Fluorescence Studies of the Volume Phase Transition and Dynamic Fluctuation in Poly(acrylamide) Gels with a Dansyl Group Induced by the Composition Change in an Acetone/Water Mixed Solvent

Yuxin Hu,*,†,‡ Kazuyuki Horie,*,‡ Hideharu Ushiki,§ Fumiaki Tsunomori,§ and Takashi Yamashita⊥

Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan, Faculty of General Education, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo, Japan, and Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, Japan

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ABSTRACT: Fluorescence studies have been made on the ionic poly(acrylamide) gels and linear poly(acrylamide) having a side-chain dansyl fluorescent probe. The gels undergo a discontinuous first-order volume phase transition at 60% acetone volume content in the mixed solvent of acetone/water at 20 °C. According to the measurements of steady-state fluorescence spectra, the fluorescence lifetime, and fluorescence anisotropy ratio, the changes in the microenvironment around the probe and in the rotational diffusion motion of the probe accompanying the phase transition were characterized as follows: (1) The phase transition from the swollen to collapsed state is accompanied by the change in hydrophobic interaction of the main chains of the gel, which is indicated by the shift of the fluorescence peak wavelength to the shorter side and the increase in lifetimes. (2) The rotational diffusion coefficient becomes infinite and shows a sharp peak at the phase transition point (60% acetone content) due to the dynamic fluctuation of the network of the gel, accompanied also by a sharp peak in the solvent composition dependence of the fluorescence peak wavelength. Some discontinuous change but no peak was observed for the rotational diffusion coefficient of the dansyl group in the linear poly(acrylamide) at an acetone content near to the transition of the gel.

Introduction

Discontinuous volume phase transitions (DVPT) and critical phenomena of polymer gels, where reversible volume changes as large as several hundred times are induced by various conditions, have attracted much attention because of their scientific interest and technological significance.[1-6] Most of the works on the DVPT of polymer gels have been devoted to investigations on the macroscopic properties such as the volume change,[1-6] mechanical behavior,[7-8] thermal behavior,[9] and kinetics of the swelling of gels.[10-11] The light scattering as an important research means was used not only to study microscopic structure and dynamics of poly(acrylamide) (PAAm) gel which does not show the DVPT,[12-13] but also to study a critical behavior of density fluctuations in PAAm gels which exhibit the DVPT.[14-15] A theoretical treatment was described for DVPT in terms of the Flory–Huggins mean-field theory which consists of four parameters, i.e., the rubber elasticity, the Flory–Huggins χ parameter, the ionic osmotic pressure, and the free energy.[1,16,17] Recently it has been noticed, however, that the detailed chemical structure, conformational change, interactions among polymer chains and between the polymer chain and solvent molecule, and microenvironment in the polymer network play a very important role in determining the DVPT. For the DVPT of poly(*N*-isopropylacrylamide) (PNIPA) gel, the environments and motions of the side group and the backbone polymer chains in terms of molecular dynamic parameters and structures were demonstrated with NMR studies by the recent work of Tokuhiro et al.[18] Their work indicated that the ionic gel of PNIPA in the collapsed state consists of two portions, the solidlike aggregates and the substantially mobile portion owing to the presence of the Donnan potential.

Although there have been a few fluorescence technique studies on polymer gels, a lot of works of fluorescence technique were devoted to the solution properties of linear PAAm or polyelectrolyte.[19] It is significant to use the fluorescence technique for studying the polymer network dynamics and microenvironment during the DVPT, in particular for studying microscopically how and why the DVPT occurs. The dansyl group has been widely used as a fluorescence probe to study conformational transition in proteins[20] and synthetic polymers.[21] This group has a special photophysical property that gives information about the local polarity and mobility of the microenvironment, as well as the binding behavior of the group.[22-24] In the recent work of Seo et al.[25] the hydrophobic interaction and the conformational change of the compact core and the micelle surface were studied with the static fluorometry and the fluorescence lifetime of the dansyl group. Their results suggested that the lifetime of the longer lifetime component in the double exponential decay becomes much longer and the emission peak wavelength shifts to a shorter wavelength in the domain of the compact core with a weaker polarity than those in the domain with a stronger polarity, and that the shorter lifetime component in the double exponential decay gives the information on the submicrodomain which is formed on the micelle surface. In our previous work,[4] the changes in microenvironments during pH-induced DVPT of PAAm gels whose side groups were labeled with a dansyl group as a fluorescent probe in an acetone/water (9/11) mixed solvent have been studied with fluorescence spectra, anisotropy, and lifetime measurements. The results revealed that there exist two transition points, the macroscopic transition point occurring at pH 5.0 and the microscopic transition

