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CP/MAS ^{13}C NMR Spectra of the Crystalline Components of Native Celluloses

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ABSTRACT: Cross-polarization/magic-angle-spinning (CP/MAS) ^{13}C NMR spectra of the crystalline components of different native celluloses have been measured in the hydrated state by using the difference in ^{13}C spin-lattice relaxation times T_{1C} of the crystalline and noncrystalline components. As a result, it has been found that the crystalline spectra of native cellulose can be classified into two groups, cotton-ramie type and bacterial-valonia type, which are referred to as celluloses I_a and I_b, respectively. The validities of the structural models previously proposed have been also discussed on the basis of the line-shape analyses of the C1 and C4 triplets of the crystalline spectra.

Introduction

It is well-known that solid-state ^{13}C NMR spectra of cellulose exhibit two types of multiplicities: one is a large splitting on the order of 3-5 ppm, which is composed of a broad resonance and a narrow line, and the other is a fine splitting of less than 2 ppm appearing in the narrow line of the former splitting.[1-18] As a result of the evaluation of the effect of crystallinity on the former splitting, we have concluded that the narrow and broad resonances should be assigned to the contributions from the crystalline and noncrystalline regions.[4,8] Although recent studies[3,5,10] suggest that the surface chains on the crystallites also contribute to the broad component, this seems to be an overestimate of that contribution.

The origin of the fine multiplicities is also still a controversial subject. Atalla and VanderHart[10,11] have proposed that all native celluloses are a mixture of two crystalline modifications, celluloses I_α and I_β, which show different fine multiplets. Analogous to their work, Cael et al.[15] have also suggested that the ^{13}C NMR spectra of different native celluloses are linear combinations of two spectra. In contrast to the preceding view, however, these two spectra are assumed to correspond to the resonances from the two-chain and eight-chain unit cell regions of cellulose.

Although both models seem very interesting, these workers did not analyze any crystalline spectrum which was not contaminated with the noncrystalline contribution. The situation is most serious for the C1 resonance, because a rather sharp line of the noncrystalline component is completely superposed on the central signal of the triplet ascribed to the crystalline contribution, as will be described later. Recently we have found that the ^{13}C spin-lattice relaxation times, T_{1C}, greatly differ for the crystalline and noncrystalline components, in accordance with the finding reported by Teeäär and Lippmaa,[12] and thus the pure spectra of the respective components can be separately recorded by using the difference in T_{1C}.[8,9,13,14,18] Moreover, we have developed a new type of MAS rotor with an O-ring seal for CP/MAS ^{13}C NMR measurements in the presence of water.[13,19] This kind of rotor is essential for cellulosic materials because the addition of water remarkably enhances the resolution of resonance lines and long-term measurements must be made without any loss of water to obtain the crystalline spectra with sufficiently high signal/noise ratios. In this paper, using these techniques, we have measured the crystalline spectra of cotton, ramie, bacterial, and valonia celluloses and compared their chemical shifts as well as multiplicities. As a result, we report that the ^{13}C crystalline spectra of these native celluloses are classified into two types, cotton-ramie type and bacterial-valonia type. The validities of the models previously proposed are also discussed.

Experimental Section

Each cellulose sample was prepared according to the methods reported in the previous papers.[4,8] After being soaked in distilled

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Table I
^{13}C Chemical Shifts of the Crystalline Components of Native Cellulose in the Hydrated State[a]

sample	C1/ppm			C4/ppm			C6/ppm			C2,3,5/ppm					
valonia	106.9	106.2	105.2	91.0	90.1	89.2	66.7	66.4	66.2	75.8	75.3	73.7	72.9	72.4	72.0
bacterial	106.9	106.3	105.2	91.0	90.1	89.5		66.4		75.8	75.3	73.8	72.9	72.5	71.9
ramie	106.9	106.2	105.1		90.0	89.2	66.7		66.2		76.1	75.3	73.6	72.5	
cotton	107.0	106.3	105.2		89.9	89.4		66.3	66.2		76.2	75.4	73.5	72.5	

[a] The chemical shift values are determined by assuming the crystalline peak of linear polyethylene to be 33.6 ppm.[20]

