(18) T. L. Brown in "Advances in Organometallic Chemistry", Vol. 3, F. G. A. Stone and R. West, Ed., Academic Press, New York, 1956.
(19) W. J. Trepka and T. W. Johnson, Phillips Petroleum Co., unpublished results.
(20) D. C. Evans, M. H. George, and J. A. Barrie, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 247 (1974).
(21) A. J. Chalk, *J. Polym. Sci., Polym. Lett. Ed.*, **6**, 649 (1968).

Hydration Effects in the ^{13}C CP/MAS NMR Spectra of Solid (1→3)-β-D-Glucans

C. A. FYFE* and P. J. STEPHENSON

The Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

M. G. TAYLOR, T. L. BLUHM, Y. DESLANDES, and R. H. MARCHESSAULT*

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada.
Received May 9, 1983

Several solid polysaccharides have been examined by ^{13}C CP/MAS NMR. It has been shown that the ^{13}C spectra of cellulose depend strongly on the source of natural cellulose I.[1,2] In addition, characteristic spectra are observed for the different polymorphic forms of cellulose.[3,4] It is clear that particular features of the ^{13}C spectra of these materials, such as peak multiplicities and line widths, reflect differences in the detailed structures of the various samples, although the precise interpretation of the observed differences is somewhat controversial. Recently, Saitô et al. have reported ^{13}C NMR studies of solid (1→3)-β-D-glucans from a variety of sources.[5] Variations in peak positions in the ^{13}C spectra of these materials were ascribed by these authors as due to conformational differences in the solids, related to the ability to form gels in aqueous media.

We have noted that the ^{13}C NMR spectra of these materials are quite sensitive to sample history. In particular, the widths of the ^{13}C resonances vary dramatically with the moisture content of the solids. Smaller variations are also observed in the chemical shifts. The present data indicate that sample history must be carefully considered in the interpretation of the ^{13}C spectra of these materials.

The ^{13}C CP/MAS spectra were obtained at 22.6 MHz, as previously described.[4] Spectra were recorded for purified curdlan and depigmented paramylon, using dry, as-received materials and in the presence of excess water. The curdlan sample was provided by the Takeda Chemical Co., Japan, and the paramylon sample, derived from *Euglena gracilis*, was a gift from Prof. Bruce Stone of La Trobe University, Australia. Figures 1 and 2 show the spectra obtained for each sample in the dry and hydrated forms.

In both cases, it is clearly seen that hydration of the solids results in a dramatic narrowing of the ^{13}C resonances. This effect is most pronounced for the C-1 and C-3 resonances of paramylon shown inset in Figure 1. In the dry material, these resonances both display fine structure similar to that noted by Saitô et al.[5] In the presence of excess water, these resonances in the paramylon spectrum are very sharp and show no indication of fine structure. Chemical shift differences are most pronounced in the C-3 region, where multiple resonances are found in the dry form while only a single line is apparent in the hydrated material. The spectral changes associated with hydration are similar, though less dramatic, for the curdlan samples.

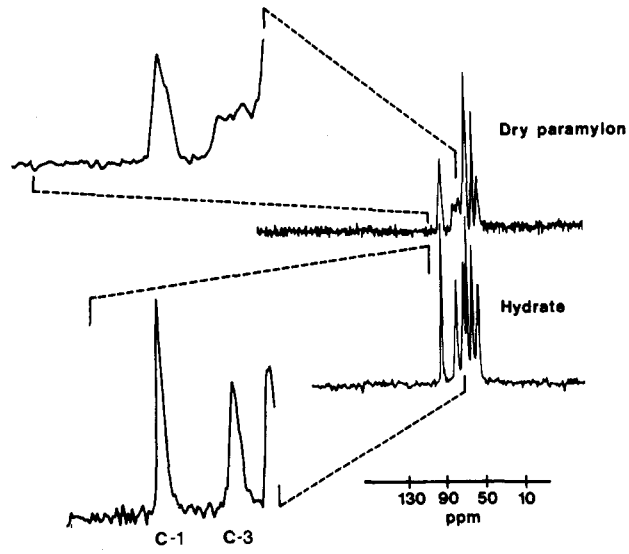

Figure 1. ^{13}C CP/MAS spectra of solid paramylon in the dry and hydrated forms.

