NMR Study of Poly(*N*-isopropylacrylamide) Gels near Phase Transition

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Received September 13, 1990; Revised Manuscript Received December 11, 1990

ABSTRACT: NMR studies have been made on the nonionic and ionic poly(*N*-isopropylacrylamide) gels near their phase transition. The gels undergo continuous second-order volume phase transition or discontinuous first-order transitions in water in response to temperature changes. The results are compared with the NMR data on the nonionic and ionic poly(*N*-isopropylacrylamide) polymers, which undergo a phase separation in water. From the analysis of the proton NMR line shapes and relaxation times, we have characterized the environments and motions of the side groups and the backbone polymer chains in terms of molecular dynamic parameters and structures. Some of the results are as follows: (1) The phase transition was characterized by the emergence of a new broad peak in the collapsed state and the disappearance of high-resolution spectra observed in the swollen state. The relaxation behavior of the broad peak characterizes the collapsed state as a solidlike aggregate. (2) The ionic gels consist of two portions, stiff and rather mobile portions. The nonionic gel has a homogeneous structure. (3) There is no appreciable change in the motions of the methylene and methyne protons in the backbone chains throughout the discontinuous phase transition. They remain mobile. (4) The methyl proton in the *N*-isopropyl group has a large mobility in the swollen state, however, the mobility decreases substantially upon collapse of the gel. It continues to decrease with rising temperature in the collapsed state, and eventually the immobilized portion becomes a significant part of the broad peak.

Introduction

Phase transitions and critical phenomena in polymer gels have attracted much attention because of their scientific interest and technological significance.[1-3] Phase transitions accompanied by a reversible, discontinuous volume change as large as several hundred times, in response to infinitesimal changes in the environmental conditions, have been observed universally in gels made of synthetic and natural polymers.[1-9] The phenomena were theoretically described in terms of the Flory–Huggins mean-field equation of state consisting of four principal terms that represent the rubber elasticity, the interactions among polymer segments and solvents, the ionic osmotic pressure, and the mixing entropy.

Most of the work on the phase transition and critical phenomena of gels has so far been limited to measurements on the macroscopic quantities such as volume,[1-9] osmotic compressibility,[11] collective diffusion coefficient,[12] shear modulus,[13] and ultrasonic absorption coefficient.[14] It has been noticed, however, that detailed chemical structures of polymers and solvent that constitute a gel play a vital role in determining the phase behavior of the gel. It is, therefore, important to study the chemical environments of gels and their changes near and at the phase transition.

Although there have been a few NMR studies on polymer gels, no study has been made on gels related to the phase transition. It is appropriate to mention, however, the recent work by Ohta, Ando, Fujishige, and Kubota on the effect of hydrostatic pressure on the gelation of an aqueous solution of poly(*N*-isopropylacrylamide).[15] A sudden shortening of proton spin–spin relaxation time (T_2) of water molecules in this solution was observed upon gelation, indicating the slowing down of the molecular motions of the main polymer chains and the side chains. Note that the gelation is a change between the solution and gel phases, whereas the phase transition of gel refers to the transition between two gel phases, one swollen and the other collapsed.

In this paper we present a NMR study of the gel–gel phase transition of poly(*N*-isopropylacrylamide) (NIPA) gels and polymers. NIPA gels were chosen because extensive studies of the phase transition and critical phenomena have been carried out on this system at the macroscopic level.[16,17] The universality class of the phase transition has been identified as that of the 3-dimensional Ising system from the determinations of critical exponents for the amplitude and decay rate of the density fluctuations as observed by dynamic light scattering spectroscopy, specific heat, critical isobars, coexistence curve, and critical kinetics.[1-8] In addition, a chronological stability of gels and a relative ease in the handling of the materials were among other factors being considered as a candidate. The gels have been most extensively studied in relation to the critical behavior and phase transition, because they undergo a swelling–shrinking phase transition in response to temperature in a single solvent, pure water, as opposed to fluid mixtures that are needed for many other gel systems.[1-7] The NIPA gels are swollen at lower temperatures and collapsed at higher temperatures with the transition temperature at around 34 °C. In general, the entropy of a system should increase as the temperature becomes higher. In the case of NIPA gels, as the temperature is raised the polymer network shrinks to a compact state and its entropy decreases. The entropy decrease of the network should be compensated by the increase of the entropy of the water molecules. Water molecules are known to form a regular, icelike structure when in contact with the hydrophobic polymer network, whereas they take a random liquidlike structure when expelled out of the collapsed polymer network. The entropy of water is smaller when the gel is swollen, and it increases when the gel collapses. The total entropy of the gel, therefore, increases upon collapse. All the hydrophobic gels known to undergo the phase transition have this reverse temperature dependence. The speculations on the melting of the icelike water, although generally well accepted, have to be experimentally tested

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0024-9297/91/2224-2936$02.50/0

by observing the microscopic behaviors of various chemical groups within the polymer network and of water molecules near and far from the polymers, in particular, near the phase transition and critical point.

Experimental Procedure

Poly(*N*-isopropylacrylamide) gels were prepared following the standard free-radical copolymerization of *N*-isopropylacrylamide (700 mM, Kodak, purified by recrystallization), with cross-linker, *N*,*N*′-methylenebisacrylamide (8.6 mM, BioRad).[9] The gelation was initiated by ammonium persulfate and accelerated by tetramethylethylenediamine. The gels thus formed were dried in a pressurized air dryer at room temperature for 3–4 days. The dried gels were then placed in D_2O and allowed to stand for about 3 days for complete equilibration. This deuteration process was repeated twice, in order to transform the NH groups into ND groups. The dried deuterated gels were placed carefully at the bottom of a 10-mm-o.d. NMR tube. This NMR tube and a tube containing a known amount of D_2O were connected to a vacuum system, and D_2O was thoroughly degassed by eight cycles of freeze–pump–thaw processes. Then, D_2O was carefully distilled over the dried gels under vacuum to let the gels swollen with D_2O. Oxygen-free N_2 gas was then introduced over the gels at about 1 atm and at room temperature. The system was maintained in the condition for more than 30 min. After that, the N_2 gas pressure was reduced to about 700 mmHg and the tube was sealed off. The N_2 gas used was from commercial sources (containing less than 5 ppm O_2 gas) and was purified further by passing through strong alkaline solutions of pyrogallol[18] and dried over calcium chloride and potassium pentoxide to remove the remaining water. The deuterium content of D_2O was 99.7%, and it was used without further purification.

