^{13}C CP/MAS NMR Study on Alkali Cellulose

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Synopsis

The phase transition from cellulose to alkali cellulose (Na-Cell) and the phase structure of Na-Cell have been investigated by CP/MAS ^{13}C NMR spectroscopy. It has been found from the ^{13}C NMR spectra that both crystalline and noncrystalline components of cellulose decrease in resonance intensities in the transition process from cellulose to Na-Cell I, suggesting that the noncrystalline and the crystalline regions of cellulose are converted to Na-Cell simultaneously. The conversion model is considered as follows: The crystalline part imposes some restriction on the swelling of the noncrystalline part of cellulose, but the conversion of both parts to Na-Cell may be possible when the swelling prevails in the whole microfibril as a result of the penetration of the alkaline solution into the crystalline part. Secondly, the ^{13}C spin-lattice relaxation times (T_1) have been measured to elucidate the phase structure of Na-Cell. Though two T_1 values are obtained for each carbon of Na-Cell except for C6 carbon, Na-Cell has a homogeneous solid structure which is composed of the crystalline regions with a small heterogeneity.

INTRODUCTION

Alkali cellulose (Na-Cell) is an important material in preparation of cellulose ether and viscose rayon. There have been a large number of investigations on Na-Cell formation, such as lattice modifications depending on NaOH-concentration and temperature. However, Na-Cell has not been completely understood for its structure, the conversion mechanism from cellulose, and its reactivity.

Up to now, X-ray diffraction technique has been mainly used in this research field, but it only provides information about the structure of the crystalline region.[1-10] Recently, cross-polarization/magic-angle spinning (CP/MAS) ^{13}C NMR technique has been applied to the characterization of the conformations, phase structures, and hydrogen bonding networks of cellulose in the solid state.[11-35]

Kunze et al.[6,36] first made use of the CP/MAS method to study the structure of Na-Cell as a function of the NaOH concentration. And two other papers followed, one for the selective coordination of sodium cation in Na-Cell[26] and another for the chain conformation during the mercerization reaction.[37] However, the conversion mechanism from cellulose to Na-Cell and the structure of Na-Cell have not been fully understood.

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In this article, the CP/MAS ^{13}C NMR spectra and ^{13}C spin-lattice relaxation times (T_1) have been measured for cellulose samples treated with a variety of aqueous alkaline concentrations, and the conversion mechanism as well as the phase structure of Na-Cell are discussed.

EXPERIMENTAL

Cellulose: Ether grade cotton linters and viscose rayon filaments cut through 60-mesh screen of cutting mill were used for cellulose material.

Alkali cellulose: One weight part of cellulose was treated with one hundred part of aqueous NaOH solution in the range of concentration from 3 to 32 weight % at room temperature overnight. Subsequently, the treated cellulose