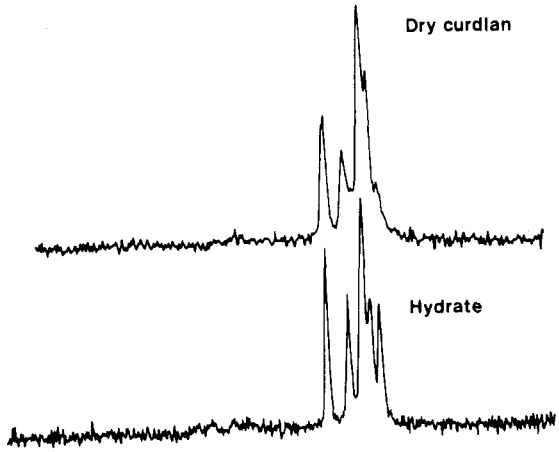

Figure 2. ^{13}C CP/MAS spectra of solid curdlan in the dry and hydrated forms.

Saitô et al.[5] interpreted the fine structure of the C-3 resonance as being characteristic of native and alkaline regenerated forms of curdlan and interpreted it in terms of helical structures, but it is now clear that this fine structure is due to hydration effects.

It is difficult to assign the cause of the observed spectral changes in an unequivocal manner. Similar variations noted in ^{13}C spectra of celluloses have been attributed to differences in morphology[2,6] or crystallinity.[7] It is interesting to note that broader lines are observed in the spectra of both dry and hydrated curdlan samples than are found in the corresponding paramylon spectra. This may reflect a lower crystallinity for curdlan relative to paramylon. The curdlan may be expected to be less crystalline since its purification process involves solubilization and reprecipitation, whereas the paramylon is examined in its native, highly crystalline form. X-ray powder diffraction studies were carried out on the two polysaccharides, using both dry and hydrated samples. Figure 3 shows the diffraction traces obtained. For paramylon, both dry and hydrated samples exhibit high degrees of crystallinity, with the greater crystalline order found in the hydrate form. In contrast, neither curdlan sample shows sharp reflections characteristic of crystalline regions. Thus, while the differences in the ^{13}C line widths between the curdlan and paramylon may be related to crystallinity effects, the decrease in widths noted on hydration of both samples cannot be attributed solely to crystallinity changes.

0024-9297/84/2217-0501$01.50/0

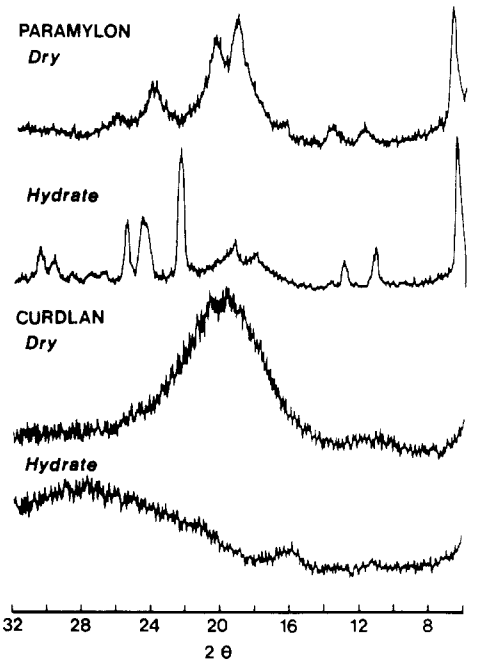

Figure 3. X-ray powder diffraction traces for paramylon and curdlan in the dry and hydrated forms.

The line broadening observed in the spectra of the dry polysaccharides is likely due in large part to distributions of chemical shifts for the individual resonances.[8] This type of line broadening results from a distribution of microenvironments within the solid sample. Hydration could alter this heterogeneity in a number of ways. X-ray diffraction studies of dry[9] and hydrated[10] (1→3)-β-D-glucans indicate that hydration is accompanied by lattice expansion, which allows water to enter the intertriplex spaces in these triple-helical solids. This lattice expansion may allow strain relief and removal of local defects in the solid. This treatment would yield a structure with greater conformational homogeneity, leading to smaller chemical shift distributions for the individual ^{13}C resonances.

Regardless of the detailed mechanism responsible for the observed spectral changes, it is seen that caution must be exercised in the interpretation of the ^{13}C spectra of these materials. Differences found in comparisons of spectra of related materials may be due only to differences in the degree of hydration of the materials. Hydration effects have been noted for another (1→3)-β-D-glucan (laminarin), (1→3)-β-D-xylan (C. A. Fyfe and P. J. Stephenson, unpublished results), cellulose[11] and oligomers of cellulose.[12] The ^{13}C spectra of other solid biopolymers may also depend strongly on hydration. Thus, the sample history with respect to exposure to water should be carefully controlled in solid-state ^{13}C NMR studies of these materials.

Registry No. Curdlan, 54724-00-4; paramylon, 51052-65-4.

