Fluorescence Studies of Volume Phase Transition in Poly(acrylamide) Gels with a Pyrenyl Probe in Acetone/Water Mixed Solvent

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

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

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ABSTRACT: The change in microenvironments and dynamics of poly(acrylamide) (PAAm) gels during the volume phase transition induced by the change in acetone content in an acetone/water mixed solvent were studied by measuring the fluorescence spectra, lifetime, and rotational diffusion coefficient of a prenyl probe attached to the side chain of the PAAm gels. The linear and cross-linked copolymers of acrylamide and sodium methacrylate were used for the experiments. The results are (a) the volume phase transition of the PAAm gels from the swollen to collapsed state is accompanied by increases in interaction between PAAm main chains and the hydrophobicity of the microenvironment, which were indicated by an increase in the monomer emission lifetimes, anisotropy ratio, and excimer emission intensity and (b) the mechanism of the volume phase transition of the gels is similar to that of the coil–globule transition of linear PAAm, which was indicated by the similarity in rotational diffusion behavior of the probe.

Introduction

The volume phase transition (VPT) of some organic polymer hydrogels such as poly(acrylamide) (PAAm) gel and poly(isopropylacrylamide) (PNIPA) gel, whose reversible volume changes as large as several hundred times are induced by various conditions, has attracted much attention because of its scientific interest and technological significance.[1-5] Until now, most of the works on the VPT of polymer gels have been devoted to investigations on the macroscopic properties such as volume change,[1-5] mechanical behavior,[6] and thermal behavior.[7] A theoretical treatment was described for the VPT in terms of the Flory–Huggins mean-field theory.[1,8,9] Recently, it has been noticed, however, that detailed chemical structure, conformational change, the microenvironment inside the gels, and various interactions in gels play very important roles in determining the properties and the VPT of the gels. These polymeric gels have also been studied extensively by light scattering[10-12] and NMR[13,14] with the aim of identifying the microstructure and dynamics.

The fluorescence technique has been widely applied to study microstructure, dynamics, various interactions, and microenvironments of organic polymer systems.[15] In our previous work,[16,17] changes in the microenvironment inside the PAAm gel, induced by the change in acetone volume content (% A)[16] or by pH change,[17] have been studied with fluorescence spectra, anisotropy, and lifetime measurements of the dansyl probe attached to the gels. The change in microenvironment of the PAAm gel during the VPT due to pH change was studied also with a pyrenyl probe.[18] The results revealed that the mechanism of the VPT induced by a change in % A is different from that induced by pH change. For the pH-induced VPT of the PAAm gel, the competitive interactions between the charge repulsive force of $-COO^-$ and the hydrophobic interaction of the polymer main chain inside the gel cause the VPT, while for the % A induced VPT of the gel, the attractive interactions among polymer main chains and the interaction between polymer side chains and solvent molecules cause the VPT.

The pyrenyl probe is used widely as a hydrophobic fluorescent probe to study the hydrophobic interactions and conformational change of linear PNIPA,[19] hydroxypropyl cellulose,[20] and polyelectrolytes.[21] The pyrene spectrum serves as a scale of the microenvironments around the probe because the relative fluorescence intensity, I_1/I_3, of the vibronic fine structures depends on the solvent dipole moment.[22] The intensity ratio of excimer emission to monomer emission, I_e/I_m, in the pyrene spectra also reflects the interactions among polymer chains and between polymer chain and solvent molecule.[20] In the present work, the PAAm gels exhibiting the VPT are studied by using the fluorescence of a pyrenyl probe attached to the side chains of the gels. For the linear polymer and the gels having different contents of cross-links and different contents of carboxylate anion groups, the absorption spectra, fluorescence spectra, fluorescence excitation spectra, anisotropy, and lifetimes were measured with the change in % A at 20 °C. The results for two gel systems and the linear PAAm are compared.

Experimental Section

Preparation of (1-Pyrenyl)acrylamide (Py). All reagents and solvents in the present work were obtained from commercial suppliers and were purified before use. (1-Pyrenyl)acrylamide was prepared from acryloyl chloride added dropwise into 1-aminopyrene in THF solvent according to the same method described in our previous paper[18] and was used as a fluorescent probe monomer. *N*-(1-Pyrenyl)acetamide was also prepared similarly from acetyl chloride and 1-aminopyrene.

