Proton MASS-NMR: A New Tool To Study Thermoreversible Transition in Hydrogels†

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ABSTRACT: The lower critical solution temperature (LCST) phenomenon in equilibrium swollen poly(*N*-isopropylacrylamide) gel has been studied by solid-state ^{1}H NMR spectroscopy. ^{1}H MASS-NMR provides considerable insight into the study of thermoreversible transition in hydrogels. It is observed that the proton resonances are inhomogeneously broadened. As a result, MASS studies even at moderate spinning speeds (2 kHz) lead to valuable information to be discerned from the NMR spectra. A clear picture of the LCST is manifested by a transition in the ^{1}H static line-width measurements. The changes in the molecular mobility within the polymeric gel are primarily governed by polymer–solvent interactions. The suppression of LCST in the presence of a surfactant, sodium dodecyl sulfate, is also demonstrated.

Introduction

Hydrogels are polymeric gels, which are hydrophilic in nature. These gels are synthesized by polymerizing various monomers with small amounts of cross-linking agents.[1-3] Equilibrium swelling in water is an important characteristic of these hydrogels. Most of the hydrogels are known to undergo discontinuous-volume phase transitions in response to a very small change in pH,[4] ionic strength,[5] solvent composition,[6] or application of an small electric field across the gel.[7] Some of these hydrogels possess lower critical solution temperature (LCST) and therefore physically exhibit reversible swelling upon variation in the temperature and are termed as thermoreversible gels.[8,9] The discontinuous- and reentrant-volume phase transitions in thermoreversible hydrogels, such as poly(*N*-isopropylacrylamide) and its copolymers, have been demonstrated by Hirokawa and Tanaka.[10,11] The existence of reentrant-volume phase transition in this gel with respect to the solvent composition has been attributed to the fact that free energy is a nonlinear function of solvent composition.[12]

The control of swelling and deswelling of these hydrogels by passing a temperature zone, above and below LCST, has very important pragmatic implications. These hydrogels find wide-ranging applications as biomaterials such as matrices for controlled release delivery systems, implants, and regeneration of the gels employed in the separation and purification processes for biomolecules.[13]

A number of techniques have been used in the past to study transition phenomena in polymer solutions and gels,[14,15] including nuclear magnetic resonance spectroscopy.[16-18] However, earlier NMR methods relied on elaborate and often time-consuming proton relaxation measurements over a wide range of temperatures and concentrations. We show here that high-resolution solid-state NMR spectroscopy, especially proton ^{1}H MASS-NMR, is a powerful technique that can be used to probe the transition phenomena in polymeric gels. This technique has very high sensitivity and, in the presence of sample spinning at the so-called "magic angle",[19] offers good spectral resolution. The utility of this technique in elucidating the structure and degree of hydration of superabsorbent polymers was earlier demonstrated by us.[20]

In this paper, we have investigated the LCST phenomenon exhibited by poly(*N*-isopropylacrylamide) gel using ^{1}H MASS-NMR spectroscopy. The choice of this polymer was due to the relative ease with which it can be synthesized, combined with its simple structure from the NMR point of view. Besides this, the polymer is known to interact strongly with surfactant[21] such as sodium dodecyl sulfate (SDS), and this makes it possible to study the effect of surfactant on the LCST behavior of the hydrogel.

Experimental Section

Poly(*N*-isopropylacrylamide) gel was prepared by free-radical solution polymerization of *N*-isopropylacrylamide monomer, with a small amount of *N*,*N*′-methylenebis(acrylamide) as a cross-linking agent. The monomer was synthesized from acryloyl chloride and isopropylamine and was purified by distillation followed by recrystallization from the mixture of petroleum ether and toluene. A total of 10 g of *N*-isopropylacrylamide and 0.1 g of *N*,*N*′-methylenebis(acrylamide) were dissolved in 60 mL of deionized and distilled water. The polymerization was initiated and accelerated by using 60 mg of ammonium persulfate and 200 μL of tetramethylethylenediamine, respectively. The reaction was carried out at 20 °C in a 6-mm-diameter glass tube under nitrogen atmosphere. The polymerization took place in about 20 min. The gels were taken out of glass tube and cut into small slabs. These slabs were suspended in deionized, distilled water for 5–6 h in order to remove unreacted monomer. Finally, these slabs were dried in a vacuum oven at 40 °C. The dried gel was obtained as powder and was slightly opaque at room temperature (22 °C). It was found to have an equilibrium swelling capacity of 9.70 g of water/g of the polymer.

