

Studies on Dynamic Behavior of Water in Crosslinked Chitosan Hydrogel

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ABSTRACT: The dynamic behavior of water in crosslinked chitosan (cr-CS) was studied at the molecular level by proton nuclear magnetic resonance (¹H-NMR) spectroscopy and positron annihilation lifetime spectroscopy (PALS). Proton line width was used as a direct parameter of local mobility during swelling. The dynamic behavior of water in hydrogel can be described by the two following processes: physical movement along free volume cavities in network and binding with hydrophilic groups of hydrogel. The formation of bound water and the effect of water on polymer network were correlated with the relaxation of hydrogel network. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 983–988, 1998

Key words: chitosan hydrogel; water behavior; ¹H-NMR; PALS

INTRODUCTION

Hydrogel is a kind of soft and wet material, and its properties are determined by the polymer network and water contained. Since the mobility and freezing–fusing behavior of water in hydrogels are different from those of free water, the study of the water state will be very helpful for understanding the structures and properties of hydrogels. Many methods, such as differential scanning calorimetry (DSC),^{1–3} nuclear magnetic resonance (NMR),^{4–6} Raman spectroscopy,^{7–8} and dielectric relaxation spectroscopy,^{9–10} etc., have been used to study the state of water in hydrogels. However, most studies have been done under

equilibrium condition, and the dynamic behavior of water during swelling is seldom approached. In a recent article, the dynamic swelling–dissolution process in a rubbery polymers has been probed through *in situ* ¹H-NMR measurements.¹¹ The change of proton line width can be used as a direct measure of the local mobility in swelling system, since this change emanates from a spatial averaging of local spin interactions by polymer motions.

The positron annihilation lifetime Spectroscopy (PALS) measurement is a powerful method to estimate the size and intensity of the free volume cavity and its size distribution in polymers.^{12–13} The ortho-Positronium (o-Ps) lifetime (τ_3) enhances with an increase in the size of free volume cavity, while the intensity I_3 of o-Ps is proportional to the number density of the cavities. The correlation between the mean radius of free volume R in polymers and τ_3 is expressed in a semi-empirical equation,¹⁴ as follows:

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$$\lambda = \tau_3^{-1} = 2[1 - R/R_0 + (1/2\pi)\sin(2\pi R/R_0)]$$

where $R = R_0 - \Delta R$ is the radius of the free volume, and $\Delta R = 1.656 \text{ \AA}$ is an empirical parameter that was obtained by fitting the measured annihilation lifetimes of cavities with known sizes, τ_3 and R , are expressed in nanoseconds and angstroms, respectively.

Several notable applications of PALS to polymeric materials, for example, hole size, content, distribution, and anisotropic structure have been reviewed by Jean,¹⁵ but less work has been done on hydrogels.^{16,17} Ito et al.¹⁶ correlated the volume phase transition of polymer gel with the variations of size and contents of free volume. Hodge et al.¹⁷ concluded that water affected the free volume characteristics of PVA in a manner depending on the state of water within the polymer.

Chitosan is a naturally occurring poly(amino-saccharide) with a repeating unit of 2-amino-2-deoxy- β -D-glucan and, which has been reported to be a promising polymer in medical and biomedical areas.¹⁸ In this article, the dynamic behavior of water in crosslinked-Chitosan (cr-CS) hydrogel was investigated by means of $^1\text{H-NMR}$ and PALS. The proton line widths of water and main polymer chain were monitored at the same time during swelling of cr-CS. The variations of o-Ps lifetime (τ_3) and intensity (I_3) with water content were also measured with PALS.

EXPERIMENTAL

Materials

Chitin (from crab shells) was purchased from Sigma Chemical Co. (Saint Louis, MO, USA). Preparation and characterization of chitosan have been reported previously.¹⁹ The *N*-deacetylation degree (DD) and the viscosity-average molecular weight of the chitosan are 72.9% and 2.3×10^6 , respectively. Glutaraldehyde is a biochemical reagent, and other reagents are at analytical grade.