Preparation of PAAm Gels and Linear PAAm. PAAm gels and linear PAAm with the pyrenyl probe were prepared by copolymerization of acrylamide, *N*,*N*′-methylenebis(acrylamide), sodium methacrylate, and (1-pyrenyl)acrylamide in DMF/water (2/3) as described previously.[16] The composition of the monomer mixture is listed in Table I. The conversion of monomers to

† Department of Reaction Chemistry, University of Tokyo.
‡ Permanent address: Chemistry Department, Jilin University, Changchun, China.
§ Faculty of General Education, Tokyo University of Agriculture and Technology.
∥ Research Center for Advanced Science and Technology, University of Tokyo.

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Table I
Composition in Molar Percents of the Monomer Mixtures for the Poly(acrylamide) Gels and the Linear Copolymer

system	acrylamide	sodium methacrylate	N,N'-methylenebis-(acrylamide)	(1-pyrenyl)-acrylamide
PPAm gel A	92.2	5.1	2.2	0.48
PAAm gel B	89.5	7.5	2.5	0.52
linear PAAm	94.4	5.1	0	0.49

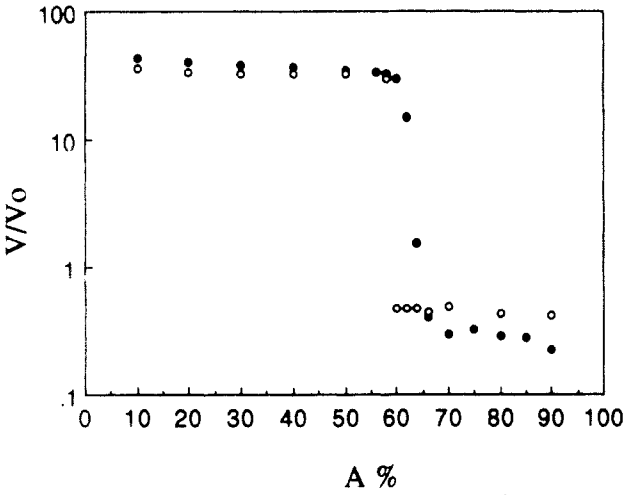

Figure 1. Equilibrium swelling of pyrenyl-labeled PAAm gels A (●) and B (○) as a function of acetone content (% A) at 20 °C in acetone/water.

copolymer was almost complete. The gels were swollen or collapsed in acetone/water mixed solvents with various acetone volume contents (% A) by standing for more than 2 weeks.

Measurements of Photophysical Properties. The photophysical properties of all the samples were measured at 20 ± 2 °C. UV absorption spectra were measured with a Jasco-660 UV/vis spectrophotometer. The steady-state excitation spectra, fluorescence spectra, and anisotropy were measured with a Hitachi 650-40 fluorescence spectrophotometer. The excitation wavelength was set at 345 nm. The fluorescence anisotropy ratio, r, was calculated from four polarized fluorescence spectra by using

$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH}) \qquad G = I_{HV}/I_{HH} \qquad (1)$$

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 grating-type monochromator. The values of r were averaged for emission from 380 to 425 nm. A Horiba NAES-1100 photon-counting apparatus with a hydrogen pulse lamp was used for detecting the transient decays of pyrenyl monomer emission at 407 nm with Toshiba UV37 and KL41 filters and to detect the transient decays of pyrenyl excimer emission at 500 nm with Toshiba Y46 and KL50 filters. The excitation wavelength was set at 345 nm. The half-width of the lamp pulse was 1.5–2.5 ns. The obtained transient decays were analyzed with the Marquardt method[23] of convoluting the system response function and varying the parameters of fitting function until the best least-squares agreement with experiments was obtained.

The PAAm gels which were swollen or collapsed in the acetone/water mixed solvent were cut into suitable sizes and placed into a quartz cell, and the original acetone/water mixed solvent was added to equilibrate the gels. The linear PAAm was dissolved in the acetone/water mixed solvent with 5.0×10^{-3} g/mL. All spectra of the gels and the linear polymer were measured in the quartz cell in the aerated atmosphere.

