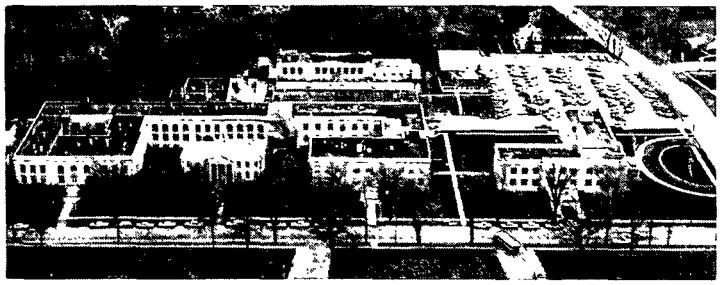
circ
W Fisher
B Leuz



THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 92

THE ^{13}C NMR SPECTRA OF CELLULOSE POLYMORPHS

R. H. ATALLA, J. C. GAST,
D. W. SINDORF, V. J. BARTUSKA AND G. E. MACIEL

MARCH, 1980

THE ^{13}C NMR SPECTRA OF CELLULOSE POLYMORPHS

R. H. Atalla and J. C. Gast
The Institute of Paper Chemistry
Appleton, Wisconsin 54912 (U.S.A.)

D. W. Sindorf, V. J. Bartuska and G. E. Maciel
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

INTRODUCTION

Our Raman spectral studies of the structures of celluloses I and II had led us to the conclusion that alternating glycosidic linkages along the cellulose molecular chain may be nonequivalent. A structure consistent with such a finding would require reassessment of many experimental studies of cellulose, in both applied and basic realms. We sought more direct evidence concerning the glycosidic linkages in cellulose by investigating the solid state ^{13}C NMR spectra of specially prepared samples of the celluloses, in collaboration with Dr. Gary E. Maciel and his associates at Colorado State University. The results confirm our interpretation of the Raman spectra.

Submitted for publication in the Journal of the American Chemical Society.

THE ^{13}C NMR SPECTRA OF CELLULOSE POLYMORPHS

R. H. Atalla* and J. C. Gast
The Institute of Paper Chemistry
Appleton, Wisconsin 54912 (U.S.A.)

D. W. Sindorf, V. J. Bartuska and G. E. Maciel*
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

We report high resolution ^{13}C NMR spectra of the two major crystalline polymorphs of cellulose and an amorphous sample, recorded using the Cross Polarization/Magic-angle Spinning (CP/MAS) technique. The spectra provide important new evidence concerning the basic structure of cellulose; they demonstrate nonequivalence of adjacent anhydroglucose units, and are consistent with conformational differences between the polymorphs.

Cellulose, which is the primary constituent of plant cell walls, is the β-1,4-polymer of anhydroglucose. Its two most common polymorphs, celluloses I and II, are usually identified with the native and the mercerized or regenerated forms, respectively (1-3). Analyses of their vibrational spectra have led to the conclusions that these two crystalline polymorphs represent different conformations of the extended molecular chains (4,5). In addition, one of us has reported evidence indicating nonequivalence of alternate glycosidic linkages along the molecular chains, and suggesting that the dimeric anhydrocellobiose must be viewed as the basic repeat unit in the crystalline structure (6). X-ray and electron diffractometric studies have led to a number of different structures over the years (1-3). An essential element in the interpretation of diffractometric data on any polymer is the assumed monomeric structure and its symmetry (7). In studies of cellulose the anhydroglucose unit has usually been taken as the basic repeat unit. The problem has been complicated by the appearance of weak reflections which are not consistent with the symmetry ascribed to cellulose. Thus the refined structures vary according to whether or not the disallowed reflections are assumed negligible (8-11). Development of the CP/MAS technique

(12,13) and its application in investigations of complex natural products suggested that the ^{13}C NMR spectra of the celluloses could contribute to resolution of the questions concerning their structures.

We report on four samples of cellulose. Two were special samples of the highly crystalline polymorphic forms I and II previously characterized by x-ray diffractometry and Raman spectroscopy (5); their preparations involved regeneration from phosphoric acid at different temperatures and in different media (15,16). The third sample was Whatman CF-1 powder, a highly crystalline cellulose I identified by fiber microscopy as fragments of acid hydrolyzed cotton linters. The final sample was a completely amorphous cellulose prepared by regeneration from the dimethyl sulfoxide-paraformaldehyde solvent system under anhydrous conditions. The ^{13}C NMR spectra were recorded using a modified JEOL FX-60Q system described elsewhere (14).