Synthesis of Crosslinked Chitosan Hydrogel

The details of synthesis of cr-CS hydrogel have been described elsewhere.²⁰ 1 g chitosan was dissolved in 0.25N acetic acid solution, then the appropriate quantity of 0.5 wt % glutaraldehyde so-

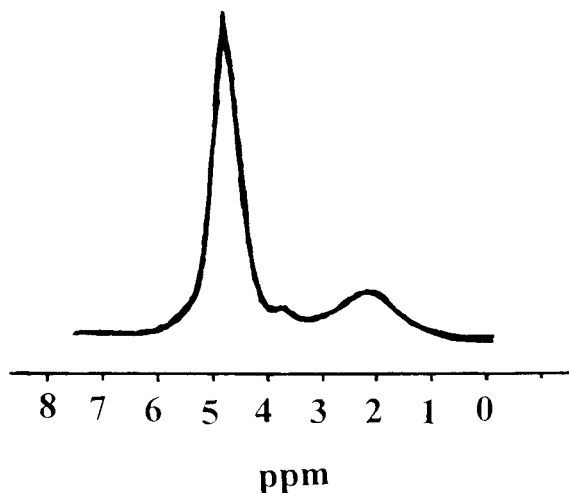


Figure 1 $^1\text{H-NMR}$ spectra of cr-CS hydrogel.

lution was added with agitation. The mixture was poured into a frame mold and maintained at 45°C for film formation. The film obtained was swollen in a $\text{pH} = 7.0$ buffer solution of potassium dihydrogen-phosphate and disodium hydrogenphosphate at 37°C for 4 h to reach equilibrium and then dried under vacuum at 70°C for two days.

$^1\text{H-NMR}$ Measurements

The NMR measurements were carried out on Varian UNITY plus-400 superconductor NMR spectrometer. Hydrogel samples were cut into pieces for NMR measurements. The small pieces, 0.12 and 0.16 g, were put into a 5 mm NMR tube; and 0.36 and 0.96 g D_2O was poured into the tube, respectively; then the line widths were measured directly from the spectra at 22°C .

Positron Annihilation Lifetime Spectroscopy

Hydrogel samples were immersed in the swelling medium at 22°C for different time intervals until a variety of water content samples were available for PALS testing. The PALS measurements were performed using an EG&G Ortec fast-slow coincidence system with a ^{22}Na resolution of 250 ps . Data were collected at 22°C using a $20 \mu\text{Ci}$ ^{22}Na kapton source sandwiched between two identical pieces of the samples. 2×10^6 counts were collected for each spectra, and 1×10^7 counts were collected for the spectra used for continuous lifetime distributions. The lifetime spectra were resolved into three components by using the program PATFIT-88, and the lifetime distributions

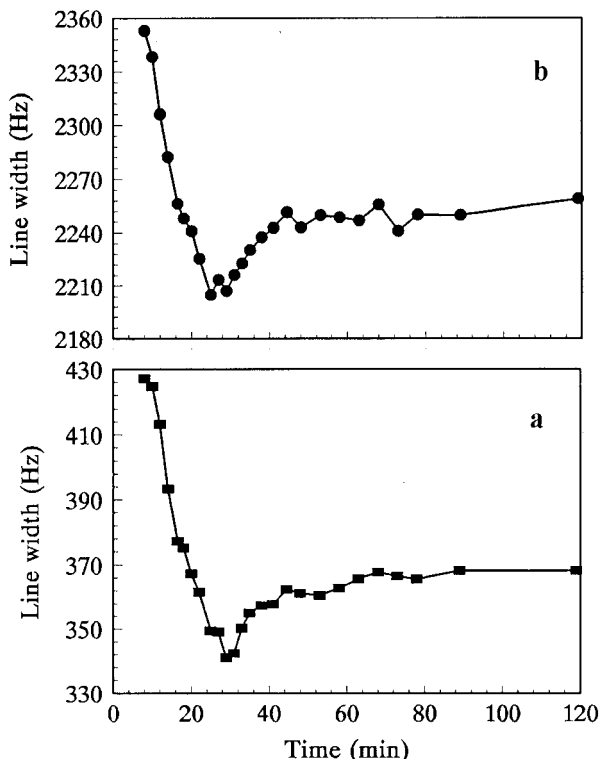


Figure 2 Variation of the (a) proton line width of water and (b) main polymer chains against time during swelling of cr-CS hydrogel with a low water content of 300 wt %.

were obtained by the Laplace Inversion of pick-off decay curve of *o*-Ps using the CONTIN computer program. The microcomputation of the program CONTIN was completed in the Laboratory of Nuclear Analysis Techniques, Chinese Academia Sinica.

