Preferential Hydration in Superabsorbing Polymers by Solid-State ^{13}C NMR Spectroscopy†

P. R. RAJAMOHANAN, M. V. BADIGER, S. GANAPATHY, AND R. A. MASHELKAR*

National Chemical Laboratory, Pune 411 008, India

Received May 7, 1990;
Revised Manuscript Received August 16, 1990

Superabsorbing polymers represent a class of macromolecules that have an ability to retain large amounts of water, typically in the range of 100–1000 g of water/g of polymer. They have potential applications in the field of agriculture,[1] medical care,[2] separations,[3] and controlled release technology.[4,5] The study of hydration of these systems and a detailed understanding of the role of water on the structure and dynamics are of paramount importance. While the effects of hydration have been extensively studied in both natural and synthetic biopolymers by a variety of techniques,[6,7] superabsorbing polymers remain to be studied in this regard.

Hydration of macromolecules has many interesting facets, one of them is the preferential process. One aspect of this process refers to a given macromolecular site showing preference for water over other solvents. The other aspect refers to water preferring to associate with a particular site in preference to other sites that may be available in the macromolecule. The former has been addressed in the case of DNA in ethanol–water mixtures.[8] For the latter case, Poole and Finney[9] have reported the process of sequential hydration using difference IR spectroscopy, where shifts in the vibrational frequencies and intensities of bands of various groups occur upon hydration.

In biopolymers, however, the tertiary structure plays a crucial role in determining the hydration pathway. Accessibility of the sites is an important factor in the hydration of biopolymers because hydrophilicity alone does not determine the sequential event of hydration. This can happen, for example, when hydrophilic sites are buried inside a hydrophobic core and hence become less accessible to water.

Nuclear magnetic resonance (NMR) spectroscopy has emerged as an indispensable tool for the study of hydration of both natural and synthetic macromolecules.[10–12] Earlier NMR studies, however, invariably used protons that offered high sensitivity but not spectral selectivity. With the advent of rare spin NMR, such as ^{13}C, together with sensitivity enhancement by cross-polarization (CP)[13] and resolution enhancement by dipolar decoupling,[14] there is a powerful technique on hand to look at the hydration process directly in the ^{13}C NMR spectrum.[15–17] The inherent advantage with ^{13}C NMR lies in the very weak spin–spin couplings amongst ^{13}C nuclei at their natural abundance, which eliminates coupled interaction between various groups. The dominant source of dipolar broadening by neighboring protons can be conveniently eliminated by strong radio frequency irradiation at the ^{1}H Larmor frequency. The resulting spectrum exhibits a powder pattern, which can now be inspected for the effects of sequential hydration.

We demonstrate in this note the process of preferential hydration by solid-state ^{13}C NMR spectroscopy on a representative superabsorbing polymer, namely, hydrolyzed starch-*g*-poly(acrylonitrile), which contains the hydrophilic groups mentioned earlier. One can precisely control the amount of water absorbed by such polymers. Moreover, these hydrophilic groups have equal accessibility for water, thus providing an excellent opportunity to study the process of sequential or preferential hydration, dictated primarily by the hydrophilicity of the associated groups.

In Figure 1 we show dipolar-decoupled ^{13}C spectra taken in two data acquisition modes, namely, using Bloch decay (A–E) and CP (F–J) methods. In the unhydrated polymer, three distinct spectral regions are identified: carbonyl (250–150 ppm), starch (125–60 ppm), and aliphatic (50–0 ppm). There is no "motional averaging" of the associated chemical shielding pattern line shapes in the dry polymer (A, F), and the resulting spectra in the two different acquisition modes are identical.