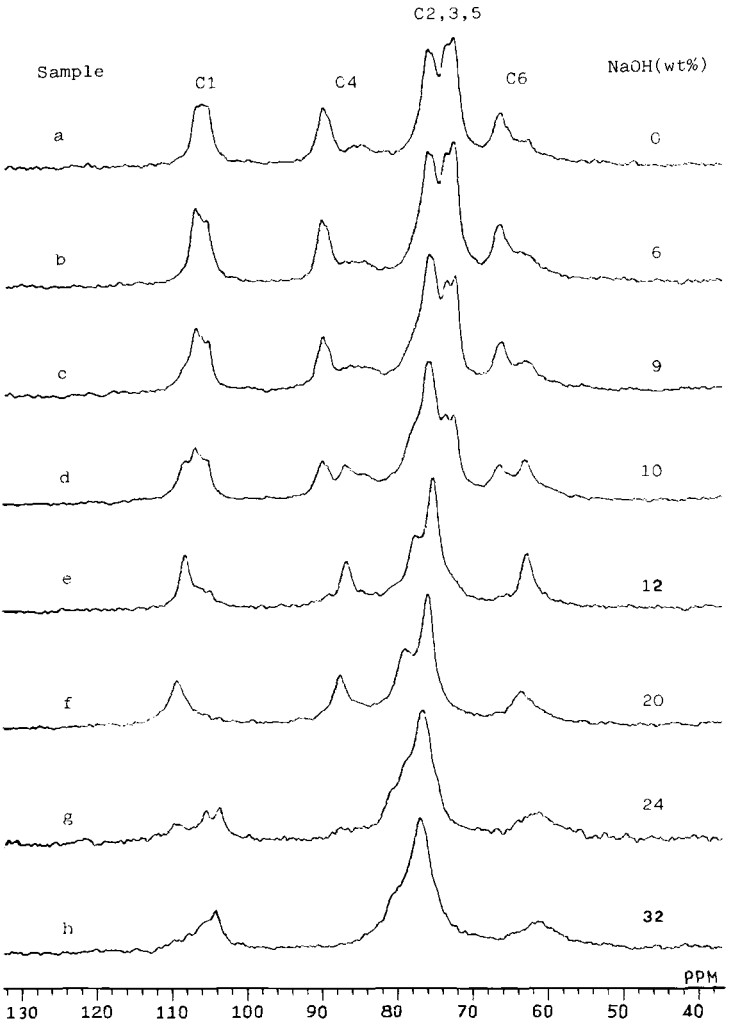

Fig. 1. 50 MHz CP/MAS ^{13}C NMR spectra of cotton linters treated with aqueous NaOH solutions of various concentrations.

TABLE I
^{13}C Chemical Shifts for Cellulose I and Na-Cell (ppm relative to Me_4Si)

Sample	NaOH conc.	C1				C4				C6				C2, 3, 5			
a	0		106.8	106.0	105.1	89.6		85.2		66.4		63.2		75.9	73.6	72.4	
b	6		106.8	106.1	105.1	89.6		85.3		66.5		63.6		75.9	73.6	72.5	
c	9		106.7	105.9	104.9	89.5		85.2		66.4		63.3		75.8	73.4	72.2	
d	10	108.3	106.7	106.0	105.0	89.8	86.9			66.3	63.0			78.2	75.8	73.5	72.3
e	12	109.0		105.9	104.8		87.4				63.5			78.5	75.9		
f	20	109.3					87.5				63.6			78.9	75.9		
g	24	109.0		105.1	103.6						60.6				76.7		
h	32				104.0						60.3				77.0		

was pressed with filter papers by hands to remove the solution retained. The alkali cellulose samples thus obtained were subjected to the measurements of CP/MAS ^{13}C NMR and X-ray diffraction.

NMR Measurements: CP/MAS ^{13}C NMR spectra were measured on a JEOL JNM-FX200 spectrometer equipped with a CP/MAS unit operating at 50 kHz for ^{13}C. The matched field strengths ν_{1C} and ν_{1H} of 52 kHz were applied to ^{13}C and ^{1}H for 1.0 ms and the field strength ν_{1H} for dipolar decoupling was reduced to 36 kHz. The recycling delay after the acquisition of an FID was 10–15 sec and magic-angle spinning was carried out at a rate of 3.0–3.2 kHz. In order to keep alkali solution in the rotor during spinning at such a high rate, we used a rotor with an O-ring seal.[23] Chemical shifts with respect to tetramethylsilane (Me_4Si) were measured using the crystalline resonance line at 33.6 ppm for a small chip of polyethylene inserted in each sample.[39,40]

The ^{13}C spin-lattice relaxation times (T_1) were measured with a slightly modified version of the method developed by Torchia.[38] The detailed procedure was described in the previous report.[19]

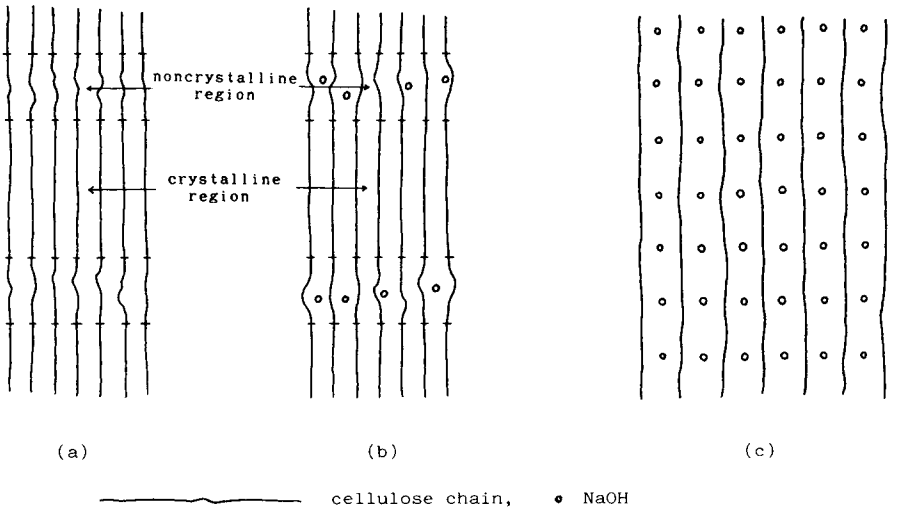

Fig. 2. Schematic diagrams of the phase transition from native cellulose to Na-Cell: (a) microfibril of cellulose, (b) transition state, (c) Na-Cell.