* To whom correspondence should be addressed.
† Permanent address: Chemistry Department, Jilin University, Changchun, China.
‡ Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo.
§ Tokyo University of Agriculture and Technology.
⊥ Research Center for Advanced Science and Technology, University of Tokyo.

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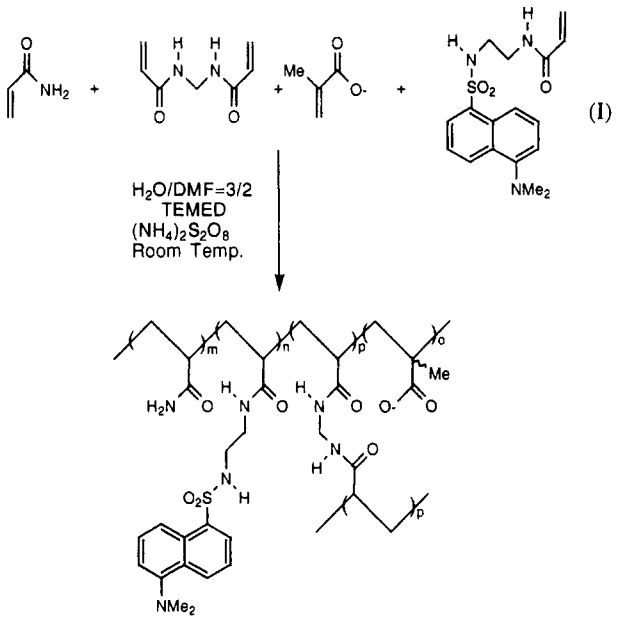

Figure 1. Syntheses of poly(acrylamide) gel and linear poly(acrylamide) with a dansyl group.

point occurring at pH 3.8. At these two transition points, the changes in the hydrophobic interaction and mobility of the backbone chains, the side groups, and the dimethylamino group in the dansyl group were demonstrated by the change in the rotational diffusion coefficient of the dansyl group.

In the present work, the discontinuous volume phase transition of poly(acrylamide) (PAAm) gel with a dansyl group was determined in an acetone/water mixture at 20 °C, and the absorption and steady-state fluorescence spectra, excitation spectra, anisotropy, and fluorescence lifetime of the dansyl group attached to the side chain of PAAm gels as well as to the PAAm linear polymer were measured as a function of the acetone volume content in the acetone/water mixed solvent. The dynamic fluctuation was revealed for PAAm gel at DVPT by sharp increases in the rotational diffusion coefficients and fluorescence peak wavelength of the dansyl group labeled to the side chain of PAAm gel.

Experimental Section

Preparation of *N*-[2-[[[5-(Dimethylamino)-1-naphthyl]sulfonyl]amino]ethyl]-2-acrylamide (I). All reagents and solvents in the present work were obtained from commercial suppliers and were purified before use. Compound I was synthesized according to the same method described in our previous paper[4] and was used as a fluorescent probe monomer.

Preparation of Poly(acrylamide) (PAAm) Gel and Linear Poly(acrylamide). PAAm gel and linear PAAm were prepared with the same methods described in our previous works.[4] Their chemical structures and the molar ratios according to the monomer feed for every monomer in 100 monomeric units are shown in Figure 1. The PAAm gels were swollen in mixed acetone/water solvents at 20 ± 1 °C in the range of 10–90% acetone volume content, and the linear PAAm samples were dissolved into the mixed acetone/water solvents in the range of 10–90% acetone volume content with the 5.0 g/L linear PAAm. After reaching the swelling equilibrium, the volume size of the PAAm gel and the photophysical properties of the dansyl probe labeled to PAAm gel and linear PAAm were measured.