Upon hydration of the polymer spectral changes ensue, since hydration causes an enhancement of polymer mobility, which tends to average the static powder-pattern line shapes. However, the observed ^{13}C spectra show that the spectral changes are not global. Early hydration at 0.38 g/g permits the hydration at the carboxylate and amide sites but precludes the hydroxyl site hydration at the starch backbone. The revealing feature of this sequential hydration process is the early collapse of the carbonyl shielding anisotropy and the unaltered powder pattern for the starch unit (Figure 1B,G).[18] In this partially hydrated state, the CP process is nevertheless effective since heteronuclear C–H dipolar interactions, necessary for polarization transfer, are incompletely averaged and there is no apparent inhibition for proton "spin diffusion".[19] Further increase in hydration, as in the 1.8 g/g sample, imposes hydration of the hydroxyl sites as well, evidenced by the increase in starch carbon resolution (Figure 1D). This further duplicates as a virtual elimination of CP except for the starch carbons (Figure 1I), due to the discriminatory ^{1}H–^{13}C polarization transfer between hydrated and unhydrated (or less hydrated) sites. The CP is totally eliminated in the highly hydrated 12.8 g/g sample (Figure 1J), but the ^{13}C spectrum can be recouped in the Bloch decay mode (Figure 1E). Herein the ^{13}C spectral resolution is indeed spectacular due to a near-zero averaging of the anisotropic interactions in the solid state because of extensive hydration-induced polymer mobility. Our observations also show that the sequential hydration process is primarily governed by the hydrophilicity of the functional groups rather than the additional cooperative factors that are important for biopolymer hydration.[9]

We have shown that the sequential hydration process in a representative superabsorbing polymer starch-*g*-poly(acrylonitrile) can be studied by solid-state ^{13}C NMR. The guiding factor is the changes in ^{13}C line shapes that occur when a given site is hydrated. The details of these line shapes can be analyzed to fit to a model for the hydration-induced dynamics. This will be reported later.

The NMR experiments were carried out on a Bruker MSL-300 FT-NMR spectrometer at ambient probe temperature (21 °C). Relevant spectral parameters are indicated in the caption to Figure 1. Different hydration levels for the samples were achieved by vapor diffusion in a humidity chamber at 100% relative humidity.

* Author to whom correspondence should be addressed.
† NCL Communication No. 4724.

