PGSE NMR Studies of Water States of Hydrogel P(Am–NaA)

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ABSTRACT: The behavior of absorbed water in equilibrium-swollen poly(acrylamide-*co*-sodium acrylate) [P(Am–NaA)] hydrogel was studied using the pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) technique. The observed nonexponential decay of the PGSE signal can be described satisfactorily by a sum of three discrete exponential terms. The self-diffusion coefficient and amount each of three phases' water can be determined quantitatively. By analysis these data, the swelling ratio of hydrogel P(Am–NaA) system in an equilibrium swollen state can be determined. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 424–427, 2000

Key words: PGSE NMR; hydrogel P(Am–NaA); absorbed water; self-diffusion

INTRODUCTION

It is well known that the solvent, especially water, in swollen polymer gels is in the form of multiphase states. Various methods have been used to study the state of water in a polymer.[1] It is widely accepted that the states of absorbed water are classified mainly as "bound," "intermediate," and "free."[2] Evidence of the existence of bound water in various water–polymer systems is based on the presence of nonfreezable water, which is measured at temperatures far below zero.

Pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) is a convenient method for measuring self-diffusion coefficients and has been applied to study diffusion in a broad spectrum of physical situations.[3] The PGSE NMR technique offers the opportunity to study the molecular displacements directly under well-defined equilibrium conditions. Self-diffusion data provide uniquely detailed and interpretable information on molecular organization and phase structure.[4,5] Self-diffusion rates are quite sensitive to structural changes and to binding and association phenomena, in particular, for colloid and macromolecular systems in solution.[6,7]

In the present article, the PGSE experiment was used for the measurement of self-diffusion behavior of water in crosslinked poly(acrylamide-*co*-sodium acrylate) [P(Am–NaA)] gels. By analysis of the self-diffusion data, we can obtain the self-diffusion coefficients and the relative contents of the multiphase states of water in gels under well-defined equilibrium conditions. Therefore, we can determine the swelling ratio of a solvent-swollen hydrogel system in an equilibrium-swollen state.

EXPERIMENTAL

Spherical beads of P(Am–NaA) gels were prepared the same as in ref. 8. All gel samples were prepared by allowing a known weight of dry gel to swell in 0.4 mL 99% D_2O for several weeks before the NMR measurements.
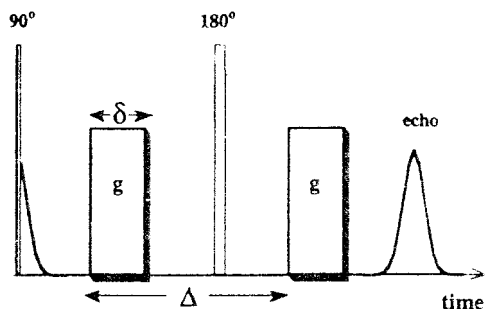
Figure 1 Pulse sequence used in a PGSE measurement.

Figure 2 Logarithm of the proton NMR signal intensity {Log(A/A_0)} versus {$\delta^2(\Delta - \delta/3)$} for the case of pure water.

The PGSE experiments were performed at 25°C (± 0.5) on a Varian UNITY plus-400M narrow-bore NMR spectrometer, operating at a proton frequency of 400.06 MHz. The spectrometer was equipped with a 5-mm PFG i.d. probe.

The pulse sequence[4] is shown in Figure 1. The magnetic-field gradient of duration δ is turned on and off between the initial 90° and refocusing 180° radio-frequency pulse and after the 180° pulse. The duration between the onsets of the gradient and radio-frequency pulse is termed Δ. Experiments were performed by varying the gradient width δ and keeping the gradient strength g and all other timing parameters constant. In processing the data of the experimental results to interpret the phase states, a simulated annealing Monte Carlo method was used.

gradient strength g can be calibrated in terms of the known self-diffusion coefficient of pure water. Figure 3 shows the same relationship as in Figure 2 for water absorbed in the swollen-state P(Am–NaA) gels with different crosslink densities. The curves in Figure 3 indicate that the diffusion of absorbed water is in the form of multiphase states.

We find that the experimental A/A_0 versus {$\delta^2(\Delta - \delta/3)$} curve of adsorbed water can be de-

RESULTS AND DISCUSSION

The quantitative relationship between echo attenuation and the self-diffusion coefficient is given by[9]

$$\text{Log}(A/A_0) = -D\gamma^2 g^2 \delta^2(\Delta - \delta/3) \qquad (1)$$

where D stands for the self-diffusion coefficient; γ, for the gyromagnetic ratio of the ^{1}H nucleus; A, for the signal amplitude; and A_0, for the amplitude with no gradients. Generally, from a series of measurements with increasing δ, the diffusion coefficient can be determined by fitting the data to eq. (1) with a non-linear least-squares fitting algorithm.