RESULTS AND DISCUSSION

¹H-NMR Studies

The change in line width provides information about the dynamics of water molecules and their local environments. Generally, the structural organization of absorbed water is sensitive to polymer mobility,²¹ which has been demonstrated to be affected by water content, so we investigated the dynamic variation of water in cr-CS hydrogels with different water content.

The ¹H-NMR spectra of cr-CS hydrogel is shown in Figure 1. Two proton peaks in Figure 1 can be observed as follows: the one at 4.8 ppm for water, and the other for protons of polymeric backbone.

Figure 2 shows the plots of variation of the pro-

ton line width of water and main polymer chains against time during swelling of cr-CS with a low water content of 300 wt %. In the early swelling stage, the higher value of water proton line width, 400 Hz, implies that the movement of water molecules in cr-CS hydrogel is restricted considerably. Upon swelling, there is a rapid decrease in line width of water, then a little increase [cf. Fig. 2(a)]. The line width narrowing with time is indicative of the enhancement of internal mobility versus time.¹¹ Due to the low value of *o*-Ps lifetime (τ_3) of cr-CS hydrogel (cf. Fig. 3), that is, low radius (R) of the cavities, the entry of water will enforce the polymer network to relax. As a result, the mobility of water increases, and the proton line width declines. The relaxation of network is also reflected in the reduced value of proton line width for main polymer chain [cf. Fig. 2(b)].

The later enlargement of water proton line width suggests a reduced mobility of water. It seems to be contradictory to the relaxation of hydrogel. The most likely explanation is that the state of water has changed. From the view of mobility, the state of water in the hydrogel has been classified into the following three types⁴: bound water, intermediate water, and free water. Because the line width of the bound water in the hydrogel was estimated to be in the order of 16 KHz,⁵ the formation of bound water will greatly contribute to the total line width. We propose that the increase of line width may be due to the increasing amount of bound water. At the beginning of swelling, it is difficult for water molecules to

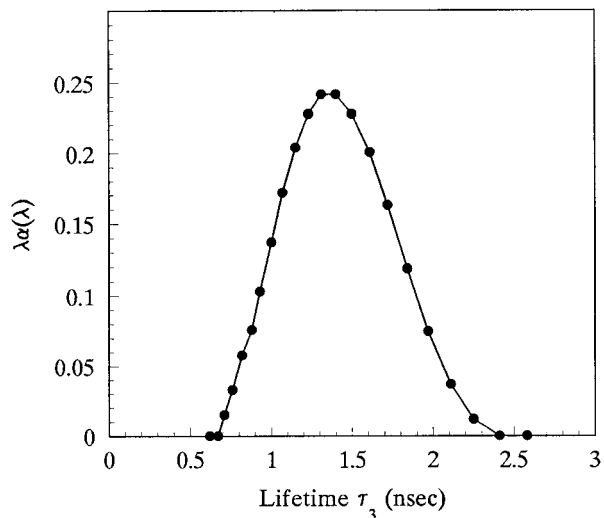


Figure 3 *o*-Ps lifetime distribution function of cr-CS xerogel.