The partially deuterated *N*-isopropylacrylamide $CH_2{=}CHCONDCD(CD_3)_2$, the major polymer component, was synthesized as follows: Five grams (85 mM) of the fully deuterated isopropylamine $NH_2CD(CD_3)_2$ (Merck, deuterium 99%) and 8.6 g (85 mM) of triethylamine were dissolved in 200 mL of benzene, and then the solution was kept at 0 °C. A total of 100 mL of benzene solution containing 7.7 g (85 mM) of acryloyl chloride (Aldrich) was added drop by drop to the above solution over a period of 60 min with vigorous stirring. The reaction mixture was kept at 0 °C while stirred overnight. Removal of triethylammonium chloride (powdered crystals) from the reaction system was essential for the successful completion of the synthesis. These crystals were removed by vacuum filtration. After 1 mg of 2,6-di-*tert*-butyl-4-methylphenol (polymerization inhibitor) was added to filtrate, benzene was removed by vacuum evaporation at 30 °C. *N*-Isopropylacrylamide-d_8 thus synthesized was purified by vacuum distillation [bp 70 °C (4 mmHg)]. The yield was approximately 65%. Absence of the methyl and the lone proton NMR peaks of the *N*-isopropyl group in the product verifies the perfect protection of the above deuterated groups throughout the synthetic processes.

The fraction of *N*-isopropylacrylamide polymers with molecular weight less than $\sim 3 \times 10^3$ was removed by dialysis.

The instrument used was a home-built multinuclei Fourier transform pulsed NMR spectrometer equipped with an Oxford wide-bore superconducting magnet operated at 8.455 T.[19] This corresponds to 359.6 MHz for the proton. The spin–lattice relaxation times (T_1) were determined by means of the inversion recovery method [180°–*t*(variable)–90°–FID]. A typical 90° pulse width for ^1H was 5–6 μs. The temperature of a sample was maintained within less than ±0.5 °C by a cryostat gas flow.

Kinetic studies of gel swelling and shrinking show that the time needed for volume and shape changes of a gel is proportional to the square of a characteristic length of the gel and reciprocal of the collective diffusion coefficient of the gel in the case of continuous phase transition.[20,21] The square-length law also holds roughly in the case of discontinuous phase transition,[20] even though mechanical instability brings about many more complications, in particular, the appearance of the surface patterns.[21] Since gels used in the present NMR study had complicated and unknown distributions of various sizes and shapes, an extra precaution was taken in order to confirm the establishment of phase equilibrium. The phase transition was approached from either higher or lower temperature sides of the critical temperature. When the phase transition or critical temperature was passed from the lower temperature side, the gel sample was left in the RF probe at a temperature only a few degrees above the phase transition or critical temperature for overnight (at least 16 h).

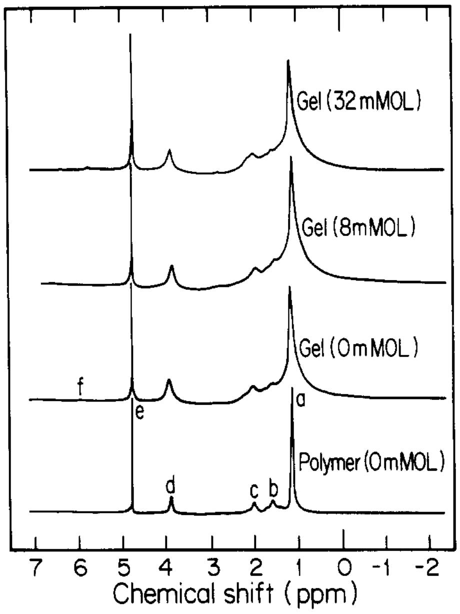

Figure 1. Proton NMR spectra of nonionic poly(*N*-isopropylacrylamide) (NIPA) gel, ionic (8 mM) NIPA gel, and ionic (32 mM) NIPA gel dissolved in D_2O at room temperature, 23 °C: (a) methyl proton of the isopropyl group, (b) methylene proton, (c) methyne proton, (d) lone proton of the *N*-isopropyl group, (e) HOD, and (f) methylene proton of cross-linking *N*,*N*′-methylenebisacrylamide.

Experimental Results

1. Overview of Proton Spectra. The proton NMR spectra of the NIPA polymer dissolved in D_2O and those for the NIPA gels containing 0, 8, and 32 mM ionic groups (total amount of NIPA plus sodium acrylate was fixed to be 700 mM) in the full swollen state are shown in Figure 1. While the polymers in gels have three-dimensional networks by cross-linking, the spectra of the gels in the swollen state resemble that of the NIPA polymer in D_2O. The assignment of the chemical groups is given in the caption of Figure 1. A noticeable broadening of the *N*-methyl protons (peak a) is observed with the increasing content of ionic groups. In addition to the sharp peaks that appear in the NIPA gels (Figure 1), there exists a very broad peak (fast decaying component in FID) centered at about 5.8 ppm (f). This peak is very small in the nonionic gel and increases with the increasing content of ionic groups.

The ^1H NMR spectrum of the monomer *N*-isopropylacrylamide shows that the methyl signal is split due to the interaction with the methine lone proton. However, any structures in the methyl peak in the NIPA polymers as well as in the NIPA gels are hidden in the broad lines, and thus the peak represents the entire methyl groups occupying various conformational positions. The same argument applies to the methylene and methine protons.