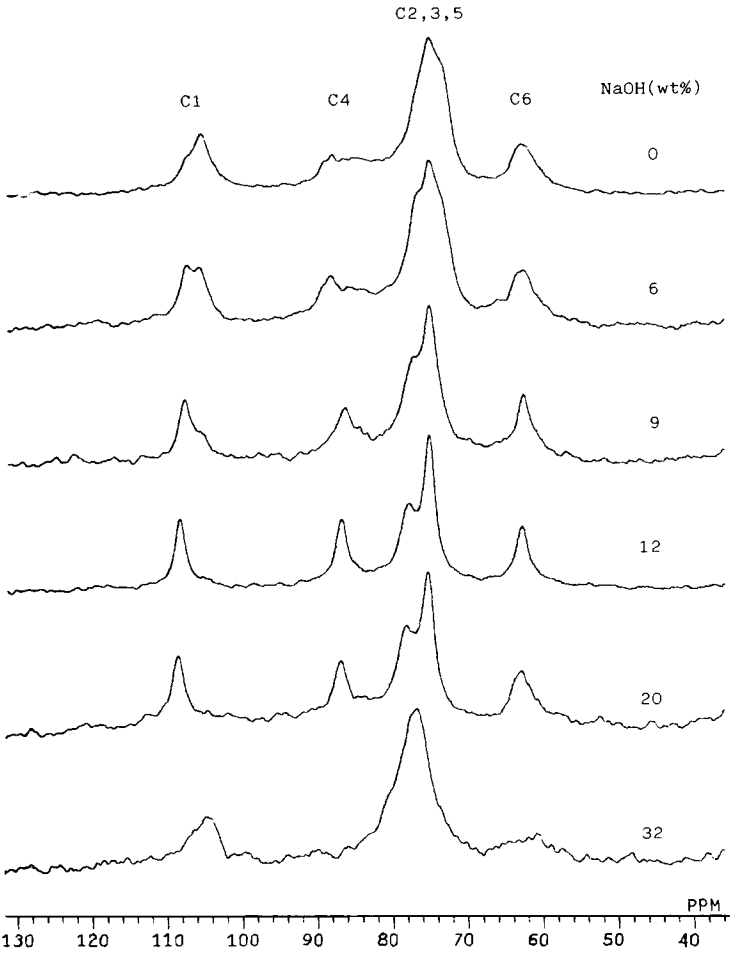

Fig. 3. CP/MAS ^{13}C NMR spectra of viscose rayon treated with aqueous NaOH solutions of various concentrations.

RESULTS AND DISCUSSION

Phase Transition from Cellulose to Na-Cell

Figure 1 shows the 50 MHz CP/MAS ^{13}C NMR spectra of linters cellulose treated with aqueous NaOH solutions of various concentrations. Chemical shifts of the observed resonances are summarized in Table I. The resonance lines of the cellulose and the alkali cellulose are assigned on the basis of the previous works.[11,12,17] The signals corresponding to cellulose remain almost unchanged up to 9%, though signals of Na-Cell are slightly recognized for C4 and C6 carbons at 9%. As the alkaline concentration increases over 9%, the peak of each carbon for Na-Cell becomes strong in intensity gradually. The process of the transition from cellulose I to Na-Cell can be seen on the spectra c, d, e, and f in Figure 1, in the range of NaOH-concentration between 9 and 20%. As the NaOH concentration increases over 20%, other types of alkali cellulose