The LCST of this polymer was reported to be 32–33 °C.[22] We also measured the LCST of the polymer that we have synthesized and found it to be 42–45 °C. This measurement was done by monitoring the volume change of an equilibrium swollen gel as a function of temperature by using a temperature-controlled bath (Julabo, West Germany). It is likely that the difference in the LCST reported earlier and that measured by us originate from the differences in the molecular weight, degree of cross-linking, and composition of the polymer. Similar studies, which show the effect of these factors on LCST, have been reported in the literature.[8,23-25] However, the LCST we have measured is consistent with our NMR measurements.

All the ^{1}H MASS-NMR spectra were taken on a Bruker MSL-300 FT-NMR spectrometer operating at a proton frequency of 300 MHz. Proton signals were observed through the decoupler channel of a double-resonance CP-MASS probe, which gave a negligible ^{1}H background signal. Relevant spectral parameters are given in the captions to the figures. The $\pi/2$ pulse was typically of 6 μs. A high-resolution spectrum in the "liquid mode" was obtained by using a 5-mm dual-tune solution probe. The

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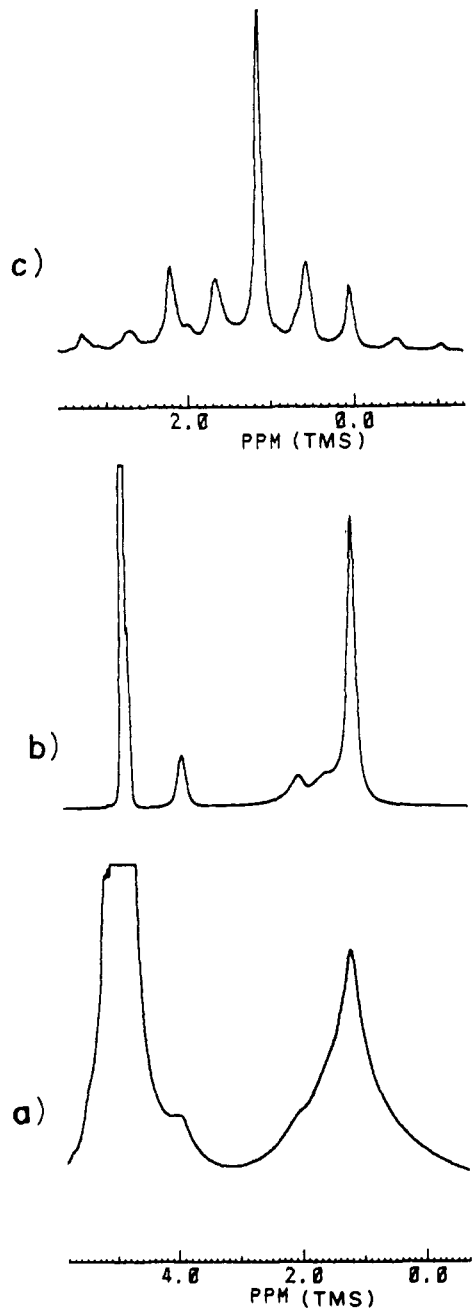

Figure 1. 300-MHz proton NMR spectra of poly(*N*-isopropylacrylamide) gel, equilibrium swollen in D_2O, showing the side-band pattern for methyl protons, taken with presaturation of the HOD peak at 4.8 ppm: (a) spectrum of nonspinning sample (400 scans); (b) MASS spectrum at ν_r = 2.1 kHz (264 scans); (c) slow MASS spectrum at ν_r = 160 Hz (100 scans).