Results and Discussion

Macroscopic Characterizations of PAAm Gels and Linear PAAm. The fluorescent probes are attached to the side chain of PAAm gels A and B and to linear PAAm. The compositions are shown in Table I. The linear polymer has the same percentage of ionic groups as that of gel A. The percentages of cross-links and ionic side groups of gel B are about 0.3% and 2.5% larger than those of gel A. The relationships of degree of equilibrium swelling for gels A and B, $V/V_0 = (D/D_0)^3$, to acetone volume content (% A) are shown in Figure 1. V and V_0 are the volumes and D and D_0 are the sample diameters after equilibrium swelling and just after preparation of the gels, respectively. The volume of PAAm gels in the swollen state was about 35 times larger than just after preparation. The volume phase transition (VPT) of the gels occurs at 64% of % A for gel A and 60% for gel B. The gels collapsed from swollen state after the VPT, where the volume of the gels decreases

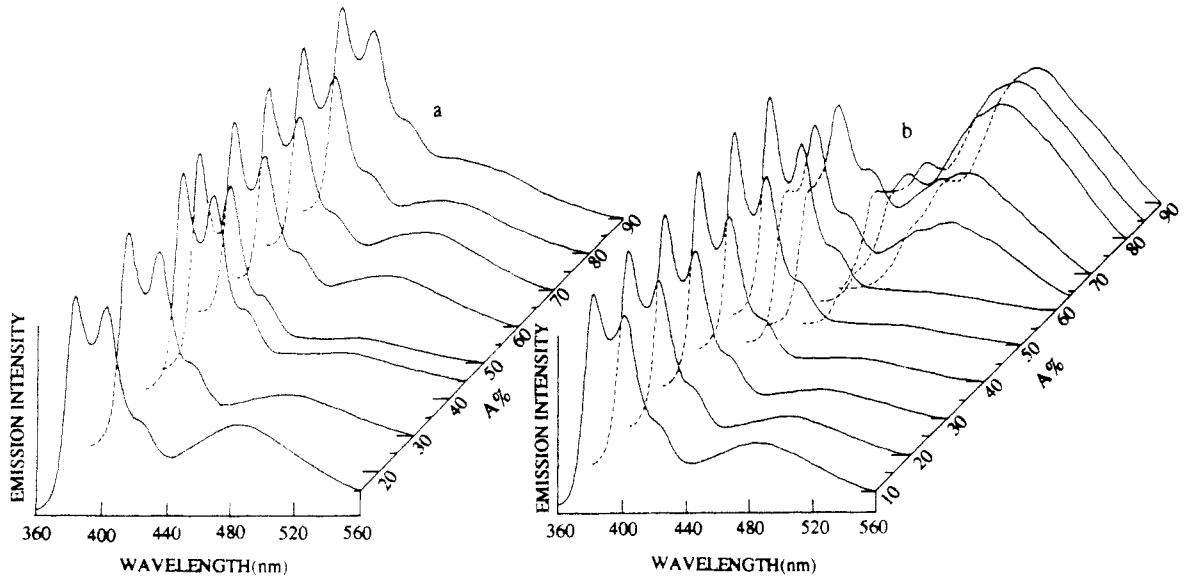

Figure 2. Typical fluorescence spectra of the pyrenyl probe attached to linear PAAm (a) and PAAm gel A (b) at various acetone contents (% A). The excitation wavelength is 345 nm.

to be about one-third of the original volume. The VPT point is affected mainly by the ionic group percent in the side chain of the polymer gel.[2,6] The swollen state PAAm gels near the VPT are semitransparent with a creamy color which become opaque with increasing % A, while swollen PAAm gels far from the VPT are transparent. The collapsed gels are yellowish solids. The creamy coloration of the swollen gels and the yellowish coloration of the collapsed gels did not affect the measurements of photophysical properties. The fluorescence anisotropy ratio, r, of the opaque collapsed gels showed a marked increase compared to that for the swollen gels (see Figure 6), which is opposite of the direction expected due to the influence of multiple scattering on r as the sample becomes opaque. The pyrenyl probe could not be detected by UV absorption in the expelled acetone/water mixed solvent.

Steady-State Photophysical Properties of Pyrenyl Probes. The absorption of the pyrenyl probe with the peak at 341 nm can be observed only above 325 nm, because of the absorption of the acetone/water mixed solvent below 325 nm. Figure 2 shows typical normalized fluorescence spectra of the linear PAAm and gel A against % A in the acetone/water mixed solvent. The pyrenyl probes in the gels and the linear PAAm show two characteristic monomer emission peaks at 385 and 407 nm and a broad structureless excimer emission centered at 480 nm. Solutions of 3.9×10^{-7} M N-(1-pyrenyl)acetamide as a model compound showed similar monomer fluorescence spectra with two peaks at 384 and 404 nm and a shoulder at 425 nm but without excimer emission for the % A range from 25% to 100%. The fluorescence intensity ratio of the peak at 384 nm to that at 404 nm of the model compound was not much affected by the solvent polarity, i.e., 1.60 in acetone, 1.54 in ethanol, and 1.71 in benzene and toluene, while the fluorescence intensity is much stronger in nonpolar solvents than in polar solvents. Identical excitation spectra were obtained for the emissions monitored at 385 and 480 nm for the swollen state of the gels and the linear PAAm, and these peaks of excitation spectra at 341 nm correspond to those of UV absorption spectra. Therefore excimer formation in these cases is supposed to obey the classical excimer formation scheme.[24] For the collapsed state of the gels, however, the excitation spectrum of the pyrenyl probe monitored at 480 nm is red-shifted, compared to that monitored at 385 nm. The excitation spectrum of the probe in the gels monitored at 480 nm is identical with the UV absorption spectrum. From these observations it has to be inferred that the excimer emission originates from loosely coupled molecular pairs of higher aggregates of the probes prior to excitation in the collapsed state of the gels.[20] The excimer emission originates predominantly from the dynamic encounter of excited- and ground-state probes in the swollen state of the gels and for all ranges of % A for linear PAAm.