The spectra are shown in Figures 1 and 2; partial assignments are noted on the basis of comparisons with solutions of the cello-oligosaccharides and a low DP cellulose (17). The most significant features in the spectra of the highly crystalline forms are those corresponding to carbons 1 and 4, which anchor the glycosidic linkages between the anhydroglucose units. The C-1 resonances for both forms and the C-4 resonance of II show very definate splittings, in each case into two lines of approximately equal intensities. These splittings provide direct evidence for the presence of two types of glycosidic linkages. Since the basic repeat distance along the chain direction is 10.3 A, or the length of an anhydrocellobiose unit, the most plausible interpretation is an alternation of nonequivalent glycosidic linkages along the chains. The differences between other features in the spectra of celluloses I and II are also consistent with differences between chain conformations proposed on the basis of Raman spectral studies (5,6).

The CP/MAS ^{13}C NMR spectrum of the amorphous sample, and, hence, its structure are clearly quite distinct from those of the I and II polymorphs. Indeed the spectrum parallels most that of the low DP cellulose in solution in dimethylsulfoxide (17) if allowance is made for a solvent shift. Broad, high shielding shoulders appear in the C-4 and C-6 regions of some samples of polymorphs I and II; these correspond to peaks a and b in the spectrum of the amorphous cellulose.

The results outlined above concerning polymorphs I and II, when taken together with the vibrational spectra and the dimensions of the unit cells, suggest that adjacent anhydroglucose units are not equivalent, and that models of the structure of cellulose need to be constructed using anhydrocellobiose as the basic repeat unit.

ACKNOWLEDGMENTS

The authors gratefully acknowledge partial support of the work from institutional funds of The Institute of Paper Chemistry and the Colorado State University Experiment Station. Drs. W. L. Earl and D. L. Vander Hart kindly shared with us the results of unpublished studies on related work.

REFERENCES

1. Jones, D. W., in "Cellulose and Cellulose Derivatives," Part IV, N. M. Bikales and L. Segal, eds., p. 117, Wiley-Interscience, New York. 1971.

2. Ellefsen, O. and Tonnesen, B. A., Ref. 1, p. 151.

3. Tonnesen, B. A. and Ellefsen, O., Ref. 1, p. 265.

4. Atalla, R. H. and Dimick, B. E., Carbohyd. Res. (1975) 39, C1.

5. Atalla, R. H., Proceedings of the 8th Cellulose Conference, Applied Polymer Symposium No. 28 (1976) 659.

6. Atalla, R. H., in "Hydrolysis of Cellulose," Jurasek and Brown, eds., ACS Advances in Chemistry Series, ACS, 1979, p. 55.

7. Kakudo, M. and Nobutami, K., "X-ray Diffraction by Polymers," Elsevier, NY, 1972, p. 285.

8. Petitpas, T., Oberlin, M., and Mering, J., J. Polymer Sci. S, 2, 423 (1963).

9. Norman, M., Text. Res. J., 33, 711 (1963).

10. Gardner, K. H. and Blackwell, J., Biopolymers (1974) 13, 1975.

11. Sarko, A. and Muggli, R., Macromolecules (1974) 7, 486.

12. Schaefer, J. and Stejskael, E. O., in "Topics in Carbon-13 NMR Spectroscopy," Vol. 3, G. C. Levy, Ed., Wiley-Interscience, New York, 1979.

13. Miknis, F. P., Bartuska, V. J. and Maciel, G. E., American Laboratory, in press.

14. Maciel, G. E., Bartuska, V. J. and Miknis, F. P., Fuel, in press.

15. Atalla, R. H. and Nagel, S. C., Science, 185, 522 (1974).

16. Atalla, R. H., Dimick, B. E., and Nagel, S. C., in "Cellulose Chemistry and Technology," J. C. Arthur, Ed., ACS Symposium Series No. 48, American Chemical Society, Washington, DC (1977), p. 30.