2. Observation of Phase Transitions by Proton NMR Spectra. Since the critical and phase transition temperatures of gels containing 0, 8 and 32 mM ionic groups are known to be 33.0, 35.7, and 37.6 °C, respectively,[17] we have studied the temperature dependences of the proton NMR spectra in these gels in the temperature range from 2 to 63 °C. Figure 2 shows the proton NMR spectra of the

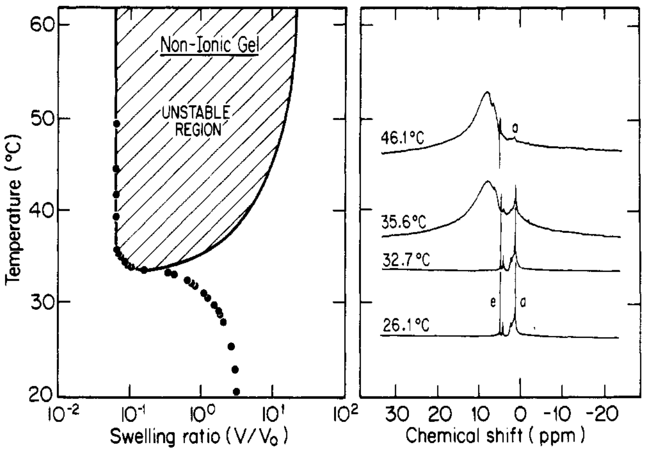

Figure 2. Proton NMR spectra and the volume of a nonionic poly(*N*-isopropylacrylamide) gel at different temperatures.

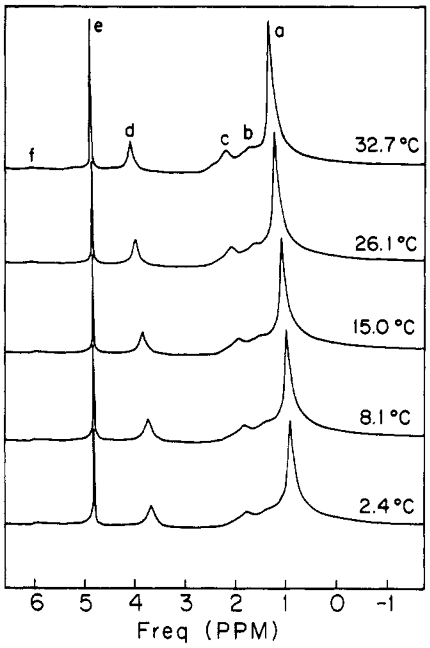

Figure 3. Temperature dependence of proton NMR spectra in the swollen state of a nonionic poly(*N*-isopropylacrylamide) gel.

nonionic gel at different temperatures below and above the critical temperature. All the spectra were obtained by using the same instrumental parameters and were recorded as the temperature was raised from 2 to 63 °C and also as the temperature was lowered backward. There was no difference in spectra between the two directions. More detailed spectral changes in the nonionic gel at temperatures below the critical temperature are shown in Figure 3. While the HOD peak (e) did not shift in the above temperature range, all the other peaks shifted toward lower field with rising temperature. Gradual narrowing of all the peaks with increasing temperature in the above temperature range was observed. This can be attributed to the motional narrowing due to more vigorous motions of molecules, and thus the CH_2 and CH peaks (b and c) are much more discernible at 32.7 °C than those at lower temperatures.

Manifestation of spectral changes caused by the phase transition in the nonionic gel is observable (Figure 2). The appearance of a new broad peak centered at 7.9 ppm and a gradual disappearance of all the peaks seen at temperatures below the critical temperature highlight this process. It should be noted that the appearance of the new band is sensitive to the temperature while the rate of this process is extremely slow; i.e., it takes a long time for equilibration of the new band. The latter is completely consistent with the results obtained in the dynamic light scattering and the kinetic swelling–shrinking experiments of the same system around the critical point.[20,21] These experiments showed the critical slowing down of density fluctuations and critical kinetics. As can be seen in the left half of Figure 2, the volume change in the collapsed state at temperatures above 34 °C is virtually zero. However, the transformation of the CH_3, CH_2, and CH peaks present in the swollen state into a part of the new broad peak still continues with increasing temperature even in the collapsed state. Kinetically, this process is not as slow as that around the critical temperature.

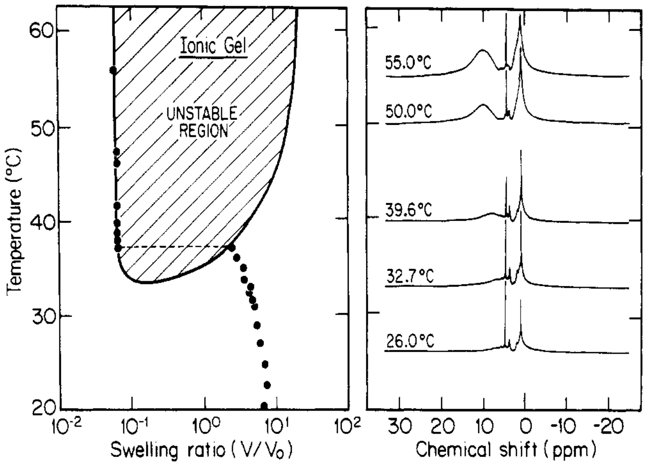

Figure 4. Proton NMR spectra and the volume of an ionic (32 mM) poly(*N*-isopropylacrylamide) gel at different temperatures.

In the ionic gel containing 32 mM sodium acrylate, the corresponding spectral changes caused by the discontinuous phase transition are substantially different from those of the nonionic gel as shown in Figure 4. The spectra below the transition temperature are virtually identical with that of the nonionic gel. Figure 5 summarizes the temperature dependence of the chemical shifts of several peaks in reference to tetramethylsilane (TMS) in the ionic (32 mM) gel. At 39.6 °C, which is only 2 °C above the transition temperature, a new broad peak can be observed at 10.3 ppm, as in the case of the nonionic gel. The new peak grows considerably with increasing temperature. In contrast to the nonionic gel, all peaks present in the swollen state become gradually broadened with rising temperature but still remain with substantial intensities after the gel is collapsed. The broadening continues even at 60 °C. The same behavior was also observed for the other ionic (8 mM) gel.