Unlike the pH-induced VPT in our previous work,[18] where the fluorescence peaks of pyrenyl probe showed red shifts from 375 to 385 nm and from 396 to 407 nm as the gel changed from the collapsed to swollen state, the fluorescence spectra for the % A induced VPT of the gels show mainly changes in the intensities of monomer and excimer emission when the gels change from swollen to the collapsed state as % A is increased. In the collapsed state of the gels, the pyrenyl probe shows an excimer emission relative to monomer emission stronger than in the swollen state of the gels. The changes in the ratios of I_e/I_m, where I_e is the excimer emission intensity at 480 nm and I_m is the monomer emissision intensity at 385 nm, are plotted in Figure 3 against % A.

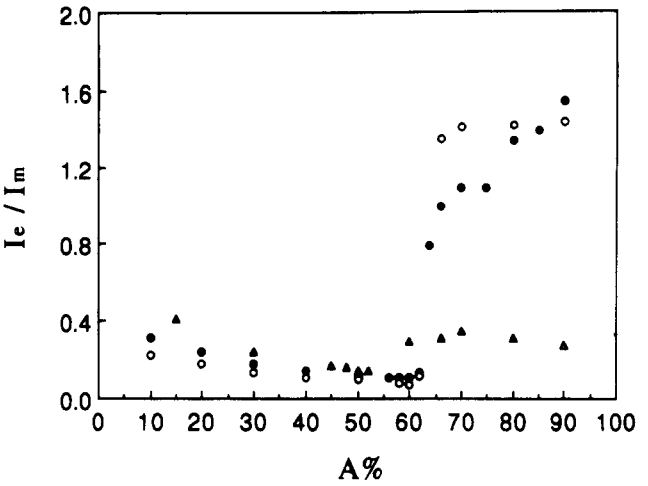

Figure 3. Changes in I_e/I_m as a function of acetone content (% A) for the pyrenyl probe attached to PAAm gels A (●) and B (○) and the linear PAAm (△), where I_e is the intensity of excimer emission at 480 nm and I_m is intensity of monomer emission at 385 nm.

In the swollen state of the gels, the decreases in the I_e/I_m from about 0.25 to 0.1 are induced by an increase in % A, since a solvation of the strongly hydrophobic pyrenyl probe and the disruption of pyrenyl dimers stabilized by hydrophobic interaction are provided by the addition of cosolvent. The values of I_e/I_m for the linear polymer in this range of % A are almost the same as those for the swollen gels. At the VPT, the I_e/I_m abruptly increases from 0.1 to 0.8 and continues to increase from 0.8 to 1.6 in the collapsed state with an increase in % A from 64% to 90% for gel A. The I_e/I_m increases abruptly from 0.1 to 1.5 at VPT and remains virtually unchanged with $I_e/I_m = 1.5$ in the collapsed state for gel B. For the linear polymer the I_e/I_m increases from 0.14 to 0.3 at 60% A and remains constant with $I_e/I_m = 0.3$ with an increase in % A from 60% to 90%. In the collapsed state of the gels, the strong hydrophobic interaction of PAAm chains leads to a situation where the solvent molecules are expelled from the network and the PAAm network becomes a rigid structure. The pendant probe in the collapsed state of the gels is fixed by the rigid structure of a close-proximity distance in a conformation possible for excimer formation. The linear polymer which is lacking in the cross-linked rigid-framed structure displays a coil–globule transition.[25] When the pyrenyl probe is connected to the network, its fluorescence behavior reflects the rigid-framed structure.