Measurements of Photophysical Properties. The Hitachi 650-40 fluorescence spectrophotometer was used for the measurements of steady-state fluorescence spectra at 20 ± 1 °C with the excitation wavelength of 345 nm. The steady-state fluorescence anisotropy ratios measured with polarizers were averaged in the range from 480 to 620 nm. The transient decays of dansyl fluorescence excited at 345 nm were detected at 550 nm by using a Horiba MAES-1100 photocounting apparatus with Toshiba KL55 and Y50 filters. The obtained fluorescence decays were analyzed with the Marquardt method[26] of convoluting the system response function and varying the parameters of the fitting function until the best least-squares agreement with experiments was obtained.

The PAAm gel which was swollen in the acetone/water mixed solvent was cut into a suitable size, and put into a quartz cell, and then the original acetone/water mixed solvent was added into the quartz cell. The steady-state spectra and time transient curves for PAAm gels and the linear PAAm were obtained under the same air conditions.

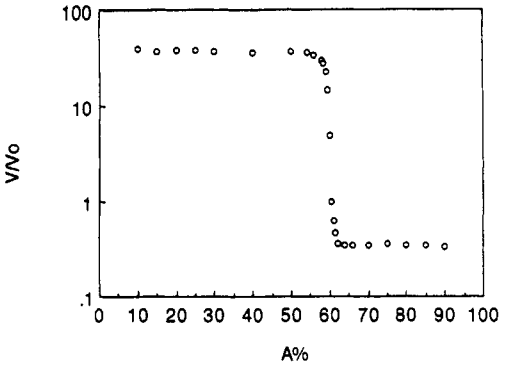

Figure 2. Degree of equilibrium swelling of PAAm gel labeled with a dansyl group as a function of acetone volume content at 20 °C.

Results and Discussion

Macroscopic Characterizations of PAAm Gel and Linear PAAm. The preparation methods of PAAm gel and linear PAAm were discussed in our previous works.[4] The fluorescent probes and ionic groups are attached to the side groups of the PAAm gels and linear PAAm, and all monomers in this system are copolymerized to gels that exhibit the DVPT at 60% acetone volume content. The relationship of the degree of equilibrium swelling of the PAAm gels, $V/V_0 = (D/D_0)^3$, to the acetone content is shown in Figure 2. V and V_0 are the volumes, and D and D_0 are the sample diameters after equilibrium swelling and at the time of preparation of the PAAm gels, respectively. Irrespective of the presence or absence of dansyl groups attached to the side group of PAAm gels, the PAAm gels swell about 35 times in volume in the acetone contents from 10% to 59.5% in the acetone/water mixed solvent. At 60% acetone content, the PAAm gel shrinks abruptly and shows a discontinuous volume phase transition, and remains collapsed about $^1/_3$ times up to 90% acetone content. The swollen PAAm gels are transparent from 10% to 54% acetone content, while the swollen PAAm gels are semitransparent with a cream color which becomes dense with increasing acetone content from 56% to 60%, and the collapsed PAAm gels are pale yellow solids from 60.3% to 90% acetone content. The yellow coloration of the collapsed PAAm gels did not affect the measurements of fluorescence spectra. The dansyl groups were not detected by UV absorption in the expelled acetone/water mixed solvent. For linear PAAm, a precipitation of PAAm was found over 70% acetone content.

Steady-State Photophysical Properties of Dansyl Groups Attached to the PAAm Gels and Linear PAAm. Both PAAm gels and linear PAAm exhibit a peak absorption at 336 nm for all acetone contents in Figure 3a. As well known, however, the absorption of acetone occurs