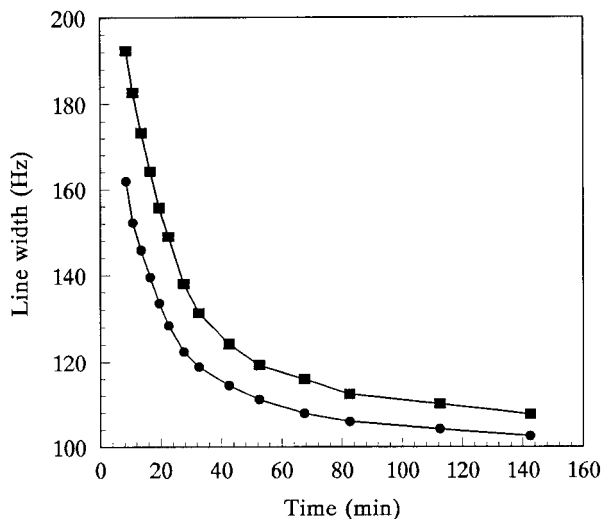


Figure 4 Plots of (■) proton line width of water and (●) main polymer chains of cr-CS hydrogel with high water content of 600 wt % as a function of time.

access hydrophilic groups of the dense cr-CS network, and most water molecules exist in a free state. With the help of relaxation of segments, more water molecules can enter in the network freely and bind to hydrophilic groups via hydrogen bonding, which results in an increase in the amount of bound water. It is worthy to note that the line width of main polymer chain protons is also enhanced after the initial reduction. It may be attributed to the state of water in hydrogel. After 30 min of swelling, the water molecules are entirely incorporated in cr-CS hydrogel network when the water content is lower. As a result, there is not enough free water to offer for the mobility of the water itself, and the polymer chain segments.

For the cr-CS system with low water content, two processes are observed during swelling: physical movement of water, and formation of bound water. In fact, the two processes take place at the same time, and which one dominates over swelling depends on the structure of hydrogel network.

The plots of proton line width of cr-CS hydrogel with high water content of 600 wt % as a function of time are shown in Figure 4. In comparison with the case of hydrogel in low water content, smaller values of line width were determined, which indicates that the mobility of water molecules and polymer chains obviously relate to relaxation of network. On the other hand, it further demonstrates that proton line width is a sensitive indicator of internal mobility. The line widths of water and polymer chain decrease rapidly, then level off. It is apparent that the physical movement of

water dominates the swelling process when water uptake reaches to a high enough level.

PALS Analysis

The dependence of τ_3 and I_3 on the water content of cr-CS hydrogel in distilled water is shown in Figure 5. The steady increase of τ_3 and I_3 was observed along with the enhancement in water content; since the measured values of τ_3 and I_3 are average values of the binary system, which is composed of water and polymer network, appropriate explanation of the data will have the aid of a model proposed by Hodge et al.¹⁷ They assumed that the observed values of τ_3 and I_3 are the sum of the weighted contribution of annihilations in bulk water and in polymer free volume cavities, as described by eqs. (1) and (2), respectively.

$$\tau_{3(\text{net})} = A\tau_{3(\text{water})} + (1 - A)\tau_{3(\text{polymer})} \quad (1)$$

$$I_{3(\text{net})} = AI_{3(\text{water})} + (1 - A)I_{3(\text{polymer})} \quad (2)$$

where A is the mass fraction of bulk water. The assumption is made that τ_3 and I_3 of water in

