NMR Characterization of Absorbed Water in Equilibrium Swollen Hydrogel P(Am-NaA)

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ABSTRACT: The behavior of absorbed water in equilibrium-swollen poly(acrylamide-cosodium acrylate) [P(Am-NaA)] hydrogel is studied with ¹H nuclear magnetic resonance (¹H-NMR). The observed non-exponential decay of the spin–spin relaxation data manifests at least two distinguishable environmental states of the absorbed water in all samples. The component, characterized by the relatively shorter T_2 , is associated with the more tightly bound water; whereas the other, characterized by longer T_2 , might be a combination of near normal and loosely bound water. Attention is directed to the way in which relaxation times and the corresponding fraction of each type of water behave as a function of the crosslink density at 25°C. There is evidence of a sudden change of the crosslink state in P(Am-NaA) hydrogel at crosslink density of about 1.0%. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1203–1207, 1999

Key words: nuclear magnetic resonance; hydrogel P(Am-NaA); absorbed water; relaxation time

INTRODUCTION

Due to their biocompatibility, hydrogels have found numerous applications in the biomedical field. The characterization of the state of water in polymer hydrogels is fundamental in understanding the physical properties of hydrogels. Various methods have been used to study the state of water in polymers,¹ such as infrared spectroscopy, dielectric relaxation spectroscopy, and thermogravimetry, and, in particular, differential scanning calorimetry (DSC) and NMR, which have been used extensively to characterize the state and dynamics of water absorbed in polymer systems.

It is widely accepted that the states of absorbed water are classified mainly as "bound," "intermediate," and "free." Evidence of the existence of bound water in various water-polymer systems, as revealed in most DSC and NMR experiments, are based on the presence of nonfreezable water with constrained motion relative to free water, at temperatures far below ambient. The reduced mobility of nonfreezable water is generally recognized. However, in contrast to this general perception, Hoeve et al. reported that the mobility of bound water corresponding to nonfreezable water was higher rather than lower.¹⁻² And more recently, Ishikiriyame and Todoki concluded that the mobility of nonfreezable water was similar to that of free water at both 298 and 222 K.³

Studies to date find that the determination of the nature and amount of different water types in the polymers depends on the experimental method used and the influence of numerous factors, for example, swelling state, equilibrium or nonequilibrium conditions, temperature, and hys-

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teresis effects in the heating and cooling cycles.⁴ In the present work, the influence of the degree of crosslinking on the fraction and mobility of each type of water in equilibrium swollen poly(acryl-amide-*co*-sodium acrylate) [P(Am-NaA)] hydrogels is investigated.

We are aware that the description of the nature of adsorbed water has been refined to take into account the thermal equilibrium states of the hydrogel in different temperature ranges (for instance, see McBrierty et al.⁵). Any sensible discussion on equilibrium swelling state must not rely indiscriminately on information derived from events at temperatures far below 0°C.

In this study, proton NMR spin-lattice (T_1) and spin-spin (T_2) relaxation times are used to characterize water behavior, paying particular attention to the separation of the proton signal of adsorbed water from that of the polymer network.

EXPERIMENTAL

Spherical beads of P(Am-NaA) gels were prepared by the standard reverse suspension polymerization of acrylamide monomer and sodium acryliote in deionized water at 15°C under a nitrogen atmosphere, using paraffin oil as a continuous phase, and a small amount of N,N-ethylenebisacrylamide as a crosslinking agent. The radical polymerization was initiated by ammonium persulfate and accelerated by tetramethylethylencediamine. The polymerized beads were then washed several times with a large amount of deionized water to remove any unreacted monomer and lowmolecular-weight oligomers before drying as a powder.

All gel samples were prepared by allowing a known weight of dry polymer to swell in about 0.4 mL 99% D_2O for several weeks before NMR measurements.