gel samples were prepared by allowing the known weight of dry polymer to swell in D_2O (99.6%; BARC, Bombay) to its equilibrium value. In the case of the gel swollen in the surfactant solution (SDS), it was ensured that the surfactant was dissolved in D_2O before subjecting the gel to swelling. The samples were allowed to homogenize for 2 days before they were transferred to the MASS rotor. The temperature of the sample was varied by controlling the temperature of the bearing air in the MASS probe using a Bruker B-VT 1000 temperature controller. The temperature stability was ±1 °C.

Results and Discussion

We show in Figure 1a the room-temperature ^1H NMR spectrum of an equilibrium swollen poly(*N*-isopropylacrylamide) gel in D_2O, taken in high-resolution solution mode. The corresponding ^1H MASS-NMR spectrum is shown in Figure 1b. Comparison of these two spectra immediately suggests that sample rotation at the magic angle offers a considerable advantage in revealing the proton resonance of the backbone and side chains of the polymer, which are otherwise obscured when the sample is static. More than 1 order of magnitude line narrowing was brought about by MASS (see Table I), similar to that observed by us[20] in hydrolyzed starch-*g*-poly(acrylonitrile) and by others[26] in polystyrene–divinylbenzene gels. It may be noted from Figure 1a that considerable averaging of static proton dipolar line width, about 30 kHz, observed in a dry polymer sample, has been brought about in the equilibrium swollen gel sample by enhanced molecular mobility in the polymer due to solvent imbibation. in the absence of this internal averaging process, it would have been far more difficult to remove the proton dipolar broadening by external averaging at the magic angle with the sample rotation speeds that we have employed (2 kHz). The ^1H MASS behavior exhibited by the polymeric gel is similar to that observed by Oldfield et al.[27] in lipids and biological membranes. The remarkable observation here is that, even under slow MASS, the proton line breaks into a spinning-side-band manifold, the envelope of which maps the residual dipolar anisotropy.[28] This feature is demonstrated in Figure 1c where a slow MASS-NMR spectrum of the same polymeric gel, taken at a sample rotation speed of 160 Hz, is also shown. While the motional models that apply to lipid systems do not necessarily operate in the polymeric gel studied here, the inhomogeneous nature of proton line broadening is at once revealing, especially through observations of intense side-band formation in Figure 1c. A similar feature was noted by us in hydrolyzed starch-*g*-poly(acrylonitrile) gel, and inhomogeneous interactions were clearly demonstrated by us using the spin-echo technique.[20] The transformation of homogeneous interactions amongst abundant homospins (protons) to an inhomogeneous one is somewhat surprising but lends itself for a physical picture in the following way: A polycrystalline polymeric solid is characterized by a static dipolar Hamiltonian

$$\mathcal{H}_{HH}^{D} = \sum_{j>k} D_{jk}(\varphi)\,(3I_{jz}I_{kz} - \bar{I}_j\cdot\bar{I}_k) \qquad (1)$$

where the spin operators have their usual meaning and φ denote different rotor orientations. Equation 1 admits that the spin operators in parentheses for different pairs "ij" and "ik" do not commute and the interaction behaves homogeneously. The condition $\nu_r \gg (M_{HH}^2)^{1/2}$, where M_{HH}^2 is the proton second moment, has to be satisfied for line narrowing by MASS to occur. However, in the polymeric

Table I
^1H Spectral Parameters of Poly(*N*-isopropylacrylamide) Gel

type of proton	line width,[a] Hz static	line width,[a] Hz MASS	chemical shift,[b] ppm	spin–lattice relaxation time (T_1),[c] ms at 22 °C
$-CH_3$	264	47	1.2	610
$>CH_2$	498	43	1.6	
>CH	196	139	2.0	
$-CH(CH_3)_2$		81	3.9	766