Figure 2 shows the plot of Log(A/A_0) versus the factor {$\delta^2(\Delta - \delta/3)$} of pure water. By calculating the slope of the straight line in Figure 2, we can obtain the value of $D\gamma^2 g^2$. Therefore, the
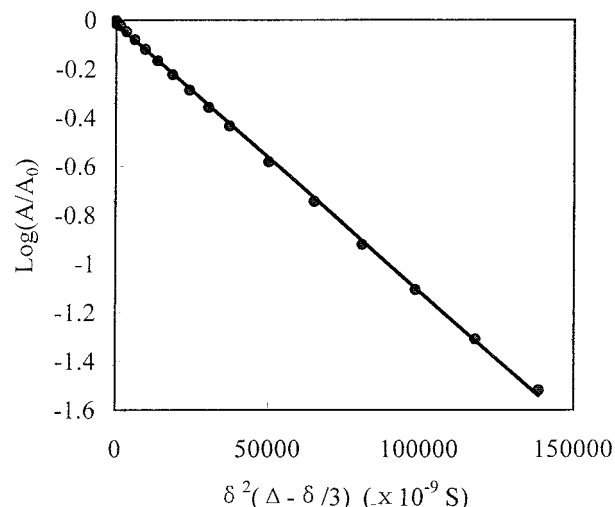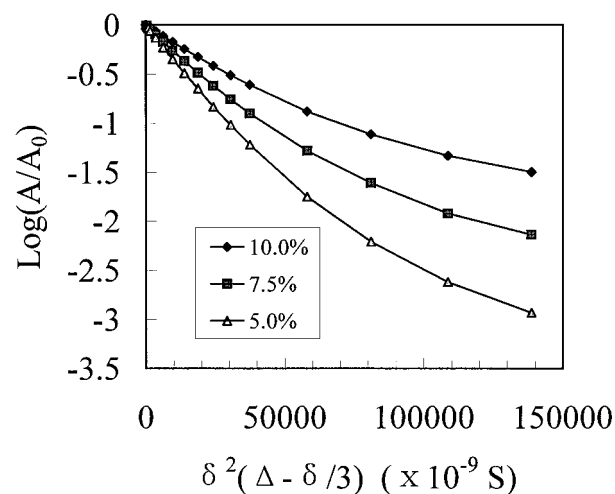

Figure 3 Logarithm of the proton NMR signal intensity {Log(A/A_0)} versus {$\delta^2(\Delta - \delta/3)$} for the case of absorbed water in hydrogels with different crosslink densities.

Table I   Self-diffusion Coefficient, D_i ($\times 10^{-9}$ m²/s) and Relative Content, P_I, of Water in Crosslinked P(Am–NaA) Gels and Swelling Ratio

Sample	Crosslink Density	$D_1(P_1)$	$D_2\ (P_2)$	$D_3\ (P_3)$	Swelling Ratio[a]	Swelling Ratio[b]
1	10.0	0.20 (13.7)	0.78 (54.2)	1.03 (32.1)	9.2	8.3
2	7.5	0.54 (22.5)	1.21 (46.8)	1.69 (30.7)	13.1	11.8
3	5.0	0.78 (14.8)	1.65 (65.0)	1.88 (20.2)	22.0	21.0
4	1.0	0.74 (10.1)	1.70 (54.4)	1.88 (35.5)	25.1	23.6

[a] Obtained by weight measurements.
[b] Obtained by PGSE measurements.

scribed satisfactorily by a sum of three discrete exponential terms:

$$A/A_0 = \sum_{j=1,3} P_j \exp(-D_j C x) \qquad (2)$$

where $C = \gamma^2 g^2$ is a constant, $x = \delta^2(\Delta - \delta/3)$; and the parameters P_j and D_j ($j = 1–3$) are the relative contents and self-diffusion coefficients of each phase state. The parameters in eq. (2) can be determined with a nonlinear least-squares fitting algorithm[8] (see Table I), and the minimized sum of quadratic deviation between the calculated values and measured data of each sample is less than 2.0.

In a previous article,[8] we studied the behavior of absorbed water in the same sample with spin–spin and spin–lattice relaxation times; the former also manifested nonexponential decay. In our experiments, we found that the nonexponential behavior of the self-diffusion data is more discriminative than that of the spin–spin relaxation. Therefore, we can describe the self-diffusion data with a sum of three discrete exponential terms, and the T_2 data, only with two. The self-diffusion coefficient is a measure only of the translational motion of the penetrant molecules and, therefore, should be a more direct indication of the mobility than the parameters T_1 and T_2.