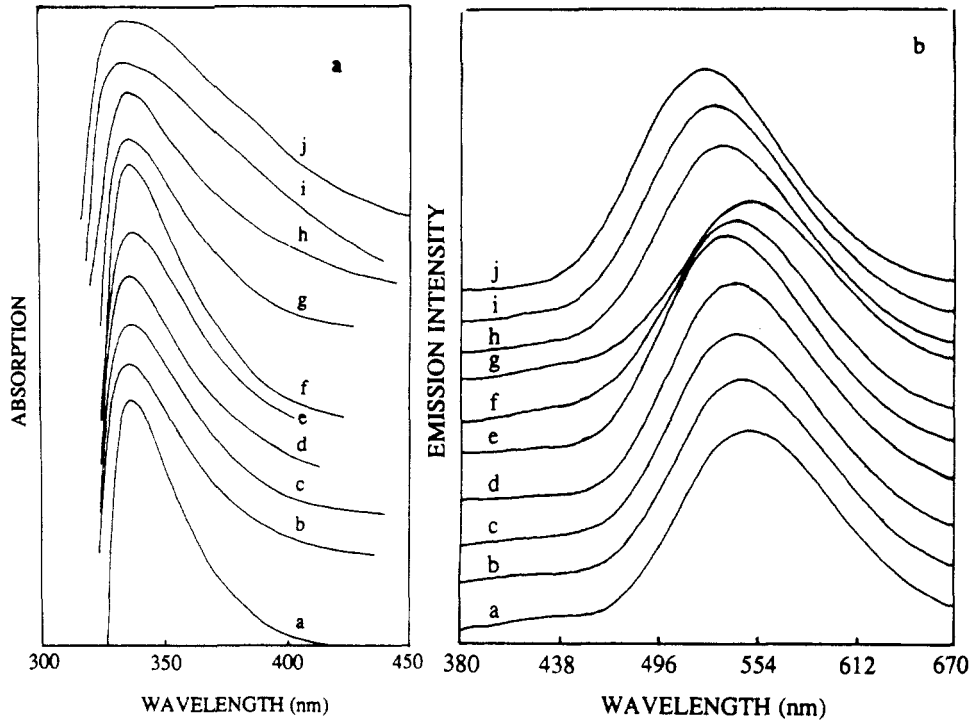

Figure 3. (a) Typical absorption spectra of the dansyl probe attached to the network of PAAm gel after equilibrium swelling at acetone contents of 10% (a), 20% (b), 30% (c), 40% (d), 50% (e), 60% (f), 60.5% (g), 70% (h), 80% (i) and 90% (j). The reference absorption is acetone. (b) Typical fluorescence spectra with the same sequence to the absorption as in (a). The excitation wavelength was set at 345 nm.

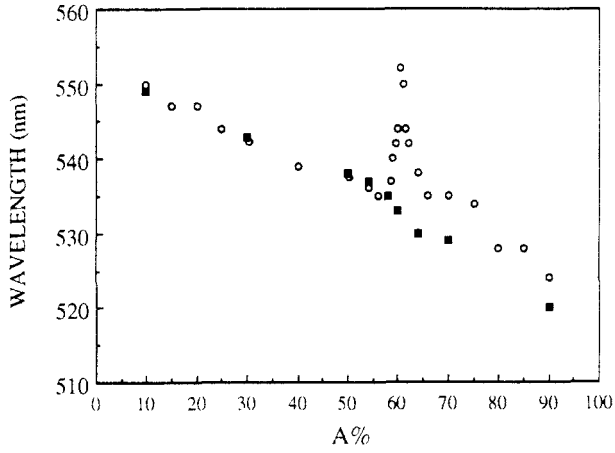

Figure 4. Acetone content dependence of the fluorescence peak wavelength of the dansyl probe attached to the PAAm gel (○) and linear PAAm (■).

below 325 nm. Therefore, 345 nm is chosen as an excitation wavelength for both PAAm gels and linear PAAm at 20 ± 1 °C. The typical normalized fluorescence spectra of dansyl probes attached to the side group of PAAm gels are shown in Figure 3b. The changes in the fluorescence peak wavelength (λ_f) of dansyl probes labeled in the side group of PAAm gels and linear PAAm are plotted against the acetone volume content in Figure 4. Although λ_f shifts to a shorter wavelength with increasing acetone content for both PAAm gel and linear PAAm in the entire range of acetone content, λ_f shifts abruptly to a longer wavelength and returns to the previous wavelength at the DVPT of the PAAm gel. At 60.3% acetone content, the emission wavelength is 552 nm which is larger than 550 nm observed for PAAm gel in water. λ_f for linear PAAm shows some stepwise shortening at about 60% acetone content. Below 60% acetone content for swollen PAAm gel, the change in λ_f of PAAm gel with acetone content is similar to that in λ_f of linear PAAm, but over 65% acetone content for collapsed PAAm gel, λ_f of PAAm gel is longer than that of the linear PAAm for the same acetone content.