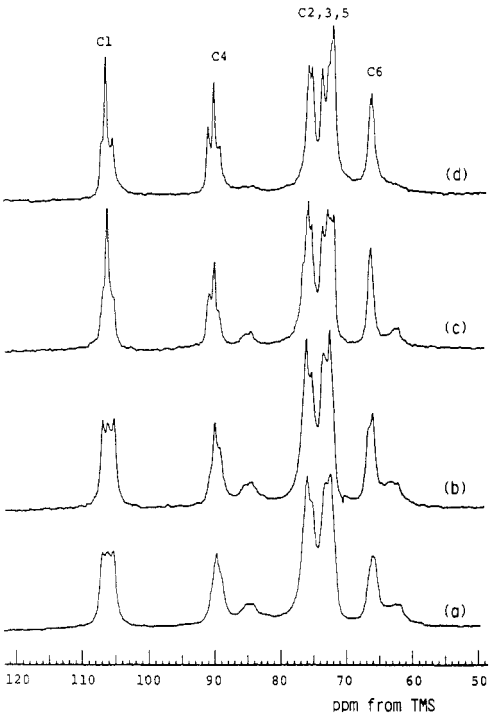

Figure 1. CP/MAS ^{13}C NMR spectra, 50 MHz, of native celluloses in the hydrated state: (a) cotton; (b) ramie; (c) bacterial; (d) valonia celluloses.

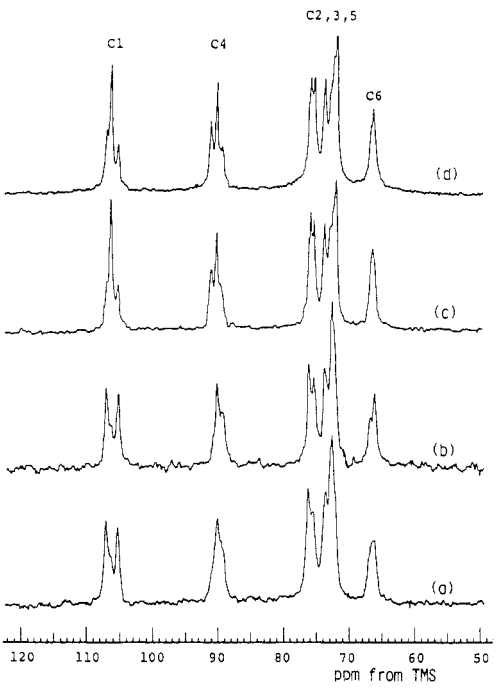

Figure 2. CP/MAS ^{13}C NMR spectra, 50 MHz, of the crystalline components included in native celluloses: (a) cotton; (b) ramie; (c) bacterial; (d) valonia celluloses.

water for about 24 h, the samples were packed into the MAS rotor with an O-ring seal. CP/MAS ^{13}C NMR measurements were performed on a JEOL JNM-FX200 spectrometer operating under a static magnetic field of 4.7 T. ^1H and ^{13}C radio-frequency field strengths $\gamma B_1/2\pi$ were 70 kHz for the CP process, while the ^1H dipolar decoupling field was reduced to 54 kHz. The MAS rate was 3.2–3.4 kHz, and the contact time was 1.0 ms throughout this work. The chemical shift relative to tetramethylsilane (Me_4Si) were determined by using the crystalline peak at 33.6 ppm[20] of linear polyethylene as an internal standard.

The pulse sequence which is used for selective observations[8,9,13,14,18] of the crystalline components is the one for ^{13}C T_1 measurements developed by Torchia,[22] where the magnetization associated with each ^{13}C species reduces from the value produced through the CP process to zero during the longitudinal relaxation. Therefore, in the system containing two components with short and long T_{1C} values, such as noncrystalline and crystalline components, the spectrum of the longer T_{1C} component can be separately recorded by utilizing the residual magnetization after the short T_{1C} contribution disappears.

Results and Discussion

Figure 1 shows 50-MHz CP/MAS ^{13}C NMR spectra of cotton, ramie, bacterial, and valonia celluloses in the hydrated state. In Figure 2, the crystalline spectra of these samples are shown. They were measured by the abovementioned pulse technique. The delay time used to suppress the noncrystalline contribution was 100 s for each spectrum. Although the conventional CP/MAS ^{13}C NMR spectra of these celluloses exhibit rather broad noncrystalline resonances at about 85 and 63 ppm, such lines completely disappear in the crystalline spectrum for each sample. It can be, therefore, assumed that the noncrystalline contribution is removed also from the C1 lines in the crystalline spectra.

As a result of the evaluation of the chemical shifts (Table I) and the multiplicities of the crystalline spectra, it has been found that bacterial and valonia celluloses give almost the same crystalline spectra, whereas ramie and cotton produce another different type of common spectra. The most prominent differences appear in the C1 resonances: an enhanced singlet with a minor doublet for bacterial and valonia celluloses, and a predominant doublet overlapping a weak singlet for cotton and ramie. It is, therefore, concluded that the crystalline spectra of these native celluloses may be classified into two groups: bacterial–valonia type and cotton–ramie type. Although these two types of spectra may not simply indicate the existence of the two types of well-defined, single-crystal forms, we refer hereafter to cotton–ramie type and bacterial–valonia type as celluloses I_a and I_b, respectively.