The behavior of the methylene and methyne protons in the main backbone polymer chains is not clearly visible in the spectrum because they are masked by the large methyl proton peak. Removal of the methyl peak is achieved by the use of partially deuterated *N*-isopropylacrylamide-d_8. For this sample, the temperature dependence of the proton NMR in the deuterated gels will depict the behavior of the main chains throughout the phase-transition process. Figures 6 and 7 demonstrate the evolution of the proton NMR spectra in the nonionic and ionic (32 mM) gels made from the completely deuterated *N*-isopropyl groups, respectively. The doublet (peaks b and c) at around 1.94 ppm is clearly assigned to the methylene and methyne protons. The methylene protons in the cross-linking molecule, *N,N'*-methylene bisacrylamide, can now be seen in the spectrum (peak f) of the nonionic gel because of the absence of the methyl peak. In the

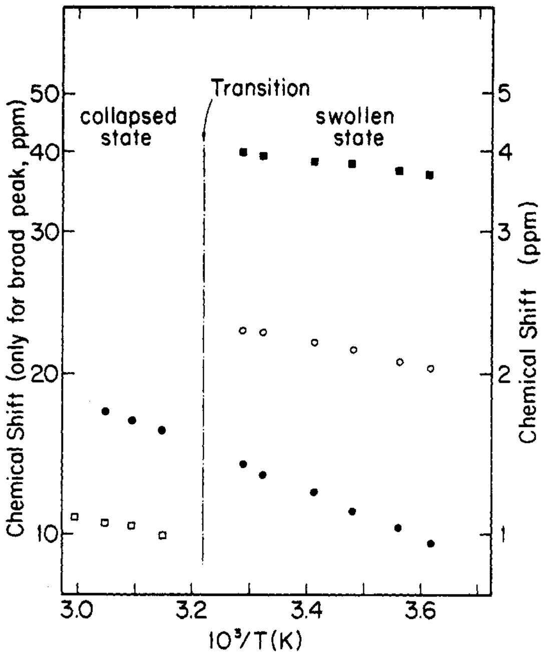

Figure 5. Proton NMR chemical shifts in ionic (32 mM) gel at different temperatures. Closed circles show the methyl proton of the isopropyl group, open circles are for the methyne proton, closed squares are for the lone proton of the isopropyl group, and open squares are for the broad peak at 10.3 ppm (refer to the left ordinate). All the chemical shifts are expressed in reference to tetramethylsilane.

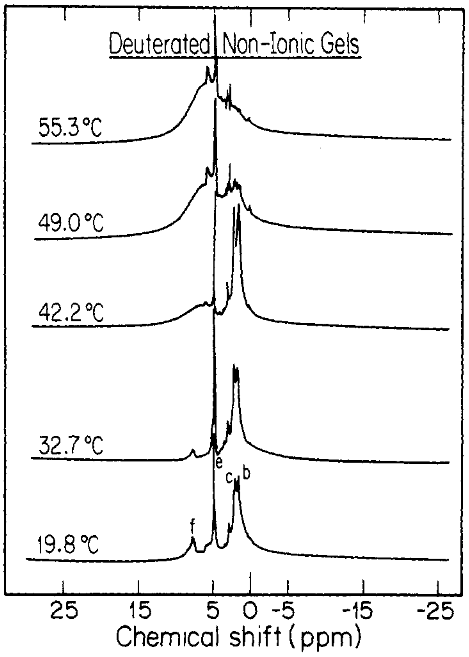

Figure 6. Proton NMR spectra in a nonionic poly(*N*-isopropylacrylamide) gel consisting of a fully deuterated *N*-isopropyl group at different temperatures.

nonionic gel, the same characteristic changes were observed in the deuterated sample as in the fully protonated samples. However, a merging of all the peaks into the broad peak that appeared in the collapsed state occurred at a temperature higher than that in the protonated sample. In the ionic gel, the spectral changes caused by the discontinuous phase transition are phenomenologically in character identical with those observed in the protonated sample.

3. Proton NMR Spin-Lattice Relaxations of NIPA Polymers in D_2O. As a reference system for studying the dynamic behavior of polymers in gels, we have determined the proton spin-lattice relaxation times (T_1) of the NIPA polymers dissolved in D_2O (70 mg of polymer/2 g of D_2O). The results are shown in Figure 8. Approximate activation energies determined from the slopes are also included in the figure captions. The significance of the sign of the slope of ln T_1 vs $1/T$(K) curves will be discussed in the Discussion section.

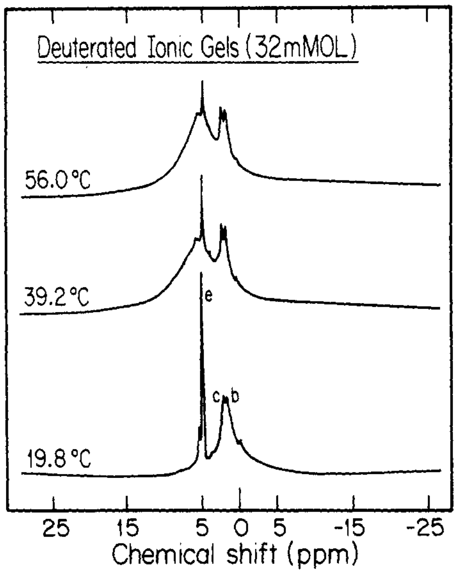

Figure 7. Temperature dependence of proton NMR spectra in an ionic (32 mM) poly(*N*-isopropylacrylamide) gel consisting of a fully deuterated *N*-isopropyl group.