As is well known, the dansyl group is a sensitive hydrophilic fluorescent probe to investigate local hydrophobic interaction, polarity, and mobility.[4,20-25] When the dimethylamino group takes a coplanar conformation with the naphthyl group in the nonpolar or the strongly hydrophobic microenvironment, λ_f of the dansyl group is about 430 nm, and when the dimethylamino group takes a twisted intramolecular charge transfer (TICT) state with the naphthyl group in the polar or the strongly hydrophilic microenvironment, λ_f is about 580 nm.[4,23] The shift of λ_f from 430 to 580 nm is determined by the twisting angle and speed of the dimethylamino group with the naphthyl group, which is induced by local hydrophobic interaction, polarity, viscosity, and free volume. For this PAAm system, the shift of λ_f gives information on the local microenvironment of dansyl probes in different domains. Below 60% acetone content, the increase in hydrophobic interaction causes the λ_f shift to shorter wavelength of the dansyl probe in Figure 4. The sharp change in λ_f to a longer wavelength and sharp return to a shorter wavelength at 60% acetone content would be caused by the PAAm network fluctuation near the DVPT, since the twisting motion of the dimethylamino group is enhanced due to the rapid fluctuation of water rearrangement. Over 60% acetone content, the suppression of the dissociation of ionic species, the increase in hydrophobic interaction between polymer chains, and the decrease in hydrophilic interaction between the PAAm chain and the mixed solvent cause the compactness of the polymer chains to produce a collapsed PAAm gel, which makes the twisting motion of dimethylamino group around the naphthyl group difficult inside the domain of the collapsed polymer chains, resulting in the presence of a higher fraction of the coplanar state of the dansyl group and the λ_f shift to a shorter wavelength.

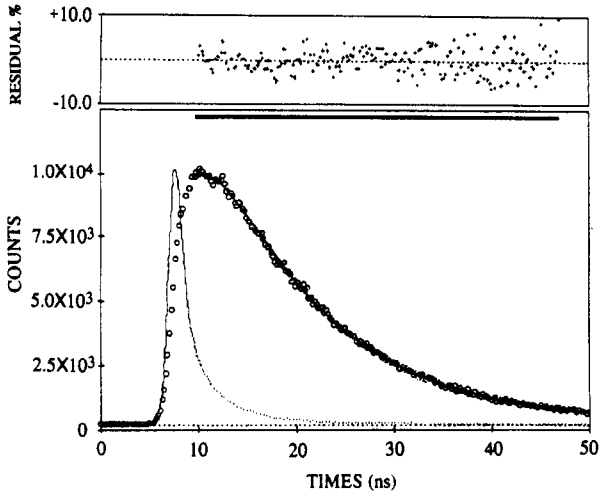

Figure 5. Fluorescence decay and a residual of the dansyl probe attached to the network of the gel at 58% acetone content: pulse lamp (- - -); residual (+); experimental data (O); curve fitting with eq 1 (—).

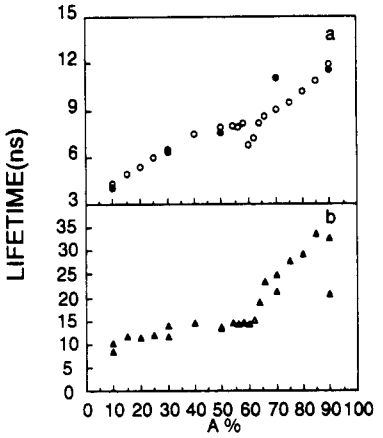

Figure 6. Fluorescence lifetimes of the dansyl probe obtained by using eq 1 in the PAAm gel (O, △) and in linear PAAm (●, ▲) for the shorter lifetime, τ_1 (O, ●), and for the longer lifetime, τ_2 (△, ▲), against the acetone content.