[a] Line widths were determined by computer deconvolution of the overlapping resonances. [b] Chemical shifts with reference to TMS (external). [c] T_1 measurements were done by using a π-τ-$\pi/2$ inversion–recovery pulse sequence and on-line least-squares analysis of the data.

gel rapid rotational or reorientational motions of polymer segments reduce the contribution of the intramolecular dipolar interactions to $\mathcal{H}_{HH}^{D}$ by a great amount. Intermolecular interactions may not be averaged to that extent since lateral diffusion is absent. Nevertheless, the system can be considered to be "motionally narrowed"[29] and the condition $M_{HH}^2\tau_v^2 \ll 1$, where τ_v is the effective correlation time, will be obeyed, leading to a frequency isolation of coupled protons. More importantly, the molecular motion projects the various proton–proton interactions along the symmetry axis of the motion. The net result is that the dipolar interaction is scaled by $P_2(\cos\theta)$, where θ is the angle between the symmetry axis and H_0. The resulting "motionally averaged"[30] dipolar Hamiltonian becomes

$$\langle \mathcal{H}_{HH}^{D} \rangle = \frac{1}{2}(3\cos^2\theta - 1)\sum_{j>k}\bar{D}_{jk}(3I_{jz}I_{kz} - \bar{I}_j\cdot\bar{I}_k) \quad (2)$$

Equation 2 admits that the entire dipolar Hamiltonian is multiplied by common factor $P_2(\cos\theta)$ and the eigenfunctions of the averaged dipolar Hamiltonian are independent of θ, whereas the eigenvalues are proportional to $P_2(\cos\theta)$. In this new basis, the spin operators commute and the dipolar interaction $\mathcal{H}_{HH}^{D}$ behaves like an inhomogeneous interaction, such as the chemical shift. The resonance frequency under MASS is given by[31]

$$\nu(t) = \nu_0 \pm \sum_{i=0}^{2}\nu_i \cos(i\nu_r t) \quad (3)$$

where the first term on the right is the rotationally invariant part leading to the revelation of individual proton resonances at their isotropic chemical shifts and the terms in the parentheses denote the time-dependent part, modulated at $\pm\nu_r$ and $\pm 2\nu_r$, leading to the formation of spinning side bands on either side of the center band and carries the information about the residual dipolar anisotropy on the spinning-side-band intensities through the coefficients ν_i. Equivalently, in the time domain, one observes a train of rotational echoes,[32] the FT of which maps the side-band pattern, as clearly seen in Figure 1C.

The limiting MASS line widths of the different proton resonances, included in Table I, show that they are not the same for all protons, the largest observed being that of the backbone proton. Also they are a factor of 4 greater than the best resolution obtained on our well-shimmed magnet. It is unlikely that the MASS lines are lifetime broadened in view of long relaxation times measured by us (see Table I). Earlier work on cross-linked polymers[33] has shown that chemical shift dispersion effects play an important role, and it is likely that such effects and/or tacticity broadening determine the ultimate MASS signal resolution in poly(*N*-isopropylacrylamide) gel.

We show in Figure 2 the ^{1}H MASS-NMR spectra of poly(*N*-isopropylacrylamide) gel recorded at different temperatures above and below the LCST. A spinning speed of 2.1 kHz was employed so that interference from spinning side bands on the polymer proton resonances is eliminated. The room-temperature spectrum (22 °C, Figure 2a) has sufficient resolution to reveal the resonances from the distinct protonic sites within the monomeric unit of the polymer, the assignments of which are also shown. The relative intensities of the various peaks also confirm the protonic count within the monomeric unit. The strong signal at 4.8 ppm occurs at the exact chemical shift for a water proton from the residual HOD. Relevant spectral parameters are collected in Table I.