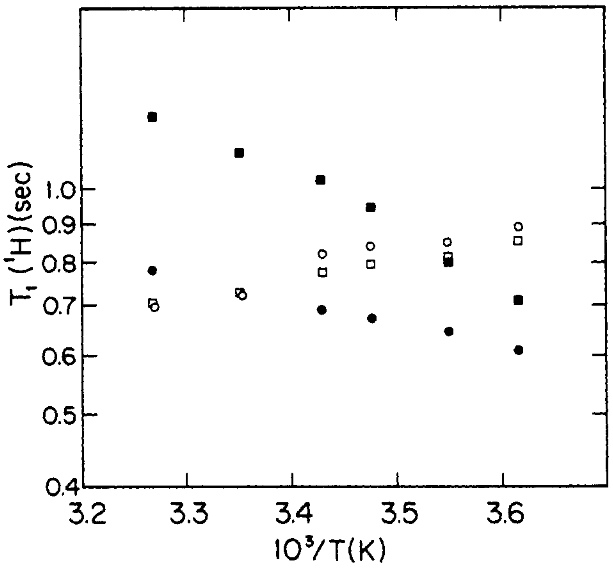

Figure 8. Proton NMR spin-lattice relaxation times of poly(*N*-isopropylacrylamide) polymers dissolved in D_2O at different temperatures. Closed circles are for the methyl proton (1.38), open circles are for the methyne proton (1.36), open squares are for the methylene proton (1.11), and closed squares indicate the lone proton of the isopropyl group (3.26), where the values in the parentheses indicate the Arrhenius activation energies in the unit of kcalories per mole.

4. Proton NMR Spin-Lattice Relaxations of the NIPA Gels. The temperature dependences of the proton NMR spin-lattice relaxation times for the NIPA polymers in the swollen state of the nonionic and ionic (32 mM) gels are shown in Figure 9 and 10, respectively. Since the methyne proton peak is partially masked by the shoulder of the strong methyl peak, the corrections are made for the intensities by subtracting the shoulder intensities, assuming that they are symmetrically located at the low-frequency side of the methyl peak. Thus, the T_1 values

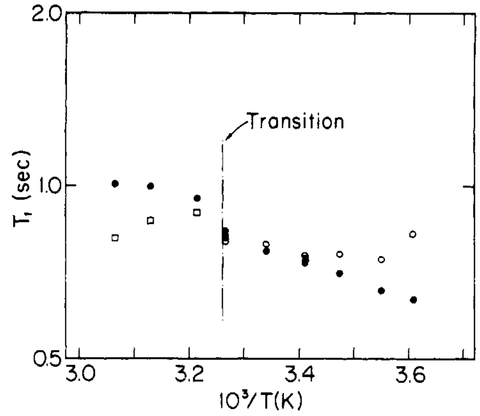

Figure 9. Proton NMR spin–lattice relaxation times in nonionic poly(*N*-isopropylacrylamide) gel at different temperatures: closed circle, methyl proton; open circle, methyne proton, closed square, methylene proton; open square, broad peak at 7.9 ppm.

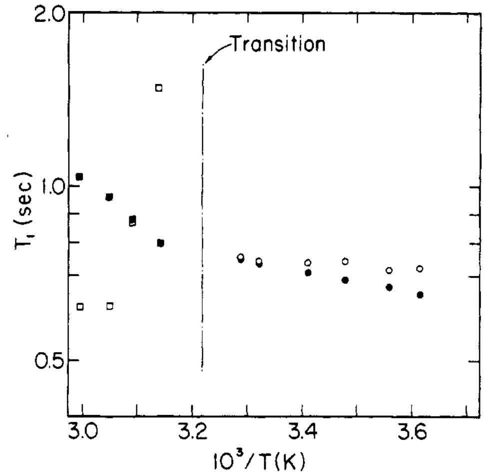

Figure 10. Proton NMR spin–lattice relaxation times in an ionic (32 mM) poly(*N*-isopropylacrylamide) gel at different temperatures: closed circle, methyl proton (swollen state); open circle, methyne proton; closed square, methyl proton (collapsed state); open square, broad peak at 10.3 ppm.

for the methyne proton are less reliable, particularly for the 32 mM ionic gel. The behavior is signficantly different between the swollen and collapsed states. The physical meaning of this aspect will be discussed in the next section.

Discussion

1. Nonionic Gels. Since it is known that polymers dissolved in water exhibit a phase separation in certain temperature ranges,[22] it is of interest to compare spectral changes caused by the continuous phase transition in the nonionic gel with those in the polymer solution. Figure 11 shows the temperature dependence of the proton NMR spectra observed in an aqueous solution (D_2O) of the nonionic NIPA polymers. A new broad peak centered at 8 ppm appears suddenly at about 34 °C, and the system enters into a two-phase state at higher temperatures. The growth of this peak with increasing temperature is significant. The line shape and the position of this peak are almost identical with those obtained in a solid dried sample of the same NIPA polymers. The spectrum at 50.2 °C of the solid polymers apparently shows the effect of motional narrowing. From comparison of these spectra, the new broad peak at higher temperatures can be regarded as that of the solid polymer. Thus, a dynamic equilibrium of two phases, that is, the polymers dissolved in solvent (D_2O) and the polymers in the form of aggregates or the dense polymer droplets floating in the solvent, coexists at the temperatures higher than about 34 °C. Phenomenologically, this can be observed as the change from a transparent solution to an opaque one with rising temperature.

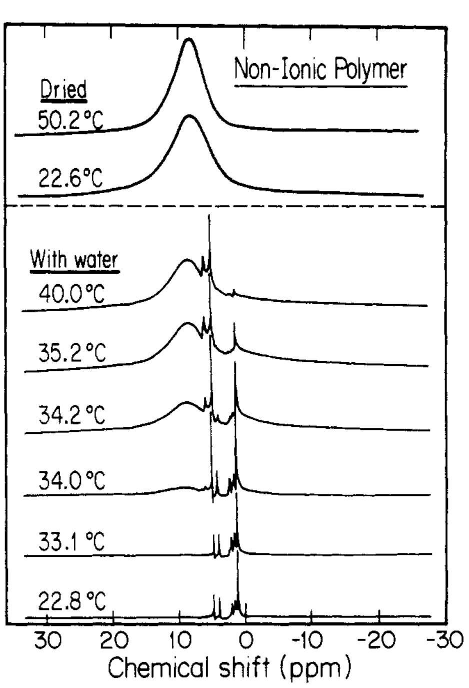

Figure 11. Proton NMR spectra of poly(*N*-isopropylacrylamide) polymers dissolved in D_2O and in dried states at different temperatures.