17. Gast, J. C., Atalla, R. H., and McKelvey, R. D., Carbohyd. Res., in press.

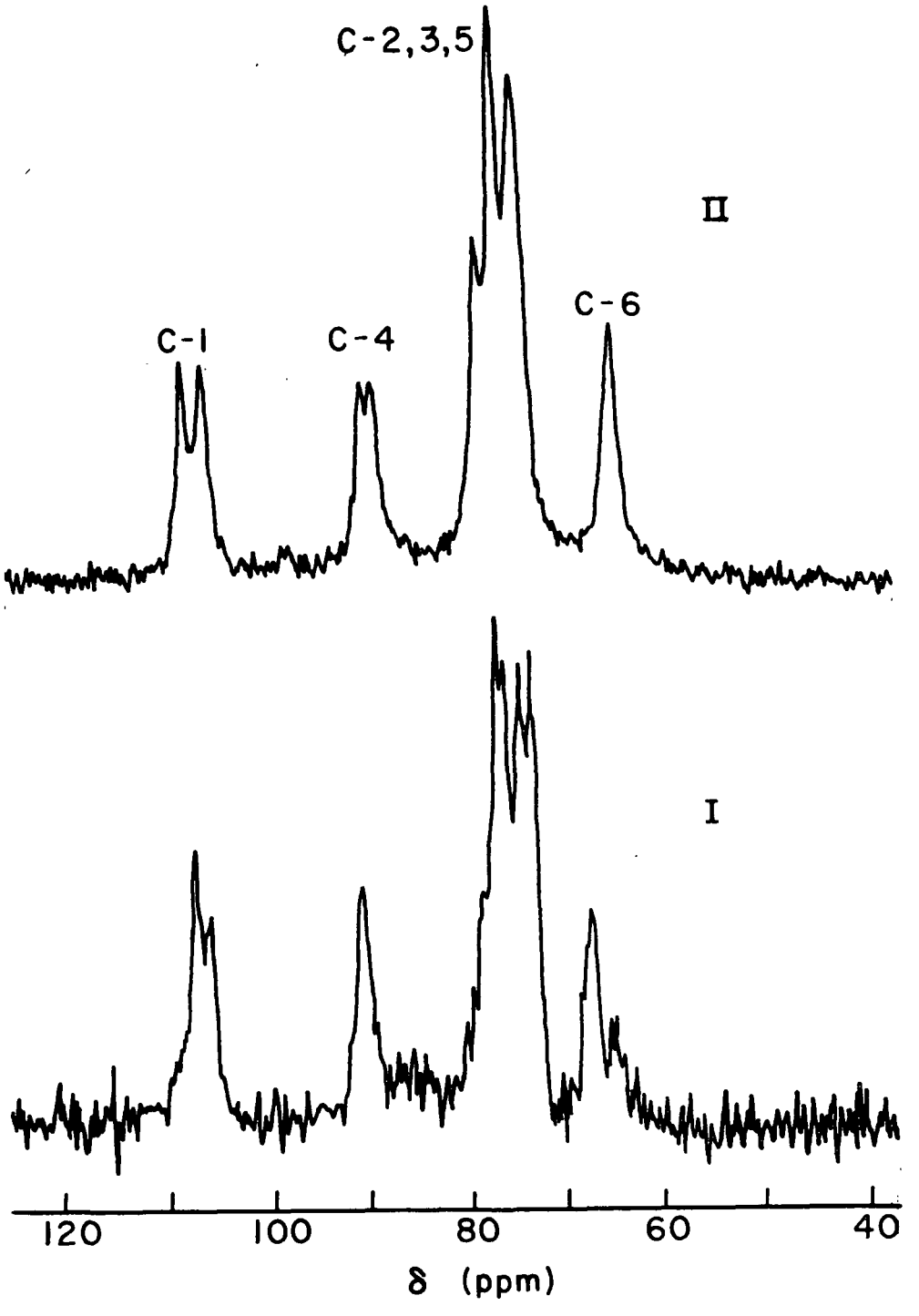


Figure 1. CP/MAS ^{13}C NMR spectra of highly crystalline cellulose I and II. Chemical shifts shown in ppm (to lower shielding) relative to TMS. Assignments of the C-1, C-4 and C-6 regions are based on analogies with pertinent liquid-state spectra. I: 13,000 3-second repetitions, 1 ms contact time, 127-ms 11-gauss ^{1}H decoupling, 0.35 cm^3 sample, 2.2 KHz spinning. II: 12,342 3-second repetitions, 1 ms contact time, 127-ms 11-gauss ^{1}H decoupling, 0.7 cm^3 sample, 2.2 KHz spinning.