The self-diffusion of absorbed water can be expressed with three coefficients, which characterizes that the gel networks has influence on the diffusion behavior of absorbed water. The component of water correspondingly with the slowest diffusion phase (with self-diffusion coefficients D_1 in Table I) is more tightly bound to the gel networks. Therefore, the motion of this component water is restricted and we think it is the so-called bound water. The component of water corresponding to the intermediate diffusion phase character-

izes that the gel networks has a loose bound to that component water and we call it "intermediate water." The fastest diffusion phase characterizes that the gel networks have no bound to this component water and we call it "free water."

The three-phase self-diffusion coefficients all decreased with increasing of the crosslink density; we think it is the obstruction effect that influences the diffusion behavior of each type of water. "The small migrating species have to make detours around the larger units in solution or gel."[10] The obstruction effect is increased with increasing of the crosslink density. The self-diffusion coefficient of free water is the same as that of pure water [1.88×10^{-9} m²/s [ref. 11] at lower crosslink density, which indicates that the obstruction effect is much weaker at a lower crosslink density. The difference in the self-diffusion coefficient between the bound water and free water and that between the high and low crosslink density are all less than one order of magnitude, which indicates that the obstruction effect and the direct interactions between water and the gel network[10] is in the same order and also that the binding of the water on the sorption sites of the gel networks is not very strong.

Peschier et al.[12] studied the diffusion of water in PHEMA hydrogels; they concluded that the total water phase in a gel diffuses as one homogeneous phase. The difference between them and us may be due to the difference in hydrogel systems.

The plot of the content of bound and intermediate water absorbed in 100 g of dry polymer versus the crosslink density is shown in Figure 4. The content of the two types of water and the sum of the two all decreased with increasing of the crosslink density, which indicates that the sorption sites decreased with increasing of the crosslink density.
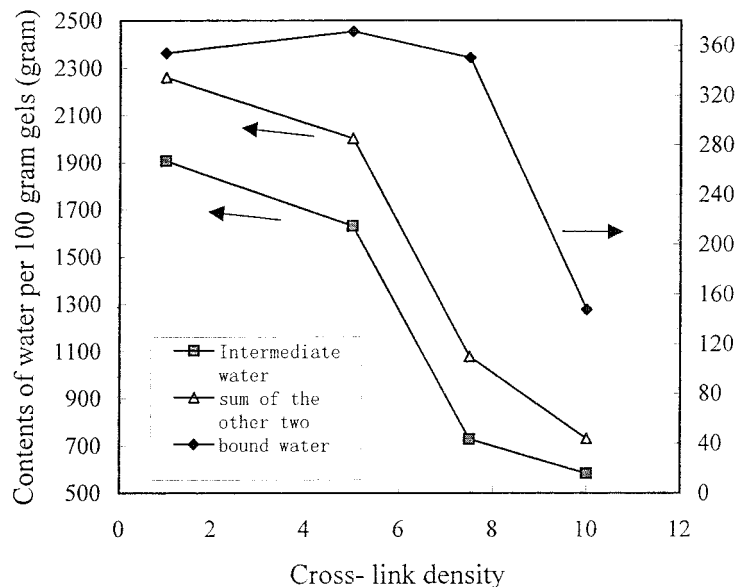
Figure 4 Amount of bound water and intermediate water versus the crosslink density.

The swelling ratio in water is defined as the mass ratio of swollen gel$_{LSG}$ to dry gel (dg). If we think that the bound and intermediate water are water inside the gel$_{wg}$ beads, where the free water is outside the gel beads, then the swelling ratio can be expressed as

$$R_w = \frac{m_{sg}}{m_{dg}} = \frac{m_{dg} + m_{wg}}{m_{dg}} = 1 + \frac{m_{wg}}{m_{dg}}$$

$$= 1 + \frac{p_1 + P_2}{m_{dg}} \times m_w \quad (3)$$

The swelling ratio calculated by eq. (3) and that by measuring the weights are also listed in Table I. We can see that they are in good agreement.

CONCLUSIONS

We studied the states of absorbed water in equilibrium-swollen P(Am–NaA) hydrogel using the PGSE NMR technique, which offers the opportunity to study the molecular displacements directly under well-defined equilibrium conditions. The self-diffusion coefficient and content of the three phases of water can be determined quantitatively. The swelling ratio of the solvent-swollen hydrogel system can be determined through simulation of the PGSE NMR data.

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