A striking difference in the temperature-dependent behavior of the NIPA polymer in water from the NIPA gel is its extreme rapidness of establishing new equilibria in response to temperature variation. In addition, it should be noted that the spectral line shapes for the polymers dissolved in the solvent remain unchanged over the entire temperature range while their intensities vary sensitively with temperature. Here, we have shown clearly that the phase transition observed in the nonionic NIPA gel is in character different from that in the corresponding NIPA polymers in water.

The new broad peak at 7.9 ppm characterizes the collapsed state of the nonionic gel. The line shape shows that a broadening effect due to the strong nuclear magnetic dipole–dipole interactions among protons dominates in this state, overcoming the motional narrowing effect. This situation can be attributed to the much closer distances among various protons of the polymers in the collapsed state than in the swollen state.

Experimental results show the following: (1) In the swollen state, the full line widths ($\Delta\nu_{1/2}$) of the methyl and lone proton peaks of the *N*-isopropyl group are about 51 and 26 Hz, respectively, at 37.2 °C. $\Delta\nu_{1/2}$ of the methyl peak was increased by about 20%, while the lone proton remains unchanged at 2.4 °C. (2) In the collapsed state, $\Delta\nu_{1/2}$ of the new broad peak was about 3.1 kHz at 35.6 °C. In the deuterated gel, (3) $\Delta\nu_{1/2}$ of the combined peak of the methylene and methyne protons was about 360 Hz at 32.7 °C in the swollen state, while (4) $\Delta\nu_{1/2}$ of the new broad peak was about 2.3 kHz at the temperature above 42 °C.

For an isolated methyl group, i.e., three protons occupying the corners of an equilateral triangle, the theoretical value[23] of van Vleck's second moment is about 5.4 G^2. If the line shape is represented by the Gaussian form, this corresponds to about $\Delta\nu_{1/2}$ = 23 kHz, if only the intramolecular interaction is taken into account. Since the methyl protons are surrounded by the other proton-containing groups in the gel, the experimentally determined line width is the sum of the intra- and the intermolecular contributions. Therefore, if the methyl protons are in the rigid lattice regime, $\Delta\nu_{1/2}$ must be greater than about 23 kHz. On the other hand, if it is in the extreme narrowing case, it must be less than 0.1–1.0 Hz. For the lone proton of the *N*-isopropyl groups, the total $\Delta\nu_{1/2}$ may be attributed to the intermolecular interactions because of the lack of nearby intramolecular protons. The intermolecular contributions to the methyl protons may have magnitude similar to the above, and, thus, the intramolecular contribution must be comparable to the intermolecular ones. However, these contributions are far smaller than the value in the rigid lattice regime, and, therefore, the effect of motional narrowing is exceedingly large but still away from completeness in the swollen state. The faster internal rotations of the methyl groups are probably accountable for the 20% reduction of line width at 32.7 °C. Since the theoretical second moment for the intramolecular proton pair of the CH_2 group is smaller than that of the CH_3 group, the larger line width of the combined peak of the CH_2 and CH protons is attributable to a less complete motional narrowing effect than the methyl group. Its effect is still eminent, however, in the swollen state. In the collapsed state, since $\Delta\nu_{1/2}$ of the new broad peak in the fully protonated gel is nearly 40% wider than that in the deuterated gel, it seems reasonable to think that the significant increase in the line width is due to an increase in the intermolecular interactions brought about by conformational transformations, because it occurs at higher temperatures where the thermal motions are greater than in the swollen state. The constant line width of the new broad peak in the deuterated gel at the temperatures covering the collapsed state supports the above idea because the peak consists of only CH_2 and (less mobile) CH protons. Although it is not possible to evaluate the intramolecular and intermolecular contributions independently, it may be allowed to assume that the intermolecular distances between protons are, on the average, in the same order of magnitude for the intramolecular distances. Thus, if we assume that about half of the line width in the collapsed state stems from the intermolecular interactions, we can estimate the ratio of the line widths in both states: In the protonated gel, the ratio is $1220/26 \sim 60$, and in the deuterated gel, it is $1150/180 \sim 6.4$.

Macroscopically, the volume contraction by a factor of 14.6 was observed from the swollen state at 32.7 °C to the collapsed state at 35.6 °C. Since the line width due to the dipolar interactions is inversely proportional to the third power of the distances of interacting proton pairs,[24] an increase in the line width is expected to be in the same order of magnitude as the volume change. The large change in the line width for the methyl protons implies that more significant conformational transformations occur in the *N*-isopropyl group through the phase transition than in the backbone groups. In terms of distance, the above values correspond to the change by a factor of 3.9- and 1.9-fold for the methyl protons and the protons in the main polymer chains, respectively. Namely, the protons in the swollen state, on the average, are located farther away than those in the collapsed state. While it is probably reasonable to use these values in order to infer qualitatively what is happening in the phase transition at the molecular level, we do not construe these values as the correct ones, because various assumptions have been made to reach the conclusion.

By integrating the experimental results for the nonionic gel as shown above, a physical picture of the process involving continuous phase transition emerges as follows: At lower temperatures at which the gels are swollen, the thermal motions of both bulky *N*-isopropyl groups and the main polymer chains are active. As the temperature rises the motions increase steadily because of the increased thermal energy. Due to the negative enthalpy and entropy of the contact free energy of NIPA polymers with water, the attractive forces among polymers and among water molecules increase with temperature. Such attractive interactions act to prevent free motions of the *N*-isopropyl groups and methylene and methyne groups in the main chains. As the attractive interactions among the hydrophobic groups of polymers increase with temperature, they can overcome the thermal motions of these groups, thus bringing all groups into a state of solidlike aggregates. This process naturally accompanies the exclusion of water molecules from the original gel system. This can be in the form of continuous second-order phase transition or of a first-order transition. While the *N*-isopropyl groups can still maintain a substantial mobility in the lower temperature range of the collapsed state, the above immobilization process seems to occur for the *N*-isopropyl groups more readily than the main polymer chains, as revealed in the fact that the disappearance of a sharp peak assigned to the mobile *N*-isopropyl protons (peak a in Figure 2) occurred at the temperatures lower than that for the methylene and methyne groups (Figure 6). The constraint of rearrangements of the polymer chains in the gels due to cross-linkings could be the main reason why the methylene and methyne peaks still persist at the lower temperature range of the collapsed state. Such a constraint will not allow completely free arrangement of polymers into the most closely packed structure of the polymers. The excluded water molecules form a system of a higher degree of randomness as compared to the water in the swollen state. Thus, the collapsing phase transition of the gel system is an entropy-increasing process as a whole.