All ¹H-NMR experiments were carried out on a Varian UNITY plus-400 FT-NMR spectrometer operating at a proton frequency of 400 MHz. Proton signals were observed through the decouple channel of a double-resonance ID (Indirect Detection) probe operating in the liquid mode. The $\pi/2$ pulse width for protons was 8.8 μ s. Spin–lattice relaxation times for 1H nuclei were measured by means of the inversion recovery [π - τ - $\pi/2$ -At (FID)] pulse sequence.⁶ The spin–spin relaxation times were measured by using a Carr–Purcell–Mciboom–Gill (CPMG) spin echo pulse sequence [($\pi/2$)_x-[τ -(π)_v- τ]_n-At].^{7,8}

RESULTS AND DISCUSSION

The proton signals of adsorbed water (sharp peak at 4.8 ppm) and hydrogel networks (dual peaks at about 2 ppm) are well-resolved [see Fig. 1(a)]. The present study at 400 MHz can resolve water and network proton signals, in contrast to earlier studies performed at lower resonance frequencies.

In order to ensure that the hydrogel samples are in their equilibrium swollen state during the measurements, the temperature of the sample is accurately kept at 25°C with an Oxford VI temperature controller equipped with the spectrometer. In P(Am-NaA) hydrogels, there exist hydrophilic groups, such as COO⁻ and CONH₂, which act as hydration sites. The adsorbed water is easily accessible to those hydrophilic groups, resulting in different water phases, which can be characterized by NMR. As compared with the single exponential decay of T_2 for pure water, in which the $\operatorname{Ln}(M_{\perp}) \sim \tau$ plot is linear, T_2 decay of adsorbed water in all the hydrogel samples with different crosslink densities (0.5, 5.0, and 10.0%) is multicomponent (see Fig. 2).

We find that at least two distinguishable spinspin relaxation times can be identified; that is, the experimental $M_{\perp} \sim \tau$ curves of adsorbed water can be described satisfactorily by a sum of two discrete exponential terms, as follows:

$$\begin{split} M_{\perp}(\tau) &= M_0 \sum_{j=1,2} P_j \exp(-\tau/T_{2j}) \\ &= M_0 f(\tau; \, P_1, \, P_2; \, T_{21}, \, T_{22}) \quad (1) \end{split}$$

in which the parameters P_j and T_{2j} are the fraction and component T_2 values of the *j*-components, respectively (j = 1, 2). The parameters in eq. (1) are determined by nonlinear least-square procedure, in which the sum of quadratic deviation, Δ^2 , between the calculated values, $M_0 f(\tau)$, and measured data, $M_{\perp}(\tau)$,

$$\Delta^{2} = \sum_{n=1}^{N} \left[M_{\perp}(\tau_{n}) - M_{0} f(\tau_{n}; P_{j}; T_{2j}) \right]^{2}$$
(2)

is minimized in the simulation.

The longer spin-spin relaxation time, T_{2L} , characterizes the relaxation behavior of the adsorbed water that is influenced least by the hydrogel network. This component is termed "associated" water, which might be a combination of



Figure 1 400-MHz ¹H-NMR spectrum of P(Am-NaA) recorded at 25°C: (a) in an equilibrium swollen state; (b) when excess surface water is removed by pressing the sample beads gently between sheets of absorbent paper.

both the so-called "near-normal" and "loosely bound" water. In Table I, we can see that T_{2L} increases with the decrease of the crosslink density of the sample up to ~ 4 s, which is comparable to the $T_2~(\sim 7~{\rm s})$ of pure water.

The shorter spin–spin relaxation time, T_{2S} , characterizes the "bound" (more tightly bound and highly dispersed) water. T_{2S} shows a relative weak tendency to decrease with the increase of the crosslink density in the range 1.0 to 10.0%, indicating more localized effects and an indication that the interaction between bound water and the network of hydrogel can be strengthened with an increase in the crosslink density within certain limits. As the crosslink density increases, T_{2S} reaches a maximum at $\sim 1.0\%$ before decreasing once again, perhaps because of a change of crosslink state in equilibrium-swollen P(Am-NaA) hydrogels.