When the temperature is increased, intensities of all proton lines diminish due to broadening of signals. The

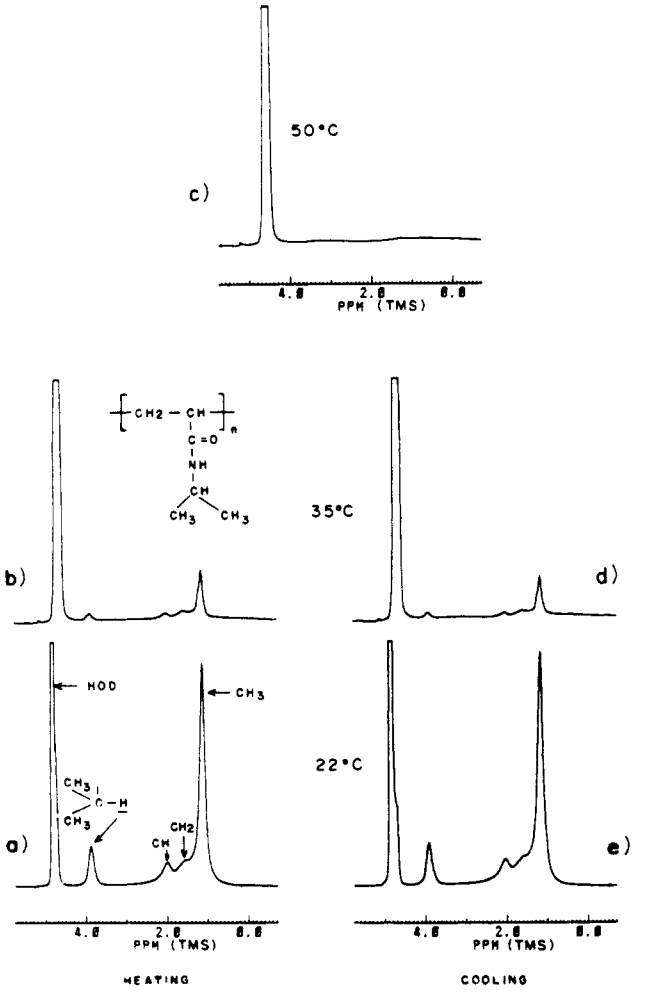

Figure 2. Effect of temperature on ^{1}H MASS-NMR spectra of poly(*N*-isopropylacrylamide) gel, equilibrium swollen in D_2O. The spectra were recorded at a spinning speed (ν_r) of 2.1 kHz (264 scans).

broadening is less severe at temperatures below LCST but becomes excessive once LCST is crossed. The behavior is very similar on the static ^{1}H spectra where external averaging by MASS is not enforced on the polymeric system and, therefore, reflects only the line narrowing by molecular motions. We have shown in Figure 3 the variation of static proton line width in the temperature range 22–50 °C. The ^{1}H resonance line width changes from a limiting value of 750 Hz at 22 °C to 3000 Hz at 50 °C, undergoing a sharp transition in the restricted temperature range of 40–44 °C. The line-width transition indeed mirrors the actual volume phase transition occurring in the gel but in a microscopic way through the associated molecular motions. Since the equilibrium swelling capacity of poly(*N*-isopropylacrylamide) gel changes as a function of temperature in the transition region,[34] decreasing with increasing temperature, solvent-induced mobility of polymer segments is progressively attenuated as the temperature is increased. The limiting value of the proton line width, viz., 3000 Hz, at temperatures above LCST shows that the proton resonance is still motionally narrowed, implying that not all water is exuded from the polymer matrix. Our results indicate that there is a dominance of polymer–solvent interactions below LCST, while at and above LCST, polymer–polymer interactions become more important. A similar inference had been drawn from light-scattering and small-angle neutron-scattering studies on LCST polymers.[35] It is also borne out from Figures 2 and 3 that spectral features are