The lack of cross-linking facilitates conformational changes to form the solidlike aggregates in aqueous solutions of the nonionic NIPA polymers. Therefore, the system establishes a two-phase equilibrium. Similar situations occur in various micellar systems as shown in their NMR experiments.[25–27]

2. Ionic Gels. To study the effects of ionization of the NIPA polymer solutions on the phase separation, we have pursued the temperature dependence of proton NMR spectra in an aqueous (D_2O) solution of the NIPA polymers containing the same amount of ionizable groups as the gels, i.e., 32 mM sodium acrylate groups. The results are shown in Figure 12. The appearance of a new broad peak centered at 9.3 ppm is clearly seen at higher temperatures, and this peak coincides with that of the corresponding solid polymers. One important difference from the nonionic NIPA polymers is a marginal growth of this component ("solidlike aggregates") with rising temperature. This means that a great portion of the NIPA polymers persist in the form of separate molecules in water without forming aggregates. Of course, the appearance or disappearance of the new broad peak is extremely sensitive to the temperature, and new equilibria are quickly established. This fast kinetic behavior is the same as that of the nonionic NIPA polymers but completely different from that of the corresponding ionic gel.

A careful comparison of the spectral changes in the fully protonated and partially deuterated ionic gels reveals that (1) there is no appreciable change in the methylene and

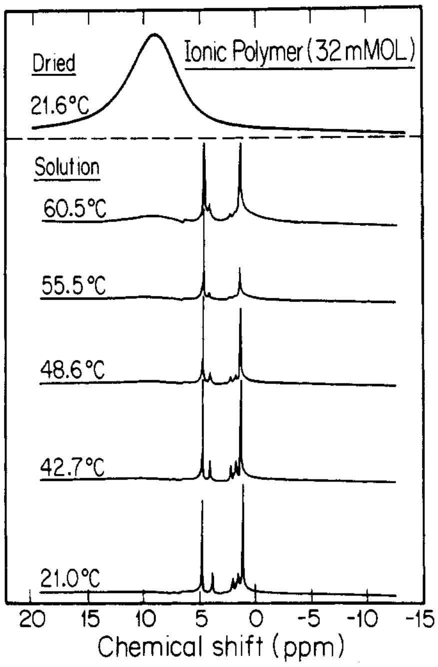

Figure 12. Proton NMR spectra of an ionic (32 mM) poly(*N*-isopropylacrylamide) polymer dissolved in D_2O and in dried states at different temperatures.

methyne proton peaks throughout the discontinuous phase transition, (2) the narrow methyl peak of the *N*-isopropyl group in the swollen state becomes a broadened peak in the collapsed state and continues to broaden with rising temperature, and (3) a substantial growth of the new broad peak within the collapsed state with increasing temperature was observed for the protonated gel. However, the intensity of the corresponding peak in the deuterated gel remains virtually constant with increasing temperature. The above results can lead to the conclusion that two different regions are recognized in the collapsed state; one region is solidlike aggregates represented by the new broad peak and the other consists of substantially mobile groups. Through the discontinuous phase transition, both *N*-isopropyl groups and groups of the main polymer chains in the swollen state become partially the solidlike aggregates upon the collapse of the gel. The other groups remain substantially mobile in both the collapsed and swollen states. However, the methyl groups turn gradually into the solidlike aggregates at temperatures higher than the phase-transition temperature.

The above-mentioned differences from those of the nonionic gel must arise from the ionic groups, which establish the Donnan potential. This potential contributes to the "stiffness" of the main polymer chains because of an increased interaction with hydrated cations. Thus, a general state of the main chains of NIPA polymers containing 32 mM ionic groups is such that certain portions of the chains are stiffer than the rest. The increased stiffness may contribute to constraints in the conformation of the polymer network in such a way that they fold over in a form where some rooms are available for bulky *N*-isopropyl groups to maintain still a substantial mobility. A comparison of the line widths in a manner similar to that of the nonionic gel gives the following values for the changes in distance by using the same assumptions: The changes are 3.2-fold and 1.50-fold in the protonated and partially deuterated gels, respectively. These are consistently smaller than those in the nonionic gel. As can be seen in Figures 2 and 4, the volume contraction by the phase transition in the ionic gel is greater than that in the nonionic gel. This stems from a more expanded volume in the swollen state of the ionic gel because the volume in the collapsed state is virtually identical in both gels. The volume contraction by the polymer networks in the ionic gel due to the phase transition is smaller than that in the nonionic gel. Therefore, the above larger volume change in the ionic gel must come from a larger amount of water retained in the swollen state of the ionic gel. The presence of the Donnan potential and the reinforcement of the water structure by sodium cations[28] should be responsible for retaining more water molecules in the gel system.

The stiffness of the main polymer chains of NIPA is also the reason why only the marginal growth of solidlike aggregates with rising temperature was observed in the aqueous solution of the ionic (32 mM) NIPA polymers.