Fluorescence Lifetime of the Dansyl Probe. The more detailed information comes from the fluorescence lifetime. Only one component lifetime of 4–30 ns depending on solvent polarity was reported for the dansyl group,[23] and two component lifetimes corresponding to different hydrophobic domains were reported for the micelle system.[25] In our works, all fluorescence decay curves at 550 nm for PAAm gels and linear PAAm shown typically in Figure 5 with a residual could be satisfactorily fitted with the double exponential function of eq 1. The

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

two lifetime components, τ_1 (4–12 ns) and τ_2 (11–33 ns) for PAAm gel, and τ_1 (4–11 ns) and τ_2 (9–21 ns) for linear PAAm, were obtained in the entire range of acetone content. The plots of the two fluorescence lifetime components against acetone content are shown in Figure 6, and the plots of preexponential factors depending on the acetone content are shown in Figure 7 for PAAm gel and linear PAAm. The shorter lifetime component, τ_1, corresponds to the TICT state where the dimethylamino group and naphthyl group in the dansyl probe are in a nonplanar excited state in a hydrophilic microenvironment, while the longer lifetime component, τ_2, corresponds to the dansyl probe with a coplanar excited state in a hydrophobic microenvironment.[4,22-25]

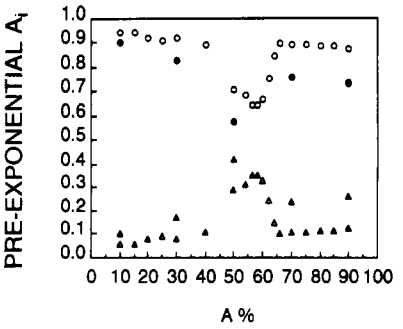

Figure 7. Relationships of preexponential factors for decay curves of the dansyl probe in the PAAm gel (O, △) and in the linear PAAm (●, ▲) with acetone content, for the first component, A_1 (O, ●), and for the second component, A_2 (△, ▲), by using eq. 1.

Figure 6a depicts the change in the shorter lifetimes, τ_1, with the acetone content. A similar change is observed for both PAAm gel and linear PAAm. τ_1 increases gradually with an increase in the acetone content in all the regions of acetone content, suggesting that τ_1 reflects directly the information of the mixed solvent. Near the DVPT of the gel, τ_1 shows a discontinuous change, and becomes suddenly shorter than that in the neighboring region of acetone content for PAAm gel due to the rapid twisting motion of the dimethylamino group around the naphthyl group caused by the network fluctuation. Figure 6b shows the change in the longer lifetime, τ_2, with the acetone content for PAAm gel and linear PAAm. Below 62% acetone content, τ_2 increases gradually from 10.3 to 15.2 ns with increasing acetone content for PAAm gel, and increases from 8.4 to 13.3 ns for linear PAAm. For over 62% acetone content, τ_2 increases about 17.5 ns from 15.2 to 32.8 ns for PAAm gel with increasing acetone content, but it only increases 8 ns from 13.3 to 21.3 ns for linear PAAm and levels off to be about 21.5 ns over 70% acetone content.

Figure 7 shows the change in preexponential factors in eq 1 for PAAm gel and linear PAAm with the acetone content. These data give only specified information on the fluorescence at 550 nm. However, the characteristic change in the preexponential factors with the acetone content for PAAm gel are the same as for the linear PAAm. In the entire range of acetone content, the shorter lifetime component, τ_1, is the main component. Near the DVPT, since the dansyl probe could not remain at a fixed excited singlet state resulting from the polymer chain fluctuation in the gel, the fraction of dansyl probes which are in the longer lifetime excited state becomes about 35%.

The results of steady-state fluorescence coincide with the results of fluorescence lifetime measurements for the PAAm system, which indicate the ionic repulsive forces and hydrophobic and hydrophilic interactions causing the swelling and shrinking of the PAAm gel and depict the polymer network fluctuation near the DVPT. The results confirm that there exist two microscopic portions in the ionic gel,[18] i.e., a solidlike aggregate portion of polymer chains and a substantially mobile portion due to the presence of the Donnan potential throughout the collapsed gels, since the longer lifetime, τ_2, in the swollen state of the gel is virtually like the shorter lifetime, τ_1, in the collapsed state of the gel.