Monomer Lifetime. Typical decay curves of the monomer emission at 407 nm and excimer emission at 500 nm for the gels and the linear polymer are shown in Figure 4. The monomer emission decay curves could be satisfactorily fitted with the double-exponential function.

$$I_m(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (2)$$

Table II summarizes the lifetimes and preexponential factors of the monomer emission corresponding to the shorter and longer lifetime components for the gels and the linear polymer depending on % A. The reason for two lifetime components in the monomer transient decays is complicated. The longer lifetime component may correspond to the usual emission of the pyrenyl group,[19a] which is quenched by the acrylamide side chain.[26] The shorter lifetime component could be due to a new path of deactivation of excited pyrenyl amide groups through intramolecular charge transfer (CT) between the pyrenyl group and the amide group directly connected to it. Fluorescence of N-(1-pyrenyl)acetamide in acetone/water

Table II
Lifetimes τ_1 and τ_2, Preexponential Factors A_1 and A_2, and Rotational Diffusion Coefficients D_{r1} and D_{r2} for Monomer Emission Decays at 407 nm of Pyrenyl Probes Attached to PPAm Gels and Linear PAAm and of *N*-(1-Pyrenyl)acetamide in Acetone/Water Mixed Solvent

	10–60% acetone content				65–90% acetone content			
	τ_1/ns (A_1)	$10^{-7}D_{r1}/s^{-1}$	τ_2/ns (A_2)	$10^{-7}D_{r2}/s^{-1}$	τ_1/ns (A_1)	$10^{-7}D_{r1}/s^{-1}$	τ_2/ns (A_2)	$10^{-7}D_{r2}/s^{-1}$
PAAm gel A	7–10 (0.96–0.92)	28–22	48–35 (0.04–0.08)	4–7	10–8 (0.9–0.8)	7–5	40–35 (0.1–0.2)	2–1
PAAm gel B	7–10 (0.94–0.9)	21–15	33–48 (0.06–0.1)	4–6	10–9 (0.9–0.8)	7–5	50–45 (0.1–0.2)	2–1
linear PAAm	7–9 (0.96–0.92)	28–15	32–35 (0.04–0.08)	6–4	6–5 (0.8–0.75)	10–8	23–25 (0.2–0.25)	2–1
N-(1-pyrenyl)acetamide	3–4 (0.4–0.3)		15–14 (0.6–0.7)		3–4 (0.3–0.4)		13–10 (0.7–0.6)	

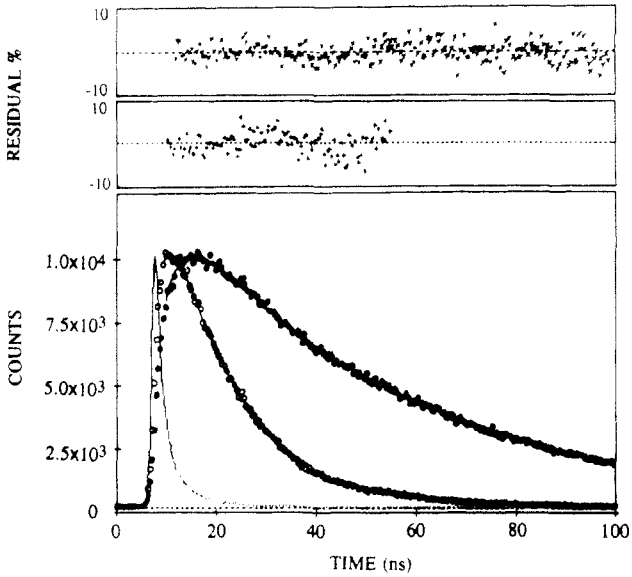

Figure 4. Monomer emission decay (○) and its residual (+) fitted with eq 2 and excimer emission decay (●) and its residual (×) fitted with eq 3 for the pyrenyl probe attached to PAAm gel A at 60% acetone content. The dotted line shows the pulse lamp profile.