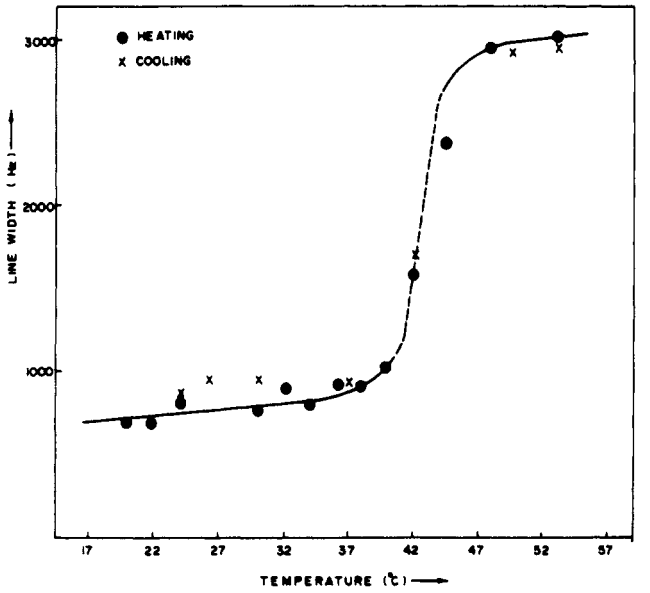

Figure 3. Variation of static proton line width of poly(*N*-isopropylacrylamide) gel, equilibrium swollen in D_2O, for the strong polymer signal at 1.2 ppm.

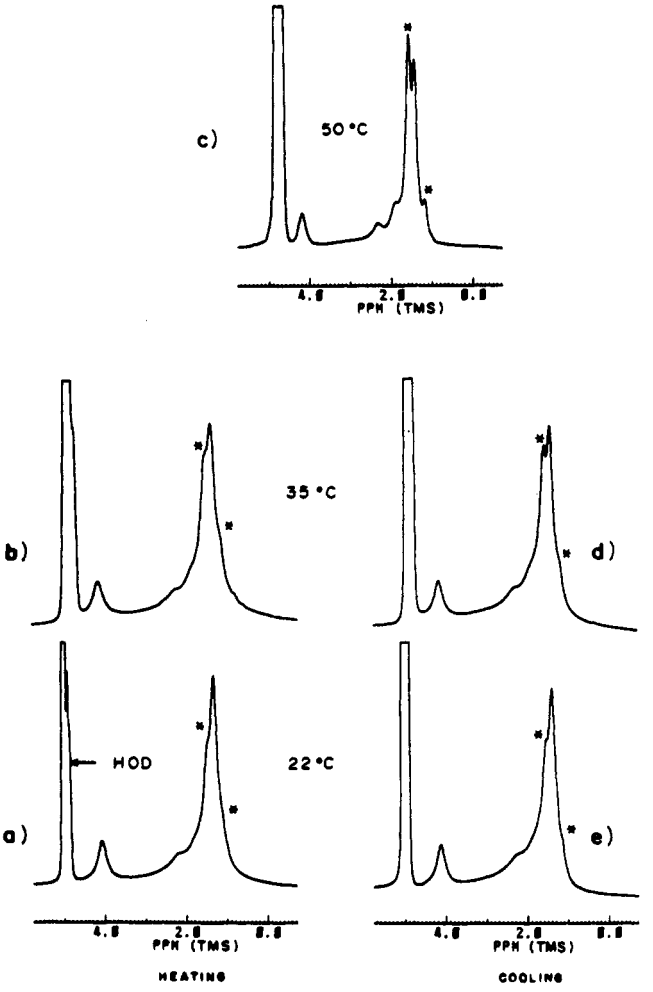

Figure 4. Effect of temperature on ^1H MASS-NMR spectra of poly(*N*-isopropylacrylamide) gel, equilibrium swollen in 1.0% SDS in D_2O. ν_r = 2.1 kHz (264 scans). (Asterisks indicate SDS signals.)

dependent only on temperature; viz., the spectra are superimposable at any given temperature regardless of whether the temperature was arrived at during a cooling or a heating cycle encompassing the LCST or otherwise (compare Figures 2a,e and 2b,d). This clearly reflects the thermoreversible nature of the hydrogel, the thermoreversibility being attributable to the reassociation of the excluded water with the polymer matrix upon a reversal in temperature.