This conclusion agrees well with the result obtained by Marrian and Mann[23] using infrared spectroscopy; the OH stretching bands of valonia and bacterial celluloses evidently differ from those of cotton and ramie celluloses. They pointed out that the differences between the two types of spectra imply a difference in molecular packing or in the degree of perfection in the crystals. On the other hand, Hebert and Muller[24] showed that two types of unit cells must be considered for different native celluloses, using the electron diffraction method. The diffraction patterns from cotton and ramie celluloses can be indexed by using the two-chain unit cell, whereas those from

Table II
Intensity Ratios of the Triplets of C1 and C4 Carbons of Native Cellulose

sample		C1/ppm 107.0	C1/ppm 106.3	C1/ppm 105.2	C4/ppm 91.0	C4/ppm 90.1	C4/ppm 89.3
valonia	obsd	1.4	2.2	1.0	1.9	2.5	1.0
	unrelaxed	1.3	2.2	1.0	2.0	2.6	1.0
	AV,[a] x = 0.52	1.0	2.2	1.0	1.1	2.1	1.0
	CKBP,[b] x' = 1.0	1.0	2.0	1.0	1.0	2.0	1.0
bacterial	obsd	1.7	4.5	1.0	1.2	1.6	1.0
	unrelaxed	1.7	4.5	1.0	1.3	1.6	1.0
	AV,[a] x = 0.69	1.0	4.5	1.0	2.2	3.2	1.0
	CKBP,[b] x' = 1.0	1.0	2.0	1.0	1.0	2.0	1.0
ramie	obsd	4.6	1.0	3.9	1.0	3.9	3.6
	unrelaxed	4.2	1.0	3.9			
	AV,[a] x = 0.106	4.2	1.0	4.2	1.0	9.4	8.4
	CKBP,[b] x' = 0.213	4.2	1.0	4.2	1.0	16.8	1.0
cotton	obsd	4.2	1.0	3.2	1.0	5.4	2.7
	unrelaxed	3.6	1.0	2.6			
	AV,[a] x = 0.122	3.6	1.0	3.6	1.0	8.2	7.2
	CKBP,[b] x' = 0.243	3.6	1.0	3.6	1.0	14.5	1.0

[a] Atalla–VanderHart model.[10,11] [b] Cael–Kwoh–Bhattacharjee–Patt model.[15]

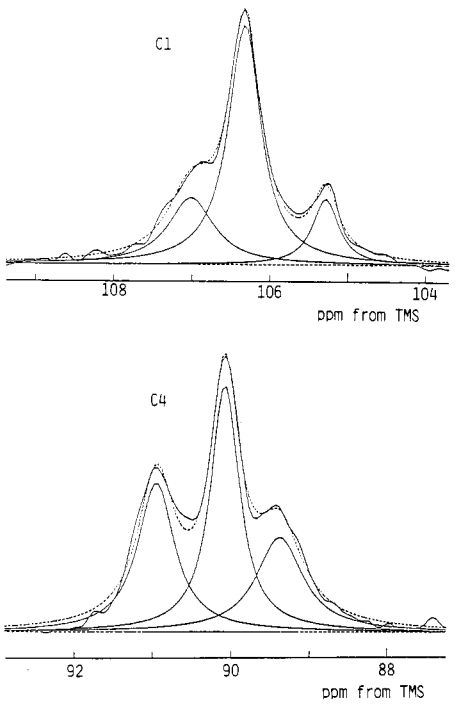

Figure 3. Line-shape analyses for the C1 and C4 triplets of bacterial cellulose. The broken line indicates the composite curve of three Lorentzians.

bacterial and valonia celluloses require a doubling of the basal plane dimensions, which indicates the existence of the eight-chain unit cell. It is not straightforward at present to explain the differences in ^{13}C NMR spectra in terms of the two types of unit cells, as will be described below, but these correspondences of the results obtained by different methods should be noted here.