3. Dynamic States of the Nonionic IA Polymers in Water (D_2O). As shown in Figure 8, the temperature dependences of proton T_1 for the nonionic NIPA polymers exhibited distinct differences between chemical groups. The T_1 values for the methyl protons in the *N*-isopropyl group increase with rising temperature. The same trend but accompanying a greater activation energy than the methyl group can be seen for the lone proton in the *N*-isopropyl group. On the other hand, temperature dependences of both methylene and methyne protons in the main polymer chains were completely opposite to the above two groups. Instead of applying rigorously whichever model[29,30] for describing molecular motions responsible for the spin-lattice relaxations, here we try to extract the general nature of molecular motions in view of the general behavior of the temperature dependence of T_1. For this purpose, it is sufficient to use a rudimentary theory[31]

$$\frac{1}{T_1} = K\left(\frac{\tau}{1 + \omega_0^{\,2}\tau^2} + \frac{4\tau}{1 + 4\omega_0^{\,2}\tau^2}\right) \qquad (1)$$

where τ is the correlation time. If the temperature dependence of τ is described by the expression

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(-\frac{E_a}{kT}\right) \qquad (2)$$

the temperature dependence of T_1 can be represented by several curves as shown in Figure 13. Here, E_a is the Arrhenius activation energy, k is the Boltzmann constant, and T is the absolute temperature in kelvin. The constant K in eq 1 includes the factors that are independent of temperature and Larmor frequency ω_0 and basically depends on the structural parameters. The T_1 is minimum when $\omega_0\tau \approx 0.67$. In this study, ω_0 is a fixed frequency, and thus the shift of the curves toward the high- or low-temperature side depends solely on the nature of the thermal motion represented by τ_0 and E_a. The absolute value of T_1 depends on the value of K. Thus, in order to examine the thermal nature of molecular motions from the temperature dependence of T_1, we basically pay attention to the location of the T_1 curve in the given temperature range.

The proton relaxation behavior of the *N*-isopropyl group follows the T_1 curve on the high-temperature side of the T_1 minimum (curve A″).

The T_1 behavior of the groups in the main polymer chains follows curve B′ in Figure 13. In other words, it implies that the *N*-isopropyl groups are a much more mobile, liquidlike state than the groups in the major polymer chains.

4. Dynamical Behavior of Nonionic and Ionic NIPA Gels. The temperature dependences of proton T_1 for the nonionic NIPA gel in the swollen state reveal certain characteristic differences from the nonionic polymers dissolved in water (Figure 9). The most notable change

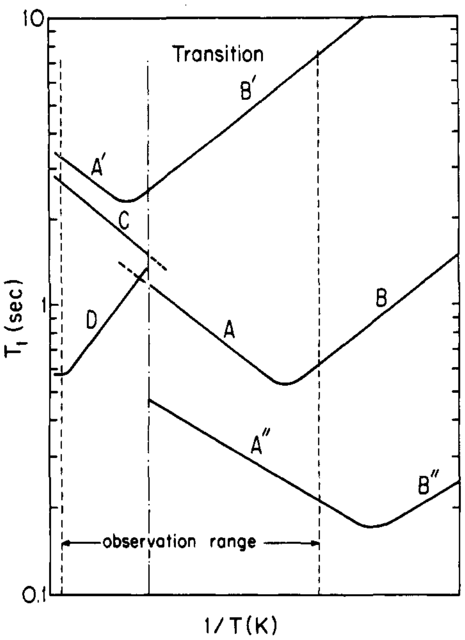

Figure 13. Conceptual sketch of the temperature dependence of spin-lattice relaxation time. When the value of ω_0 is fixed, the curve A-B shifts to curve A′-B′ if τ becomes long and shifts to curve A″-B″ if τ becomes short. The slopes in the semilogarithmic plot are determined by the value of E_a in eq 2. The absolute value of T_1 also depends on K in eq 1.

was that the T_1 minimum appeared at about 11 °C ($1/T = 3.5 \times 10^{-3}$ K^{-1}) for the methyne proton curve. The behavior of the methyl protons in the *N*-isopropyl group (curve A″) is similar to that for the polymers in water, and, thus, this group in the nonionic gel is dynamically quite mobile. Although the measurement of T_1 for the methylene protons was possible only at two higher temperatures, the trend is identical with that of the methyne proton. Thus, it can be said that the temperature dependence of T_1 for the protons in the backbone polymer chains shifted toward low temperature when compared to the T_1 curves for the same group of the NIPA polymers dissolved in water (the curve A′-B′ shifted to the curve A-B in Figure 13). This means that the dynamic state of the backbone polymer chains in the swollen state of the nonionic gel approaches the liquidlike state. The correlation time τ for the overall motions of methyne proton is easily estimated to be $\sim 3.0 \times 10^{-10}$ s at 11 °C (T_1 minimum) (Figure 9). This value falls in the common range of correlation times for molecular liquids.

While a mimimum was absent from the methyne proton T_1 curve in the ionic (32 mM) gel, the sign of the slope changes clearly between the gel and polymers in water (Figure 8 and 10). This corresponds to the shift from curve B′ to curve A″ in Figure 13. Approaching the "liquidlike" state of the backbone polymer chains in the swollen state is more evident in the ionic gel than the nonionic one.

There is certainly a systematic change in the activation energy for the methyl proton relaxation. They are 1.38, 1.46, 1.10, and 0.86 kcal/mol for the NIPA polymers in water, nonionic, ionic (8 mM), and ionic (32 mM) gels, respectively. The same similarity was also found for the methyne proton relaxation, that is, 1.37, 0.81, 0.73, and 0.71 kcal/mol, respectively. These facts are consistent with the above finding that the polymers are dynamically more "flexible" when incorporated within the gel than in water.

Turning now to the relaxation behavior in the collapsed state, the proton T_1 for both the methyl and broad peaks exhibits totally different temperature dependences. At the critical or transition temperature, there is clearly a gap in the T_1 values as well as a break in the slopes of T_1 curves. For systems other than gels, these are always observed when the first-order phase transition occurred. It is of interest to note that the chemical shift of the methyl group in the collapsed state (Figure 5) does not show such a distinct gap or break with respect to those in the swollen state. It is quite reasonable that the T_1 curve of the broad peak follows curve D in Figure 13. Even though the methyl T_1 in the ionic gel follows curve C in Figure 13, it is accompanied by a much higher activation energy as compared to that in the swollen state. Altogether, the collapsed state can be dynamically characterized as a solidlike state.

More NMR studies on gels near the critical point or first-order phase transition will be invaluable to further elucidate the local environmental changes of the polymer, solvent, and counterions.

Acknowledgment. The work was supported by the NSF, DMR-8920401, and the Kao Corp. TT. thanks a partial financial support from the NIH, RR-00995, and the NSF, DMR-8511789, through its support of the Francis Bitter National Magnet Laboratory.

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