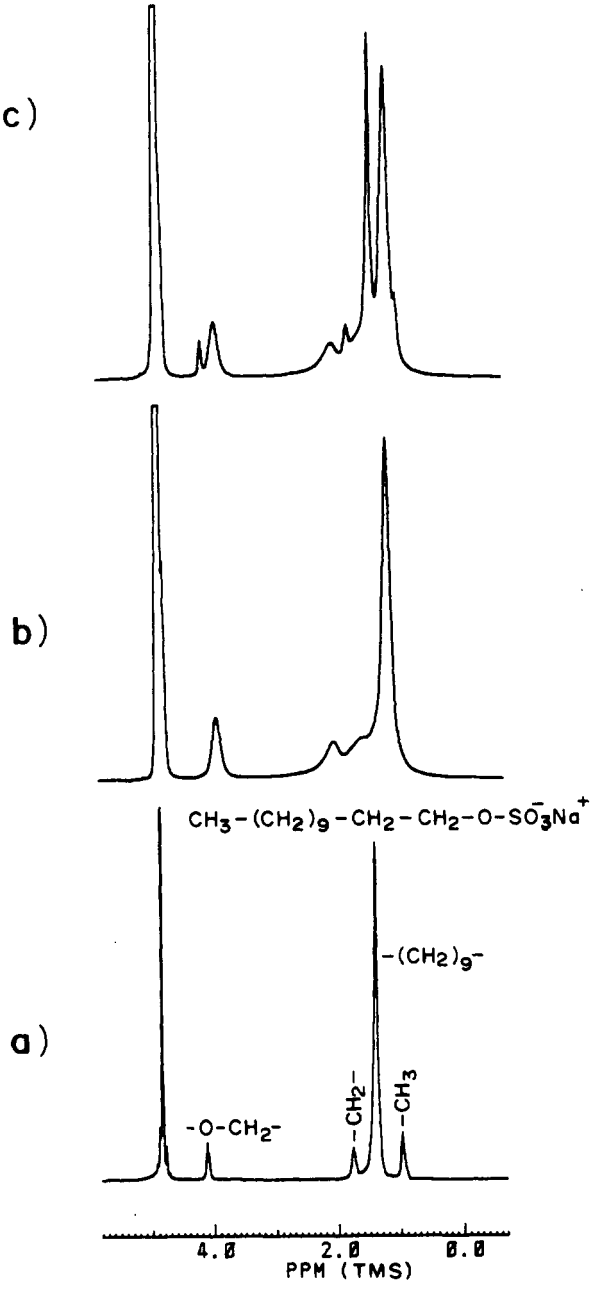

Figure 5. Identification of proton resonances due to SDS: (a) solution-mode ^1H spectrum of 1.0% SDS in D_2O; (b) ^1H MASS spectrum of equilibrium-swollen gel in D_2O (ν_r = 2.1 kHz); (c) arithmatic addition of a and b.

It has been noted that the viscosity of poly(*N*-isopropylacrylamide) solution increases severalfold in the presence of a surfactant such as sodium dodecylsulfate (SDS).[21] Further, the polymer is not precipitated from these solutions even on boiling. This has been ascribed to the interaction of the polymer with the surfactant through hydrophobic bonding.[36] The suppression of LCST in the presence of a surfactant can be monitored through ^1H MASS-NMR as well. We show in Figure 4 the temperature dependence of ^1H MASS-NMR spectra of poly(*N*-isopropylacrylamide) gel swollen to equilibrium in 1.0% solution of SDS in D_2O. As an aid in the identification of the polymer and SDS peaks, we further show in parts a and b of Figure 5 the room-temperature ^1H Bloch decay NMR spectrum of 1.0% SDS in D_2O and the ^1H