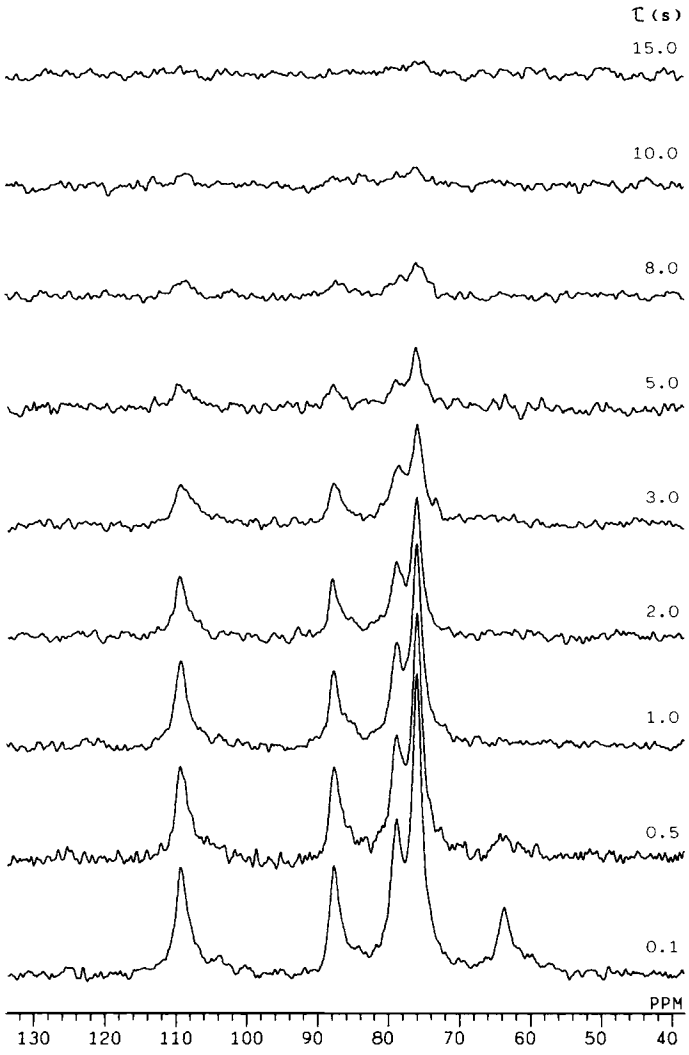

Fig. 4. Partially relaxed 67.8 MHz ^{13}C NMR spectra of sample f at different τ values which were measured by the Torchia pulse sequence[38] for CP T1 measurements.

seem to be formed. These changes of CP/MAS spectra in cellulose alkalization process corresponds closely to those of the X-ray diffractograms obtained for the same samples, as shown below.

On the other hand, it is noted that, as the NaOH-concentration increases, the intensities of C4 and C6 resonances of cellulose decrease in both noncrystalline and crystalline components which are assigned to the upfield broader and downfield sharper lines, respectively.[14,18] Concomitantly, a single line appears for each carbon of Na-Cell (see spectra Figures 1(c)–1(e)). These results suggest that the crystalline and the noncrystalline phases of cellulose simultaneously are converted to the Na-Cell phase. This is in contrast with the well known model that the reactions to produce cellulose derivatives take place first in the noncrystalline regions, and then in the crystalline ones.

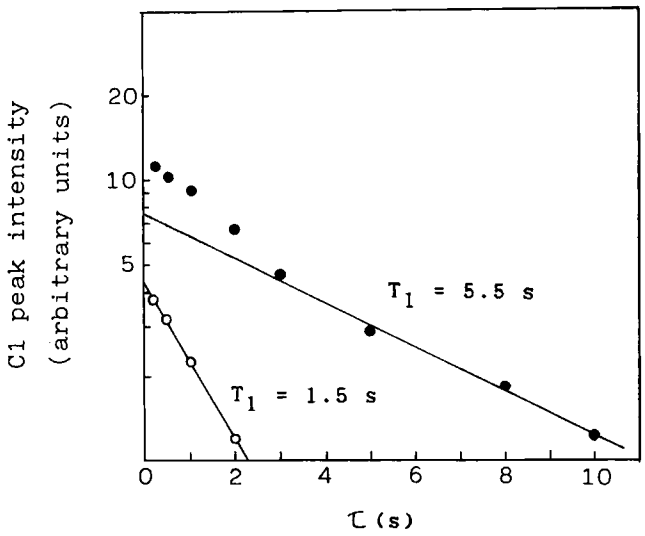

Fig. 5. The semilogarithmic plots of C1 peak intensity for sample f as a function of τ obtained by using the Torchia pulse sequence.[38]

To explain such interesting behavior of cellulose during alkalization, we propose a model for the transition process from native cellulose to Na-Cell, which is shown in Figure 2. Here, a part of the microfibril is drawn without considering the polarity of the cellulose chain, because the existence of parallel or antiparallel chains is still one of controversial problems of cellulose. It is plausible to assume that the crystalline part imposes some restriction on the swelling of the noncrystalline part in the microfibril (Fig. 2(a)), because the conformations of the noncrystalline chains are considerably hindered in native cellulose.[18,28] When an alkaline solution penetrates into such a noncrystalline part, this part may not swell enough to change to Na-Cell at lower NaOH concentrations (Fig. 2(b)). However, as the NaOH concentration increases and the alkali penetrates also into the crystalline region, higher swelling will be possible in both crystalline and noncrystalline regions. Consequently, the

TABLE II
^{13}C Spin-Lattice Relaxation Times[a] of Cellulose and Na-Cell Samples

Sample	NaOH conc (wt %)		T_1 (s) C1	C4	C2, C3, C5	C6
a[b]	0	Crystalline	194, 148, 204	212, 233	208, 196, 155, 175	217
		Noncrystalline	12	17	11, 9.2, 8.7	8.4, 0.17
e	12		1.4, 5.7	1.9, 5.7	1.3, 9.2[c]	0.3
f	20		1.5, 5.5	1.4, 4.5	0.9, 4.4	0.3

[a] Measured with JNM-GX 270 spectrometer.
[b] Ref. 41.
[c] Containing the contribution of residual cellulose components.