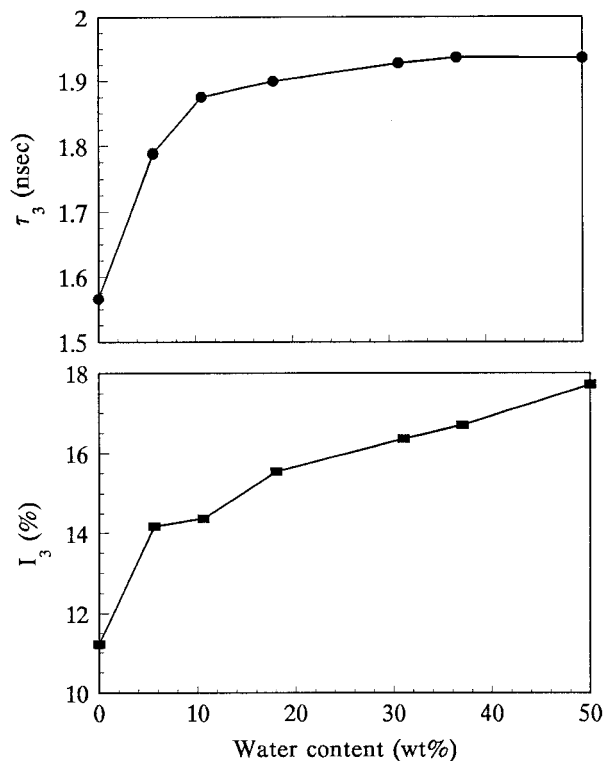


Figure 5 Dependence of o-Ps average lifetime (τ_3) and o-Ps intensity (I_3) of free volume cavities on water content of cr-CS hydrogel in distilled water.

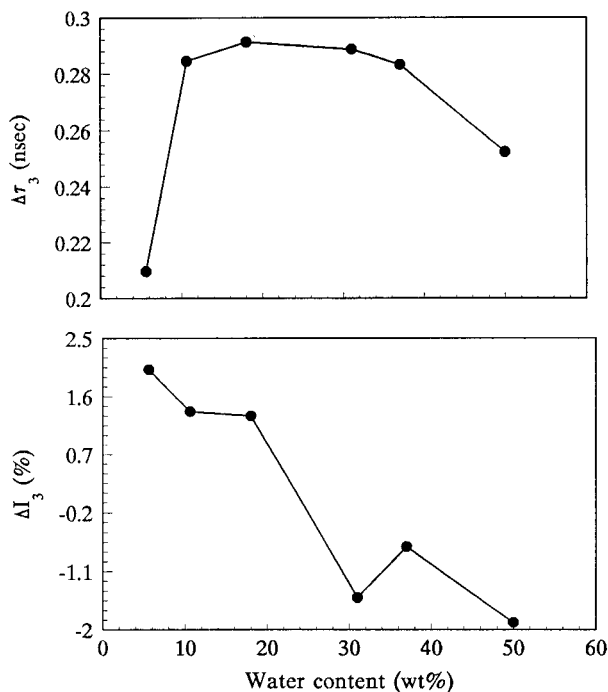


Figure 6 Plots of $\Delta\tau_3$ and ΔI_3 against water content of cr-CS hydrogel in distilled water.

polymer are equal to that of bulk water at the same temperature and are constants as a function of concentration. $\tau_{3(\text{water})}$ and $I_{3(\text{water})}$ are taken as 1.80 ns and $28 \pm 2\%$, respectively.

According to eq. (1), the maximum value of $\tau_{3(\text{net})}$ should be 1.80 ns, while the experimental value of $\tau_{3(\text{net})}$ in cr-CS hydrogel surpassing 1.80 ns when water content reaches 10%. It is probable that part of the water molecules absorbed by the network form clusters, which force the rigid network to spread apart, enlarging free volume cavities.¹⁷

As for τ_3 and I_3 , they begin to increase at extremely low water content. Many investigations^{21,22} have shown that water molecules exist in an isolated state, i.e., bound water, when the water content is lower. If so, the value of τ_3 and I_3 would not increase due to the fact that o-Ps pickoff occurs in bulk water only if water clusters have reached a critical size.¹⁷ Therefore, we suggest that individual water molecules bonded to the hydrophilic groups via hydrogen bonding coexist with water clusters in the early stage of swelling. This interpretation is consistent with the result of ¹H-NMR discussed in the last section.

In order to further clarify the dynamic behavior of water during swelling, the values of $\tau_{3(\text{net})}$ and $I_{3(\text{net})}$ were calculated according to eqs. (1)

and (2) under the assumption that the value of $\tau_{3(\text{polymer})}$ and $I_{3(\text{polymer})}$ is constant as a function of water content. The difference between calculated values of τ_3 , I_3 , and measured ones are plotted as a function of water content in Figure 6. The positive value of $\Delta\tau_3$ and ΔI_3 indicate that the free volume of polymer network is not constant, and the relaxation of network leads to an increase of free volume. It is worthy to note that there is a turning point at 31% water content, at which ΔI_3 becomes negative and $\Delta\tau_3$ reaches a maximum. This may be due to the gradual formation of bound water during swelling. Because o-Ps pickoff cannot occur in single water molecule, the measured values of τ_3 and I_3 of hydrogel will definitely decrease with the increase of water molecules bonded to the hydrophilic groups of cr-CS network. This interpretation strongly supports the results of ¹H-NMR.