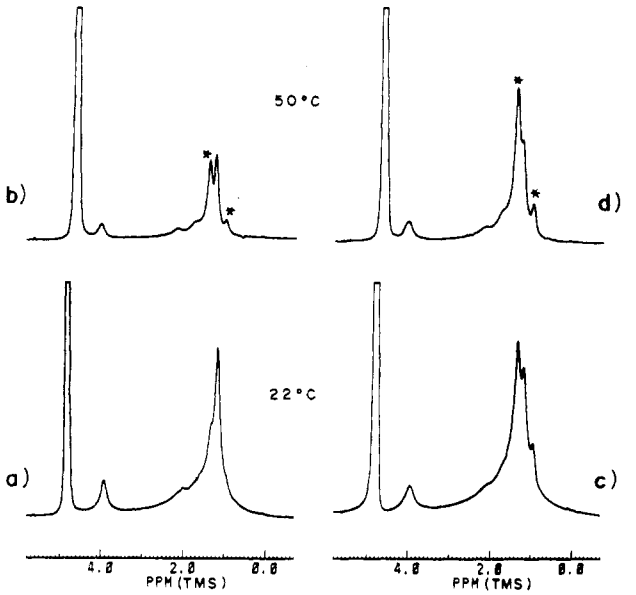

Figure 6. Effect of surfactant concentration on ^1H MASS-NMR spectra of poly(*N*-isopropylacrylamide) gel, equilibrium swollen in 0.1% (a and b) and 0.2% (c and d) SDS in D_2O at two different temperatures indicated. ν_r = 2.1 kHz (264 scans). (Asterisks indicate SDS signals.)

MASS-NMR spectrum of poly(*N*-isopropylacrylamide) gel, equilibrium swollen in D_2O. The arithmatic addition of these two spectra is also shown (Figure 5c) and compared with the room-temperature ^1H MASS-NMR spectrum of the polymeric gel, equilibrium swollen in 1% SDS in D_2O (Figure 4). The ^1H MASS-NMR spectra of the polymer gel in 1.0% SDS (Figure 4a) exhibit broader proton resonances than the corresponding arithmatically added spectra (Figure 5c). The broadening noticed in Figure 4a is presumably due to the interaction of SDS with the polymer, resulting in the broadening of the signals due to SDS or the polymer or both. Nevertheless, the SDS peaks can be identified and assigned as shown in Figure 4. The spectra shown in Figure 4 exhibit unaltered spectral features over the entire temperature range except for a slight improvement in the proton line resolution at 50 °C. Our results clearly indicate that no lower critical solution temperature behavior, formerly observed in the absence of surfactant, is now exhibited by the polymeric system in the presence of a surfactant. The marginal increase in the MASS spectral resolution at 50 °C (compare parts a and c of Figure 4), especially for the methyl protons, points to an enhancement of polymer chain mobility by thermal effects alone. Since LCST is suppressed and since the solvent is not excluded, the effect of increased temperature would be to reduce the residual dipolar couplings, further rendering MASS to be far more effective, in line with our observations.

We also examined the effect of surfactant concentration on the polymer by ^1H MASS-NMR. The spectra shown in Figure 4 are taken at a surfactant concentration well above the critical micellar concentration (cmc) (0.3%).[37] We show in Figure 6 the ^1H MASS spectra obtained at two concentrations (0.1 and 0.2%) below the cmc of SDS. The spectra show that, to a large extent, the spectral behavior resembles that for a surfactant free polymer. However, there is a small amount of the admixture of properties observed in Figures 2 and 4. Our observations indicate the possibility of the coexistence of both the phases, viz., a major one in which polymer–polymer interactions dominate (LCST envisaged) and a minor one in which polymer–solvent interaction dominates (LCST suppressed).

Conclusions

We have shown that ^1H MASS-NMR can be conveniently used to investigate the LCST phenomena and the polymer–surfactant interactions. The high sensitivity associated with the proton observation and the fine spectral resolution due to the application of the MASS technique offer considerable scope for similar studies in a variety of hydrogels that exhibit transition phenomena. The transition in the ^1H static line width of the polymer with respect to the temperature clearly reflects the thermoreversible volume phase transition in the gel through the effects of solvent-induced polymer mobility.

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