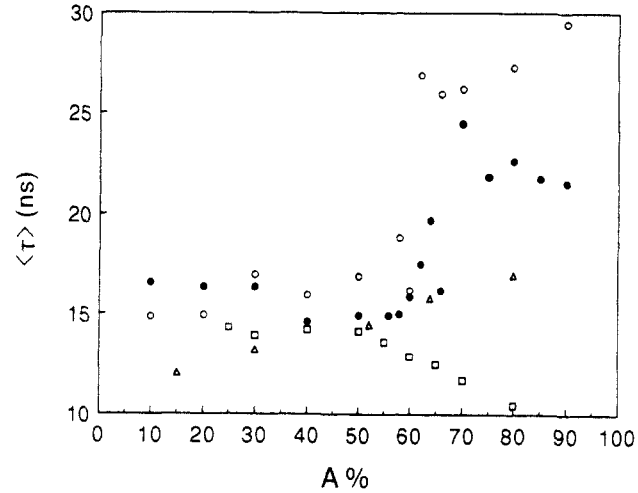

Figure 5. Plots of the average lifetime, $\langle\tau\rangle = \sum A_i\tau_i^2/\sum A_i\tau_i$, of monomer emission of the pyrenyl probe attached to PAAm gels A (●) and B (○) and the linear PAAm (△) as well as emission of *N*-(1-pyrenyl)acetamide (□) depending on acetone content (% A).

mixed solvents showed also double-exponential decay irrespective of % A with lifetimes given in Table II. The much larger τ_2 values for the probes attached to the PAAm chain compared to τ_2 values for the model *N*-(1-pyrenyl)-acetamide in the same mixed solvent suggests a hydrophobic and less mobile microenvironment around the pyrenyl groups in the polymer gels.

In the swollen state of the gels, the τ_1 in monomer emission with the lifetime of 7–10 ns is the dominant component since the more than 90% monomer emission comes from the preexponential factor A_1. In the collapsed state of the gels, owing to the strong hydrophobic microenvironment and the restraint on the motion of the probe, the intramolecular charge transfer and quenching by neighboring amide groups are inhibited, leading to a decrease in the shorter lifetime component, A_1, and an increase in the longer lifetime component, A_2, with an increase in % A.

Overall information on the monomer emission of the probes is characterized by the average lifetime $\langle\tau\rangle$, which is plotted in Figure 5 against % A with $\langle\tau\rangle = \sum A_i\tau_i^2/\sum A_i\tau_i$. Changes in $\langle\tau\rangle$ demonstrate the sensitivity of the pyrenyl fluorophore to the microenvironment. For linear PAAm, $\langle\tau\rangle$ is linear in % A, whereas a discontinuous change in the $\langle\tau\rangle$ occurs at the VPT of gels A and B. In the swollen state of the gels, the $\langle\tau\rangle$ of the gels is larger than that of linear PAAm. In this % A range, the $\langle\tau\rangle$ of gel A decreases with an increase in % A, while the $\langle\tau\rangle$ of gel B increases. In the collapsed state of the gels, the $\langle\tau\rangle$ of gel B is larger than that of gel A. The intramolecular quenching with a new path of deactivation of excited pyrenyl amide groups and the intermolecular quenching by the PAAm chain are affected by the microenvironment around the pyrenyl probe and the mobility of the probe. Because gel A has fewer cross-links and carboxylate anions than gel B, the hydrophobic interaction between the polymer main chains and the mobility of the probe decreases in the order linear polymer > gel A > gel B. In the collapsed state of the gels, the mobility of the strongly hydrophobic probe in gel B is more restricted than in gel A, which leads to more intramolecular quenching of the probes in gel A than in gel B. These results are in good agreement with those of the steady-state fluorescence measurements described above and with those of the rotational diffusion motion of the probe described below. Significant data for $\langle\tau\rangle$ for gels are near the VPT of the gels. The $\langle\tau\rangle$ suddenly drops and rises again for gel A in the % A range from 64% to 70% and for gel B in the % A range from 58% to 66% in Figure 5. This similar change in $\langle\tau\rangle$ for both gels near the VPT can be interpreted by a dynamic fluctuation of the polymer network of PAAm gel, as also deduced from the behavior of a dansyl probe in the same system.[17]

Excimer Lifetime. The excimer emission decay curves at 500 nm, a typical one shown in Figure 4, could be satisfactorily fitted with a three-exponential function.

$$I_e(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (3)$$

The obtained lifetimes and preexponential factors of excimer emission are summarized in Table III, with a moderately fast buildup lifetime τ_1, a negative value of A_1, and two decay lifetimes τ_2 and τ_3.