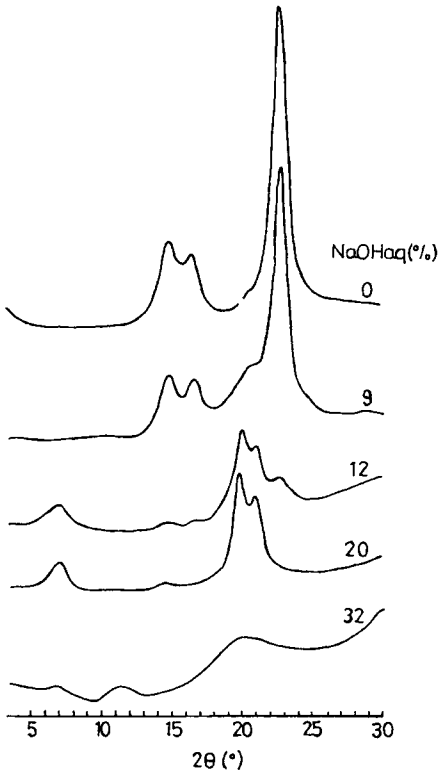

Fig. 6. X-ray diffractograms of cotton linters treated with aqueous NaOH solutions of various concentrations.

whole microfibril may convert to Na-Cell as shown in Figure 2(c). In the transition region, poorly ordered crystalline parts may more easily convert to Na-Cell compared with the highly ordered crystalline parts.

Figure 3 shows the CP/MAS ^{13}C NMR spectra of rayon treated with the aqueous NaOH solutions of different concentrations. The conversion of cellulose to Na-Cell seems to take place at somewhat lower concentrations for rayon than for linters: Rayon is almost converted to Na-Cell in a 9% aqueous NaOH solution. Such easy conversion of rayon to Na-Cell may be attributed to the weakness of hydrogen bonding network, poorly ordered crystalline regions, and the low degree of polymerization of this sample. However, the crystalline and noncrystalline regions seem to be also converted to Na-Cell at the same time as in the case of linters, though the noncrystalline part of rayon is less restricted than that of linters.[18,28]

Phase Structure of Na-Cell

Figure 4 shows the partially relaxed ^{13}C NMR spectra of sample f shown in Table I, which were obtained by Torchia's pulse sequence for T_1 measurements.[38] In Figure 5 the logarithmic peak intensity of the C1 line is plotted against the time τ for the longitudinal relaxation. It is clearly seen from this figure that there are two components with different T_1 values. Similar two components

were also recognized for some resonance lines of samples e and f, whose T_1 values are compiled in Table II. For comparison the T_1's of the crystalline and noncrystalline components of the original cellulose are also shown in Table II. Both T_1 values of Na-Cell are extremely short compared with the T_1's of the crystalline and noncrystalline components of the cellulose. This indicates that the cellulose chains undergo much enhanced motion in Na-Cell possibly due to the highly swollen structure in which the molecular chains are coordinated with Na^+ ion and water molecules. The assignments of the two components with different T_1 values are not easy at the present time. According to the analysis of the decay curve shown in Figure 4, the fraction of the longer T_1 component increases with increasing NaOH concentration and it reaches to at least 70% for sample f. Nevertheless, the X-ray diffractograms simply indicate the increase in intensity of Na-Cell in the same range of NaOH concentration, as shown in Figure 6. In addition, each line of the diffractogram is considerably narrow and no contribution from the disordered region can be observed for these samples. Therefore, it is plausible to point out that both two components with different T_1 values should be attributed to the crystalline region of Na-Cell. Though the detailed information on the structural difference between those components has not been obtained yet, ^{13}C NMR spectroscopy is useful for detecting such a small structural difference. They will not be so different in conformation and molecular mobility each other, judging from no or small difference in ^{13}C chemical shifts and T_1 values for them.

Consequently, the phase structure of the Na-Cell is considered as follows: the Na-Cell is composed of only crystalline regions in which there is such a small structural heterogeneity as can be reflected on NMR spectra but not be detected in X-ray diffractogram.

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