Dynamic Fluctuation of the PAAm Network and the Rotational Diffusion Coefficient of the Dansyl Probe. The dynamic fluctuation would be realized when the system is near the DVPT. In order to monitor the changes in the rotational mobility of the dansyl group attached to the polymer chains, the fluorescence anisotropy

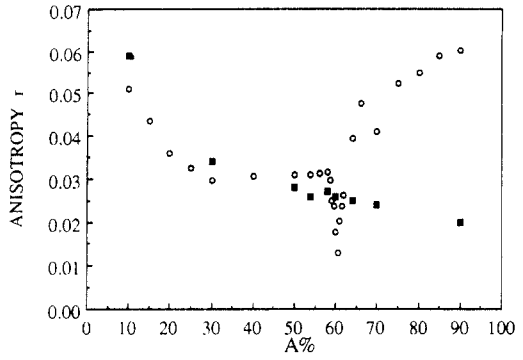

Figure 8. Fluorescence anisotropy ratio, r, of the dansyl probe attached to the PAAm gel (○) and linear PAAm (■) against acetone content. The values of r are average ones for wavelengths from 480 to 620 nm.

ratio, r, was calculated from four polarized fluorescence spectra by using

$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH}) \quad (2)$$

$$G = I_{HV}/I_{HH}$$

where I is the fluorescence intensity and the subscripts represent the orientation of polarizers (V is vertical, and H is horizontal) which are located for incident light (the first subscript) and for emitted light (the second subscript). The G value was used for correcting the depolarization characteristics of the apparatus having grating-type monochromators. Figure 8 depicts the fluorescence anisotropy ratios, r, depending on the acetone content. Below 55% acetone content, it is shown that the anisotropy ratio decreases with increasing acetone content and remains a constant from 30% to 55% acetone content for both PAAm gel and linear PAAm. Over 65% acetone content, the anisotropy ratio of the dansyl probe increases for PAAm gel and decreases for linear PAAm with increasing acetone content. It is important that a discontinuous change and an approach to zero of the anisotropy ratio for PAAm gel take place near the DVPT. The rotational diffusion coefficient D_{ri} of dansyl probes labeled to the side chains of PAAm gels and linear PAAm can be calculated from the anistropy ratio, r, with the lifetime τ_i (τ_1 or τ_2) on the basis of the Perin–Weber equation (eq 3), where k_B is the

$$r_0/r = 1 + (k_BT/v\eta)\tau_i = 1 + 6D_{ri}\tau_i \quad (3)$$

Boltzmann constant, η is the viscosity of the solvent around the dansyl probe, T is the absolute temperature, v is the rotational volume of the dansyl probe, and r_0 is the limiting value of r in the medium where no rotational diffusion occurs or the Brownian motion is frozen. The value of r_0 = 0.325 was obtained from our previous work.[4]

The rotational diffusion coefficients, D_{ri}, calculated from the values of r and τ_i by using eq 3 are given depending on the acetone content in Figure 9. Although some values of anisotropy ratios for acetone content below 55% in Figure 8 are larger than those for acetone content over 65% for PAAm gels, the D_{ri} displays a regular change with the change in the acetone content except for the region of DVPT. The change in the D_{r1} of the gel against acetone content is shown in Figure 9a. The change in the D_{r1} with acetone content for PAAm gels is similar to that for D_{r2}. However, the change in the D_{r1} of the linear polymer is different from that of D_{r2} for the linear polymer, but is similar to that of D_{r1} for the gel except for the DVPT region. The D_{r1} for the dansyl probe which locates inside

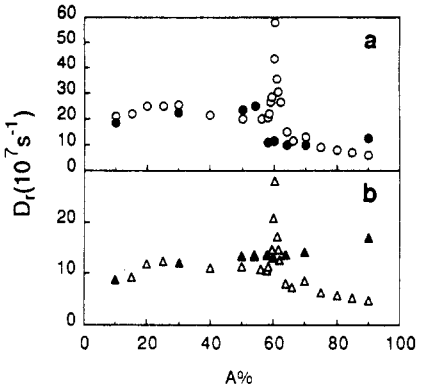

Figure 9. Changes in the rotational diffusion coefficient, D_{ri}, of the dansyl probe attached to the PAAm gel (○, △) and linear PAAm (●, ▲) against acetone content by using eq 2 with the values of lifetime τ_1 (○, ●), lifetime τ_2 (△, ▲), and r_0 = 0.325.