The coplanar state of the excimer is formed in both the swollen and collapsed states of the gels and in the linear polymer within the lifetime of the monomer excited state due to a dynamic encounter of excited- and ground-state probes, which is reflected by the buildup lifetime, τ_1. Of course, we cannot eliminate the possibility of a partial formation pyrene excimer from the preformed ground-

Table III
Lifetimes and Preexponential Factors for Rise (τ_1, $-A_1$) and Decay (τ_2, A_2, τ_3, A_3) of Excimer Emission at 500 nm of Pyrenyl Probes Attached to PAAm Gels and Linear PAAm in Acetone/Water Mixed Solvent

			τ_3/ns (A_3)	
	τ_1/ns ($-A_1$)	τ_2/ns (A_2)	10–60 A%	65–90 A%
PAAm gel A	4–5 (0.2–0.4)	6–10 (0.2–0.5)	52–46 (0.7–0.8)	50–53 (0.8–0.5)
PAAm gel B	4–6 (0.4–0.7)	6–10 (0.6–0.7)	52–43 (0.3–0.4)	50–53 (0.3–0.4)
linear PAAm	4–5 (0.3–0.5)	6–8 (0.4–0.5)	48–50 (0.5–0.6)	

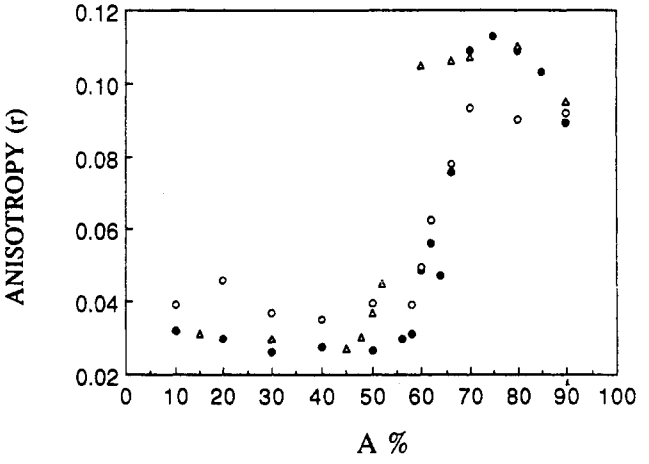

Figure 6. Plots of the fluorescence anisotropy ratio, r, of the pyrenyl probe attached to PAAm gels A (●) and B (○) and the linear PAAm (△), versus acetone content (% A). Values of r are the average ones from 380 to 425 nm.

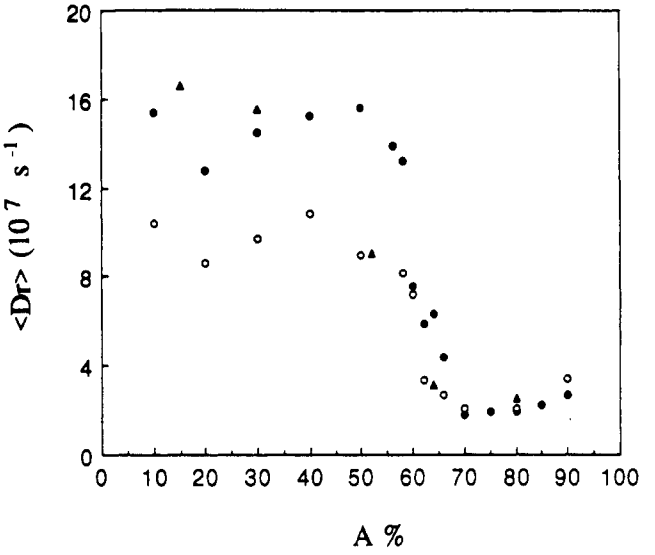

Figure 7. Plots of the average rotational diffusion coefficient, $\langle D_r \rangle$, of the pyrenyl probe attached to PAAm gels A (●) and B (○) and the linear PAAm (△), against acetone content (% A) using $r_0 = 0.400$ based on the average lifetime $\langle \tau \rangle$.

state pyrene aggregates[20] especially in the collapsed states of the polymer gels. Though the lifetimes τ_1 and τ_2 did not depend significantly on % A, in spite of the fact that individual experimental values are rather scattered within the range shown in Table III, the change in the excimer emission lifetime, τ_3 is sensitive to the microenvironment around the probe dimer; i.e., τ_3 of the gels decreases gradually with the increase in % A in the swollen state and shows a discontinuous change at the VPT of gels A and B, to a limiting value of 50–53 ns. The reason for two decay lifetimes τ_2 and τ_3 in the present system is not clear but may be related to the two decay components for the monomer emission of the 1-amido-substituted pyrene probe.