For relaxation dominated by magnetic dipoledipole interactions between proton nuclei, and assumed isotropic rotational motion, the correlation time τ_c can be deduced from the following expression⁹:

$$\frac{1}{T_2} = \frac{3}{20} \left(\frac{\gamma^4 \hbar^2}{r^6} \right) \left(3\tau_c + \frac{5\tau_c}{1 + \omega^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega^2 \tau_c^2} \right) \quad (3)$$

where γ and ω are the gyromagnetic ratio of proton and Larmor frequency, respectively. The interproton distance of water r is taken as 1.54 Å. Correlation times deduced for T_{2S} and T_{2L} are listed in Table I. The longest correlation time of bound water $(\tau_C^{(B)} \sim 3.5 \times 10^{-11} \text{ s}$ in the 10.0% crosslink density sample) is about 20 times the correlation time of pure water ($\sim 0.22 \times 10^{-11} \text{ s}$). The shortest correlation time of associated water ($\tau_C^{(A)} \sim 0.4 \times 10^{-11} \text{ s}$ in the 0.5% crosslink density sample) is comparable to that of the pure water. For each sample, the differences in correlation time between the bound water and associated water is less than one order of magnitude. This difference is far lower than was observed in methacrylate hydrogels [$\tau^{\text{(free)}}$



Figure 2 Spin-spin relaxation for three hydrogel samples and pure liquid water (dashed line: fitted with the linear least-squares method).

 $\sim 10^{-11}$ s, $\tau^{(\rm intermediate)} \sim 10^{-9}$ s, and $\tau^{\rm (bound)} \sim 10^{-6}$ s],¹⁰ which indicates a less heterogeneous range of water mobility in P(Am-NaA).

Figure 3 shows some representative spin-lattice data for water protons in P(Am-NaA) hydrogel samples with different crosslink densities (10 and 1.0%). Spin-lattice relaxation is exponential throughout, and it is a function of the degree of crosslinking.

When excess surface water is removed by pressing the sample beads gently between sheets of absorbent paper prior to NMR observation, the proton signal of adsorbed water is considerably broadened [see Fig. 1(b) and contrast it to Fig.

Table I T_{2L} , T_{2S} and their Relative Proportions are Listed, Along with Correlation Times of a Series of Swollen Equilibrium Samples with Different Crosslink Densities

Sample	Crosslink Density (%)	$\begin{array}{c} T_{2l} \\ (\mathrm{S}) \end{array}$	$T_{2s}\left(\mathbf{S}\right)$	P_{2l}	P_{2s}	$(imes \ 10^{-11} \ { m S})$	$\stackrel{\tau_{2s}}{(\times \ 10^{-11} \ \rm S)}$	T_1 (S)
1	10.0	0.88	0.45	65.1	34.9	1.8	3.5	5.63
2	7.5	1.60	0.74	77.3	22.7	1.0	2.1	8.46
3	5.0	1.97	0.87	58.2	41.8	0.8	1.8	8.02
4	1.0	2.47	1.06	79.9	20.1	0.6	1.5	14.2
5	0.5	4.04	0.85	75.9	24.1	0.4	1.9	11.2



Figure 3 Signal decay: spin-lattice relaxation for two samples and pure liquid water.

1(a)]. Clearly, surface bulklike water is removed to leave a predominance of water that is perturbed by the hydrogel network.

The fact that two phases characterized explicitly by transverse relaxation $(T_{2S} \text{ and } T_{2L})$ coexist, whereas only single T_1 is observed, which is an indication that the spin-lattice relaxation of different phases is strongly coupled.

Similar behavior was found in water vapor adsorbed on silica gels and explained on the basis that the lifetime of water in adsorbed phases were so short that only an average T_1 could be experimentally observed.¹¹

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