0024-9297/91/2224-1423$02.50/0

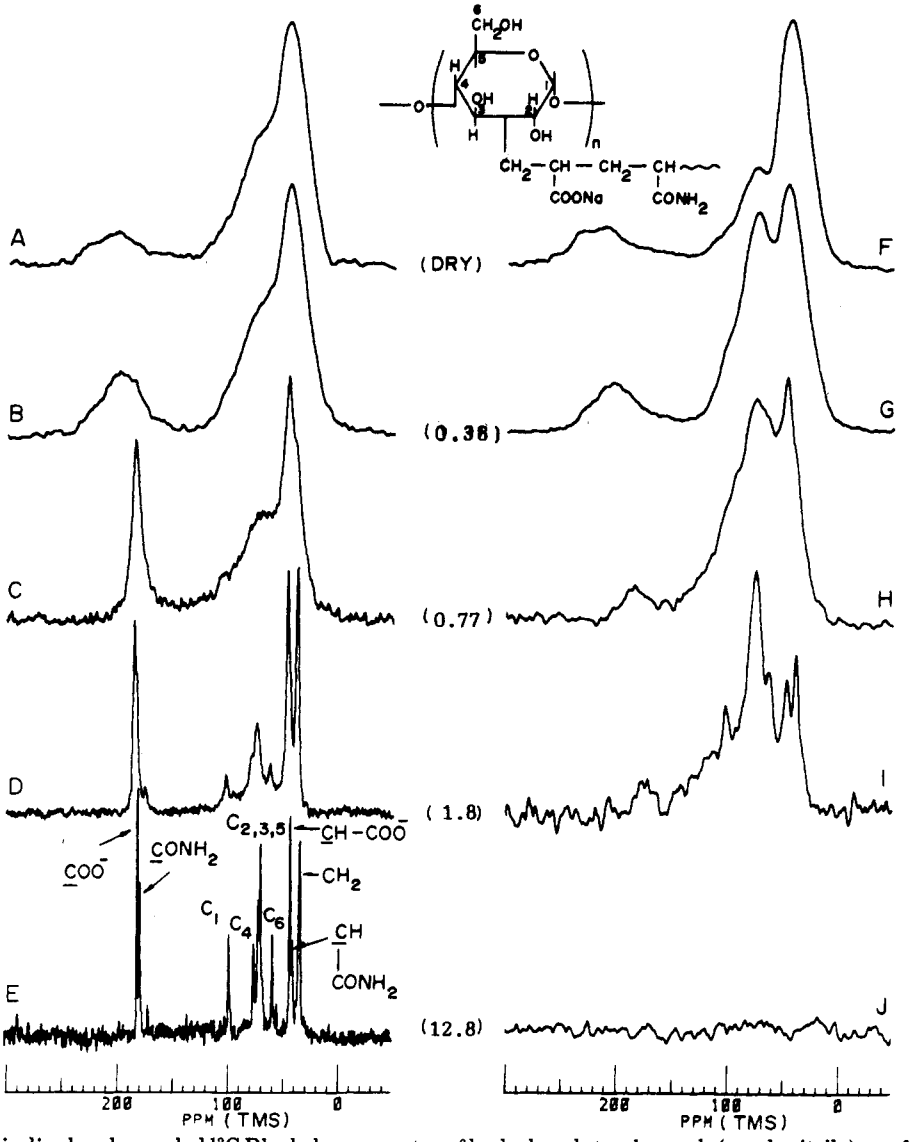

Figure 1. (A–E) Static dipolar-decoupled ^{13}C Bloch decay spectra of hydrolyzed starch-*g*-poly(acrylonitrile) as a function of hydration. All the spectra were taken with a 45° flip angle and a recycle time of 20 s. Number of scans: (A) 2900, (B) 4700, (C) 1600, (D) 1300, (E) 5700. (F–J) Static dipolar-decoupled ^{13}C CP spectra as a function of hydration. All the spectra were obtained by using a CP pulse sequence with an applied radio frequency field of 50 kHz and a mixing time of 1.0 ms. Number of scans: (F) 416, (G) 8100, (H) 16 100, (I) 12 200, (J) 10 200. Hydration levels are indicated in parentheses.

References and Notes

(1) Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russel, C. R. *Starke* **1974**, *30*, 237.
(2) Masuda, F. *CEER, Chem. Econ. Eng. Rev.* **1983**, *15*, 19.
(3) Freitas, R. F. S.; Cussler, E. L. *Sep. Sci. Technol.* **1987**, *22*, 911.
(4) Ratner, B. D.; Hoffman, A. S. In *Hydrogels*; Andrade, J. D., Ed.; ACS Symposium Series 31; American Chemical Society: Washington, DC, 1976; p 1.
(5) Hoffman, A. S.; Afrassiabi, A.; Dong, L. C. *J. Controlled Release* **1986**, *4*, 213.
(6) Pessen, H.; Kumosinski, T. F. *Methods in Enzymology*; Hirs, C. H. W., Timasheff, S. N., Eds.; Academic: New York, 1985; Vol. 117, p 219.
(7) Jelinski, L. W.; Dumais, J. J.; Choli, A. L.; Ellis, T. S.; Karasz, F. E. *Macromolecules* **1985**, *18*, 1091.
(8) Gekko, K.; Sakaki, T.; Shindo, H. *Polym. J.* **1988**, *20*, 751.
(9) Poole, P. L.; Finney, J. L. *Biopolymers* **1984**, *23*, 1647.
(10) Kuntz, I. D., Jr.; Brassfield, T. S.; Law, G. D.; Purcell, G. V. *Science* **1969**, *163*, 1329.
(11) Fung, B. M. *Methods in Enzymology*; Parker, L., Ed.; Academic: New York, 1986; Vol. 127, p 151.
(12) Bahneider, D.; Doskocilova, D.; Dybal, J. *Polymer* **1985**, *26*, 253.
(13) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(14) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(15) (a) Ganapathy, S.; Chacko, V. P.; Bryant, R. G. *Macromolecules* **1986**, *19*, 1021. (b) Jackson, C. L.; Bryant, R. G. *Biochemistry* **1989**, *28*, 5024. (c) Swanson, S. D.; Kennedy, S. D.; Bryant, R. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 111.
(16) Horii, F.; Ito, T.; Kitamaru, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 27.
(17) Sarkar, S. K.; Sullivan, C. E.; Torchia, D. A. *J. Biol. Chem.* **1983**, *258*, 9762.
(18) It may be noted here that we do not differentiate between the sequential hydration of the carboxylate and amide functions, in view of the spectral overlap of their shielding tensors. The distinction can, however, be made by a detailed line-shape analysis for the carbonyl region. Nevertheless, one can anticipate the hydration of the carboxylate group first because of its greater hydrophilicity.[9]
(19) Akasaka, K.; Takegoshi, K.; Terao, T.; Ganapathy, S. *Can. J. Chem.* **1988**, *66*, 2014.