References and Notes

(1) W. L. Earl and D. L. VanderHart, *J. Am. Chem. Soc.*, **102**, 3251-3252 (1980).
(2) W. L. Earl and D. L. VanderHart, *Macromolecules* **14**, 570-574 (1981).
(3) R. H. Atalla, J. C. Gast, D. W. Sindorf, V. J. Bartuska, and G. E. Maciel, *J. Am. Chem. Soc.*, **102**, 3249-3251 (1980).
(4) C. A. Fyfe, R. L. Dudley, P. J. Stephenson, Y. Deslandes, G. K. Hamer, and R. H. Marchessault, *J. Macromol. Sci., Rev. Macromol. Chem.*, in press.
(5) H. Saitô, R. Tabeta, and T. Harada, *Chem. Lett.*, 571-574 (1981).
(6) G. E. Maciel, W. L. Kolodziejski, M. S. Bertran, and B. E. Dale, *Macromolecules*, **15**, 686-687 (1982).
(7) F. Horii, A. Hirai, and R. Kitamaru, *Polym. Bull.*, **8**, 163-170 (1982).
(8) D. L. VanderHart, W. L. Earl, and A. N. Garroway, *J. Magn. Reson.*, **44**, 361-401 (1981).
(9) Y. Deslandes, R. H. Marchessault, and A. Sarko, *Macromolecules*, **13**, 1466-1471 (1980).
(10) C. T. Chuah, A. Sarko, Y. Deslandes, and R. H. Marchessault, *Macromolecules*, in press.
(11) D. L. VanderHart, National Bureau of Standards Report NBSIR 82-2534, 1982.
(12) R. L. Dudley, C. A. Fyfe, P. J. Stephenson, Y. Deslandes, G. K. Hamer, and R. H. Marchessault, *J. Am. Chem. Soc.*, **105**, 2469-2472 (1983).

Similarity Applied to the Statistics of Confined Stiff Polymers

THEO ODIJK

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. *Received May 14, 1983*

In a recent paper[1] we introduced a so-called deflection length for describing the statistical properties of wormlike chains trapped in pores. Scaling-type laws were derived for equilibrium as well as dynamical quantities, the latter pertaining to polymers confined in networks. Our results for the rotational diffusion coefficient agree with a somewhat different approach due to Doi,[2] who obtained some of the numerical coefficients as well. At present it is not known if the calculations outlined in ref 1 and 2 have any bearing on the modification of the dynamics of mutually entangled rodlike polymers.[3-6] There still seems to be a major missing link between experiment (e.g., ref 7) and theory (ref 3-6, 1, and 2).

Our derivation of the deflection length was very heuristic. Hence, we would like to point out in this Note that it can be obtained much more rigorously from the partition function by a similarity analysis.[8]

Consider a wormlike chain of contour length L trapped in a infinitely long, cylindrical pore of diameter D. In our Cartesian coordinate system (x, y, z) the axis of the pore is along the z direction. The canonical variable is $\vec{u}(s) = \partial\vec{r}(s)/\partial s$ with $\vec{u}^2 = 1$. Here, $\vec{r}(s)$ is the radius vector of a point of the coil at a contour distance s from one end to that point. The partition function is given formally by the following path integral:[9]

$$Z(\vec{u}(0),\vec{u}(L),P,L,D) = \int_{\substack{\vec{u}(0)\ \text{fixed} \\ \vec{u}^2(s)=1}}^{\vec{u}(L)\ \text{fixed}} \mathcal{D}[\vec{u}(s)]\ \exp\left\{-\tfrac{1}{2}P\int_0^L \left(\frac{\partial\vec{u}}{\partial s}\right)^2 ds\right\} \quad (1)$$

with the additional restriction

$$\left[r_x(0) + \int_0^s u_x(t)\,dt\right]^2 + \left[r_y(0) + \int_0^s u_y(t)\,dt\right]^2 \le \tfrac{1}{4}D^2 \quad \text{for all } s \quad (2)$$

Here, P is the persistence length. Now, if $D \ll P$, the chain cannot fold along the z axis (see ref 1). Furthermore, $u_x(s) \ll 1$ and $u_y(s) \ll 1$. In that case, eq 1 can be rewritten as follows:

$$Z(u_x(0),u_y(0),u_x(L),u_y(L),P,L,D) = \int_{u_x(0),u_y(0)}^{u_x(L),u_y(L)} \mathcal{D}[u_x(s)]\mathcal{D}[u_y(s)] \times \exp\left\{-\tfrac{1}{2}P\int_0^L \left[\left(\frac{du_x}{ds}\right)^2 + \left(\frac{du_y}{ds}\right)^2\right] ds\right\} \quad (3)$$

Although eq 3 is not exact, we can make it as exact as we want to by letting DP^{-1} become smaller and smaller.

0024-9297/84/2217-0502$01.50/0