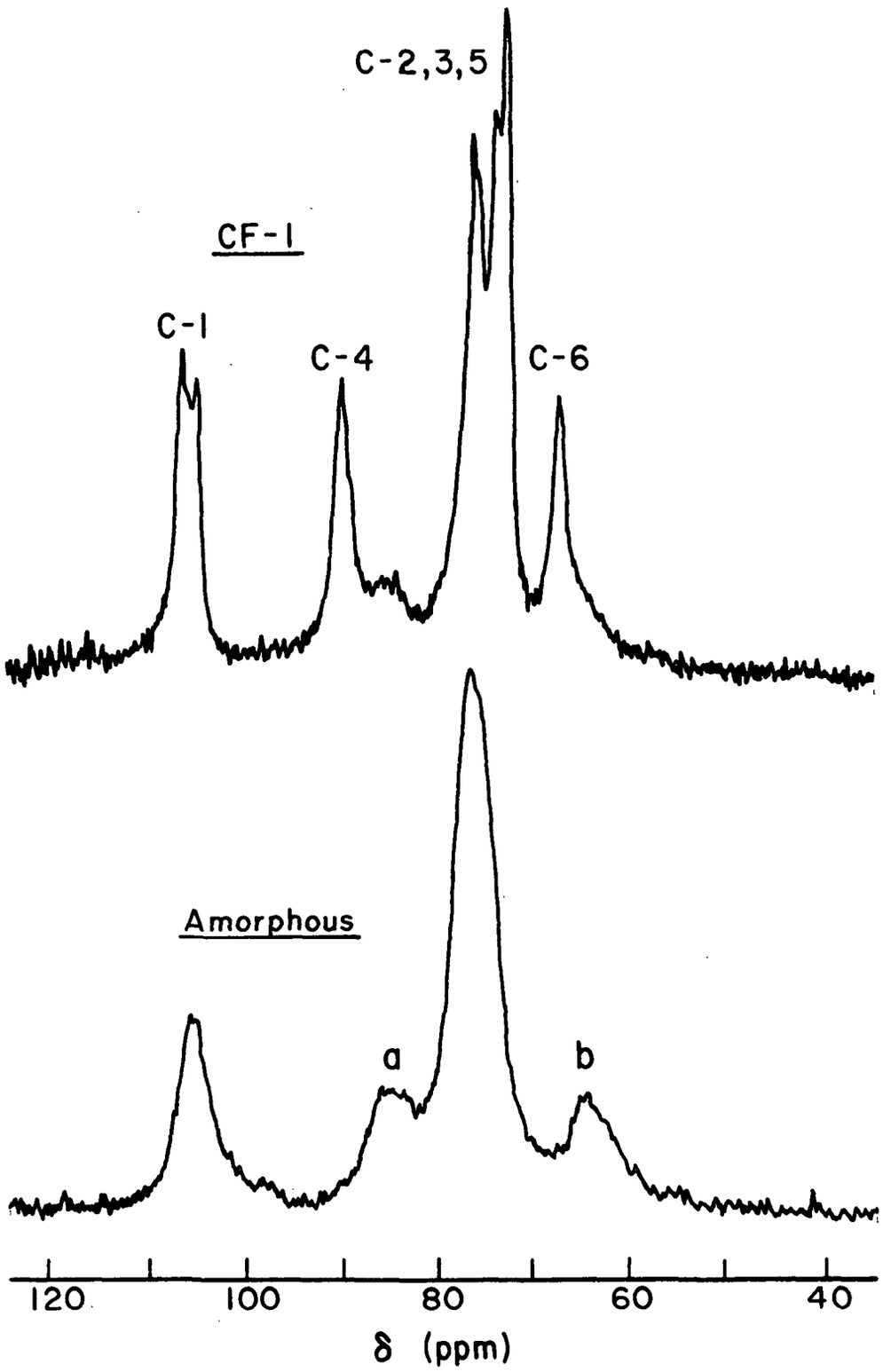


Figure 2. CP/MAS ^{13}C NMR spectra of native I (Whatman CF-1) and amorphous celluloses. Chemical shifts are in ppm (to lower shielding) relative to TMS. CF-1: 12,000 3-second repetitions, 1 ms contact time, 127-ms 11-gauss ^{1}H decoupling, 0.7 cm^3 sample, 2.2 KHz spinning. Amorphous: 8116 4-second repetitions, 1 ms contact time, 127-ms 11-gauss ^{1}H decoupling, 0.7 cm^3 sample, 2.2 KHz spinning.