the microenvironment of the solvent molecules below 60% acetone content is about 22×10^7 s^{-1}. The PAAm gel becomes collapsed at 60% acetone content, and the linear PAAm shows a coil–globule transition at 55% acetone content monitored by a discontinuous change in D_{r1} as is shown in Figure 9a. The D_{r1} of the dansyl probe which is encircled with the microenvironment of the polar side group of the PAAm system over 60% acetone content is about 9×10^7 s^{-1}. From this result, it is shown that the Donnan potential contributes to the mobile domain of the polymer main chains in the collapsed or globular state owing to an increase in the interaction with hydrated cations.[18] Thus, in the region of the acetone content corresponding to the collapsed state of the PAAm gels, not only for PAAm gel but also for the linear PAAm, the motion of the dansyl probes is moderately constrained.

Figure 9b shows the change in the rotational diffusion coefficient of the longer lifetime component, τ_2, corresponding to a coplanar state. Below 60% acetone content in the swollen gels, the D_{r2} for the dansyl probe which is located inside the microenvironment of the loose PAAm network increases slightly with increasing acetone content from 10% (9×10^7 s^{-1}) to 25% (11×10^7 s^{-1}) and remains virtually unchanged for acetone content from 25% to 58%, because the PAAm networks are relaxed by the strong hydrophilic interaction with solvent molecules. Over 65% acetone content in the collapsed gels, the D_{r2} of the dansyl probe whose mobility is rigorously restricted by the dense PAAm networks decreases to about 3.0×10^7 s^{-1} with increasing acetone content, since a part of the dansyl probes are trapped entirely by the hydrophobic domain of the main chain network aggregate from which the polar solvent molecules are expelled. However, in this range of acetone content, the D_{r2} for the linear PAAm also continues to increase with the increase in acetone content. The reason for the increase in D_{r2} of linear PAAm is due to the lack of a constraining cross-linking point.

A striking characteristic for D_{r1} and D_{r2} is their extremely large values near the DVPT. This change in the values of D_{r1} and D_{r2} is completely consistent with the results of steady-state and lifetime measurements described above. The rapid microscopic transition of the network between the solidlike network aggregate and the liquidlike polar group assembly together with the increase in the mobility of solvents would be considered to take place because of the density fluctuation and unequilibrium situation near DVPT. Thus, in spite of the facts that the collective diffusion coefficient of the network becomes zero and the relaxation time becomes infinite in the macroscopic volume phase transition,[11,18,27] the rotational diffusion coefficient

of the side group of the network is supposed to become infinite owing to the rapid microscopic fluctuation of the network and solvent.

Conclusion

The interactions between the polymer network and solvent molecules and the conformational change in polymer networks of poly(acrylamide) (PAAm) ionic gels having dansyl groups are studied with the fluorescence technique in the swollen and collapsed states induced by the change in acetone content. The dynamic fluctuation at the discontinuous volume phase transition (DVPT) is demonstrated by the fluorescence wavelength and rotational diffusion coefficient of the dansyl probe. These results reveal the conclusion as follows: The PAAm gel exhibits a typical DVPT behavior at 60% acetone content. In the swollen state of the gel, the hydrophobic interaction increases with the increase in acetone content inside the gel as was shown with the shift of the fluorescence peak wavelength to the shorter side and the increase in the fluorescence lifetime. In the collapsed state, the gels separate into two phases where one is the solidlike aggregate of the polymer main chains and the other is the polar side group assembly. Even in this collapsed state, the fraction of the TICT state of the probe is predominant, and the lifetime and rotational diffusion of the probe in the polar side group assembly are identical with those of the longer lifetime component in the swollen state. Near the DVPT the dynamic fluctuation of the networks is demonstrated by a sharp characteristic change in the fluorescence peak wavelength and by the divergence of the rotational diffusion of the probe. The fluorescence technique as an effective method for studying the DVPT and critical point of gels and demonstrating the microscopic interaction and conformational change in polymer gels will be further elucidated in forthcoming publications.

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Registry No. PAAm Gel, 141848-40-0; Linear PAAm, 141879-13-2; CH_3COCH_3, 67-64-1; H_2O, 7732-18-5.