Two structural models[10,11,15] have been proposed in order to explain the origin of the multiplicities of C1 and C4 lines, as already mentioned above. However, these models were used for the analyses of conventional CP/MAS ^{13}C spectra that contain also a noncrystalline contribution. Thus, we have examined the validity of the models using the crystalline spectra shown in Figure 2. Figure 3 shows the results obtained by computer line-shape analyses for C1 and C4 resonances of bacterial cellulose, where each line for the triplets is assumed to be a Lorentzian.[25] The composite curve of three Lorentzians is in good accord with the observed triplets. Similar good agreement was obtained for the C1 and C4 triplets of other samples. In these analyses, the Lorentzian lines have different line widths, indicating the irregularity of the contents of the multiplicities. Similar irregularity was also observed for T_{1C} relaxation, yielding different values for the respective sublines of the triplets,[26] as well as for intensity ratios as shown below.

In Table II are summarized the observed intensity ratios of the respective lines in C1 and C4 triplets of the native celluloses which were obtained by the computer line-shape analyses mentioned above. However, since the T_{1C} values of the respective lines of the triplets were not the same,[26] these ratios are somewhat distorted by the relaxation. Therefore, unrelaxed intensity ratios, which were estimated by using the T_{1C} values, are also shown in Table II. The calculated ratios shown in the table were obtained for models proposed by Atalla and VanderHart[10,11] (AV model) and Cael et al.[15] (CKBP model). For example, the predicted relative intensities of the C1 triplets are given by $(1 - x):2x:(1 - x)$ for the AV model and by $(2 - x'):2x':(2 - x')$ for the CKBP model, where x and x' are the fractions of I_α crystals and the eight-chain unit cells in their models, respectively. As is clearly seen in Table II, both models are inappropriate for the description of the unrelaxed experimental intensity ratios. In particular, the disagreement between the calculated and the observed values is more serious for the C4 triplets. We are now trying to analyze these data by using other structural models, particularly taking into account the effect of the possible composites of different types of crystal forms for each cellulose.

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SANS and SAXS Studies on Molecular Conformation of a Block Polymer in Microdomain Space. 2. Contrast Matching Technique†

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ABSTRACT: We critically tested the contrast matching technique in the small-angle neutron scattering from block polymers to study the molecular conformation of a block polymer chain in microdomain space. It was found that the blending of deuteriated and undeuteriated block polymers with a composition to produce zero contrast ("contrast matching") does not always result in true contrast matching even in the case of the two block polymers mixed at a molecular level in the microdomain space. The true matching is expected to occur only in the case when the deuteriated block polymers overlap each other in the domain space to produce uniform segmental density of their own at the given composition, giving rise to the zero contrast between each microdomain. However, even in the event of incomplete contrast matching, the suppression of the domain scattering by 2 orders of magnitude was attained, which enabled us to measure the component of the radius of gyration of the block polymer chain parallel to the interface with much better accuracy than the previous work without the contrast matching. The component was again found to be 70% of the component for the unperturbed chain.

I. Introduction

In a previous paper[1] we reported an analysis of the molecular conformation of a block polymer chain in a microphase-separated domain space by small-angle neutron scattering (SANS) with a deuterium labeling technique;[1-7] i.e., A polymer chains of an AB diblock polymer were labeled with deuterium, and the labeled block polymer was mixed with an unlabeled AB diblock polymer having the same degree of polymerization and the same composition in order to study the molecular conformation of an A block chain in the A domain space. Assuming (i) identical degree of polymerization for labeled and unlabeled block polymers, (ii) homogeneous mixing of labeled and unlabeled block polymer chains in the microdomain space, and (iii) no volume change on the mixing of the two block polymers, the SANS intensity from the mixture is given by

$$I(q) = \phi_D(1-\phi_D)(a_H - a_D)^2\phi_A P(q) + [a_H(1-\phi_D)/V_A + a_D\phi_D/V_A - a_B/V_B]^2 S(q) + I_{in} \quad (1)$$

where ϕ_D is the volume fraction of the deuterium-labeled polymer chain in the A microdomain, a_H and a_D are the scattering length of the protonated and deuteriated A monomer unit, respectively, $P(q)$ is the molecular scattering function of the A block chains, $S(q)$ is the scattering function from the microdomain structure, ϕ_A is the volume fraction of the A microdomain, and I_{in} is the net incoherent intensity. Thus the coherent intensity from the mixture is given by simple addition of the *domain scattering* and the *molecular scattering* from which the radius of gyration of the block polymer chain is obtained.

The conformation analysis of a block polymer chain in domain space is an interesting problem from the viewpoint of statistical mechanics of *confined chains*, i.e., random walk chains confined in a certain domain space with one end at the interface, while satisfying the uniform space-filling requirement with their segments. The chain in the domain space was found to be expanded along the direction perpendicular to the interface, and its dimension along this direction was found to control the domain size.[8-13] All

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