Dynamics of PAAm Gels and Linear PAAm. Figure 6 shows the anisotropy ratios, r, of the pyrenyl probe in the gels and the linear polymer against % A. In the swollen state of the gels, the r is about 0.03. Near the VPT, the r values of the gels increase sharply with an increase in % A and remain unchanged in gel B, but for the gel A the r decreases with the increase in % A after reaching a maximum at 75% in the collapsed state for the gels. The r of the linear polymer increases from 50% and remains virtually unchanged above 58% with an increase in % A. The rotation diffusion coefficient of the pyrenyl probe in these systems can be obtained from the Perrin–Weber equation

$$r_0/r = 1 + (k_B T/\upsilon\eta)\tau = 1 + 6D_r\tau \qquad (4)$$

where D_r is the rotational diffusion coefficient, τ is the lifetime of the monomer emission, η is the viscosity of the solvent, υ is the rotational volume of the pyrenyl probe, and r_0 is the limiting value of r in a medium where the Brownian motion is frozen. By extrapolation of r to infinite viscosity in water/glycerol, $r_0 = 0.400$ was obtained for the probe monomer with the pyrenyl group (1-pyrenyl)-acrylamide.

The rotational diffusion coefficients of the probe, D_{ri}, obtained from eq 4 are given also in Table II. In the swollen state of the gels, D_{r1}, the major component based on A_1, are about 2×10^8 s^{-1} and do not show a significant % A dependence. In the collapsed state of the gels, however, the rotational diffusion coefficients of both lifetime components become significant. In this % A range, the probes in these systems are divided into two groups according to the rotational mobility, one group rigorously restricted in mobility (for this group D_{r2} is about 1×10^7 s^{-1}) and the other group located at more relaxed sites (for this group D_{r1} is about 6×10^7 s^{-1}). The D_{r1} for this shorter lifetime component in the collapsed state of the gels is similar to D_{r2} for the longer lifetime component (6×10^7 s^{-1}) in the swollen state of the gels. The similarity in D_{r1} for the collapsed state and D_{r2} in the swollen state was also observed in the PAAm gel with a dansyl probe.[16] The unit for D_r in the ordinate of Figure 6 in ref 17 should be corrected to 10^7 s^{-1}. The change with % A in the averaged rotational diffusion coefficient, $\langle D_r \rangle$, calculated from $\langle \tau \rangle$ in Figure 5 is shown in Figure 7, where the marked decrease in $\langle D_r \rangle$ is observed at the VPT of the gels from the swollen to collapsed state. The tendency for the linear PAAm is similar to that for the gels, which indicates that the mechanism of phase transition of the PAAm gel is the same as the mechanism of coil–globule transition of the linear PAAm. In the range of % A corresponding to the swollen state of the gels, the interaction between the polymer chain and solvents dominates the interaction between the polymer chains. Ionic repulsion between ionized carboxyl side chains plays a role to some extent. The difference in $\langle D_r \rangle$ for the gels A and B would be due to the difference in cross-linking density for these gels. The interaction between polymer chains becomes predominant at 64% for gel A, at 60% for gel B, and about at 58% for the linear polymer, where the gels collapse and the linear polymer changes to the globular state. A sharp peak of the rotational diffusion coefficient at the VPT[16]

which was observed for the VPT of the PAAm gel with a dansyl probe induced by the change in solvent composition was not observed in the present case with the pyrenyl probe. The reason is not clear, but the difference in the spacer distances of the chromophores from the main chain might be related to it.

Based on the above results together with those of Tanaka et al.,[13] we have to consider two types of interaction between the labeled polymers and solvent molecules: the interaction between polymer chains and the interaction between solvent molecules and polymer chains. The macroscopic phase transition is dominated mainly by the competition between these two types of interactions. In the swollen state of the gels, because of the strong hydrophilic interaction of PAAm chains with the solvent in which water is predominant, the PAAm gels were swollen to only one phase, while the linear PAAm is in the coil state. The ionic repulsion between ionic side chains is also important for the stabilization of the swollen state. In this % A range, the excimer of the pyrenyl probe can be formed only in a small portion due to the low concentration of the pyrenyl groups in the swollen PAAm network. The mechanism of the VPT of the gel is supposed to be the same as that of the coil–globule transition of the linear polymer. As % A increases, the network is brought into the collapsed state since the hydrophobic interaction between the polymer main chains increases while the interaction between polymer chains and solvents decreases. In the collapsed state of the gels, the coexistence of the two phases of the gels[13] is suggested from the results of lifetimes and D_{ri} (Table II); one phase is an aggregated state, and the other phase is in a rather relaxed state of the PAAm network. The nonpolar aggregates of the part of the PAAm chain are surrounded by a cage of highly organized solvent molecules tightly bound through hydrophobic interaction of hydrogen bonding.[20] In this % A range, a major part of the probes are located in the aggregated state of polymer main chains leading to the intense excimer formation.

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