CONCLUSION

Dynamic behavior of water in cr-CS hydrogel can be described as the following two processes: physical movement along free volume cavities of network, and formation of bound water with hydrophilic groups of network. Which process dominates swelling depends on the structure of the hydrogel. Bound water is likely to impede the mobility of the main polymer chain, especially for hydrogel with low water content.

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REFERENCES

1. A. Takizawa, T. Kinoshita, O. Nomuram, and Y. Tsujita, *Polym. J.*, **17**, 747 (1985).
2. M. B. Ahmad and M. B. Huglin, *Polymer*, **35**, 1997 (1994).
3. D. S.-G. Hu and M. T. Lin, *Polymer*, **35**, 4416 (1984).
4. F. X. Quinn, E. Kampff, G. Smyth, and V. J. McBrierty, *Macromolecules*, **21**, 3191 (1988).
5. Y. N. Atsuko, I. Kazuhiko, T. Minoru, and T. Hiroshi, *J. Appl. Polym. Sci.*, **39**, 2443 (1990).
6. J. Maquet, H. Thévenean, M. Djabourov, J. Leblonk, and P. Papon, *Polymer*, **27**, 1103 (1986).

7. B. H. Stuart, *Polym. Bull.*, **35**, 727 (1995).
8. B. H. Stuart and D. R. Williams, *Polymer*, **35**, 1326 (1994).
9. A. Kyritsis, P. Pissis, and J. Grammatikakis, *J. Polym. Sci., Part B: Polym. Phys.*, **33**, 1737 (1995).
10. M. B. Ahmad, J. P. Omahony, M. B. Huglin, T. P. Davis, and A. G. Ricciardone, *J. Appl. Polym. Sci.*, **56**, 397 (1995).
11. I. Devotta, V. Pvemnath, M. V. Badiger, P. R. Rafamohanan, S. Ganapathy, and R. A. Mashelkar, *Macromolecules*, **27**, 532 (1994).
12. C. M. McCullagh, Z. Yu, A. M. Jamieson, J. Blackwell, and J. D. Mcgervey, *Macromolecules*, **28**, 6100 (1995).
13. L. Xie, D. W. Gidley, H. A. Hristov, and A. F. Yee, *Polymer*, **35**, 14 (1994).
14. H. Nakanishi, S. J. Wang, and Y. C. Jean, in *Positron Annihilation Studies of Fluids*, S. C. Sharma, Ed., World Science, Singapore, 1988, p. 292.
15. Y. C. Jean, *Mater. Sci. Forum*, **59**, 175 (1995).
16. K. Ito, Y. Ujihira, T. Yamashita, and K. Horie, *Abstract for 4th International Symposium on Polymer Gels*, Tsukuba, Japan, 1995, p. 83.
17. R. M. Hodge, G. H. Edward, G. P. Simon, and A. J. Hill, *Polym. Prep.*, **34**, 839 (1993).
18. T. Sannan, K. Kuritta, K. Ogura, and Y. Iwakura, *Polymer*, **19**, 458 (1978).
19. K. D. Yao, T. Peng, M. F. A. Goosen, J. M. Min, and Y. Y. He, *J. Appl. Polym. Sci.*, **48**, 343 (1993).
20. Y. L. Guan, L. Shao, and K. D. Yao, *J. Appl. Polym. Sci.*, **61**, 2325 (1996).
21. H. W. Starweather, in *Water in Polymers*, S. P. Rowland, Ed., ACS Symposium Series 127, American Chemical Society, Washington, DC, 1980, p. 433.
22. E. G. Chatzi and J. L. Koeing, *Appl. Spectrosc.*, **40**, 847 (1986).