^{13}C nuclear magnetic resonance studies of cellulose acetate in the solution and solid states

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Solution and solid state nuclear magnetic resonance studies are reported on heterogeneously acetylated cellulose. Comparison of the spectra obtained indicates that there are both ordered and disordered regions within the solid phase but solution state n.m.r. does not reveal the presence of both of these domains. It is proposed that the initial acetylation occurs in disordered regions which may thereafter be solubilized, but that subsequent acetylation permits the preservation of order in the sample. Unlike nitration, acetylation appears to occur rapidly, and no evidence for the presence of partial acetylation of anhydroglucose units was found.

(Keywords: cellulose acetate; heterogeneous reaction; carbon-13 nuclear magnetic resonance; magic-angle spinning; *N*-methylmorpholine-*N*-oxide; morphology)

INTRODUCTION

Cellulose acetate is normally produced commercially by the action of acetic anhydride in the presence of glacial acetic acid, with a sulphuric acid catalyst. The product is obtained in powder or flake form suitable for subsequent processing. Acetylation can however be carried out so that the fibrous nature of the original cellulose is, to some extent, retained[1]. It is now reasonably well-established that the two types of acetate, which are chemically equivalent, are in fact polymorphic forms analogous to the cellulose (I) and (II) structure of the parent molecule. Recent X-ray diffraction studies have revealed significant differences in the packing geometry of the unit cells in each case[2,3].

During the last few years the importance of structure and morphology to the dynamic behaviour of cellulose and its derivatives has been recognized[4-7] and it is for this reason that the present study has been undertaken in an attempt to correlate the molecular and supramolecular structure of these materials with dynamic observations. In the present series of papers data will be presented on the behaviour of a series of cellulose acetates generated using heterogeneous acetylation conditions.

During the last four years, a number of papers have been published on the ^{13}C n.m.r. of cellulose and its derivatives[8]. Prior to the availability of magic-angle-spinning solid state n.m.r. high resolution spectra were obtained using various 'solvents' for cellulose. The spectra obtained were often of poor quality and even when high accumulation levels were used contained considerable noise levels. A more important point is that most, if not all, of these 'solvents' react chemically with the cellulose to form various types of complex, an example being the combination of paraformaldehyde and dimethylsulphoxide to give a cellulose hemiacetal, and as such would be expected to alter the chemical shifts of the relevant carbons. *N*-methylmorpholine-*N*-oxide was reported to be a useful solvent for cellulose[9], and a number of spectra obtained with this solvent have been recorded[8,10]. In this paper we will discuss whether or not true solution spectra are obtained and also attempt to identify the structural implications of the data obtained at present. In subsequent papers we will report the results of X-ray diffraction, positron annihilation, and dielectric and dynamic mechanical measurements, and attempt to interpret this data on the basis of the information revealed by the present study.

EXPERIMENTAL

Synthesis of cellulose acetates

The series of cellulose acetates used in this study was prepared from cotton linters by heterogeneous acetylation using the method described by Tanghe *et al.*[11]. A 10 g portion of cotton linters (cleaned and dewaxed Holden Vale type II, supplied by Drs T. J. Lewis and F. S. Baker, PERME Waltham Abbey) was placed in a 250 ml conical flask, and a mixture of glacial acetic acid (80 ml), toluene (120 ml) and 71–73% perchloric acid (2 ml) was

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added. The mixture was shaken vigorously for a few minutes, and then as much of the liquid as possible was poured into another flask containing 50 ml acetic anhydride. This mixture was swirled and immediately poured back into the flask containing the linters. The purpose of this procedure was to minimize the possibility of a high initial concentration of acetic anhydride contacting the fibres closest to the neck of the flask and hence generating material which might have higher than average degrees of acetylation. The flask was stoppered and maintained at 30°C for periods between 5 min and several hours with periodic shaking of the flask. At the end of the required period the acetylated linters were removed and washed twice or three times in ethanol and then several times in water in order to remove residual traces of acid. Washing was continued until 1 drop of 0.05 M NaOH was sufficient to impart a faint permanent pink to a 100 ml aliquot of the wash water containing phenolphthalein. The acetate was washed a final time in ethanol and subsequently dried *in vacuo* overnight at 60°C.

All samples were stored in screwcapped glass jars until they were required and before any subsequent experiments were performed the samples were dried overnight in a draught-assisted oven at 90°C. The degree of acetylation was determined using a standard method[12].

Solution ^{13}C n.m.r. spectra

Solution ^{13}C n.m.r. spectra were obtained by dissolving the cellulose or cellulose acetate sample in a mixture of dimethylsulphoxide (DMSO) and *N*-methylmorpholine-*N*-oxide. It was found that the samples with degrees of acetylation greater than 20% could be dissolved in DMSO only at elevated temperatures. The composition of the solvent mixture used for cellulose and the 0.5 degree of substitution (*DOS*) sample was composed of 200 mg of polymer in 2 ml of a 80:20 mixture of DMSO-D6 and the morpholine derivative at 90°C. The higher acetates were dissolved using similar quantities in DMSO-D6 only.

The spectra of these solutions were recorded on a Varian 300 MHz Fourier transform instrument at the University of Manchester. The spectra were recorded at 90°C using TMS as the internal reference with approximately 10^5 transients accumulated for each spectrum.

^{13}C n.m.r. spectra of solid samples

The ^{13}C n.m.r. spectra of the solid cellulose acetates were obtained using a home-built double-resonance spectrometer (with a Bruker (CXP200) probehead) at the University of East Anglia. In all cases the spectra were recorded at ambient temperature and at a ^{13}C frequency of 50.3 MHz. The samples (*ca.* 70 mg) were enclosed in Andrew/Beams design rotors constructed of Macor and Delrin (base) and were spun at the magic-angle (54.7°) with respect to the B_0 field and at rates of the order of 3 kHz. The spectra were all obtained using cross-polarization from ^1H to ^{13}C with Hartmann–Hahn matching fields of 40 kHz amplitude, a ^1H decoupling field of 60 kHz, and flip-back. Cross-polarization times were typically 2 ms, the number of transients per spectrum was approximately 25000 and the recycle delays were 1.5–2 s. Other details are given in the Figure captions.

The ^1H spin relaxation times were obtained using a home-built pulse spectrometer operating at 60 MHz with a 90° pulse duration of *ca.* 1 μs. The spin-locking field used for $T_{1\rho}$ measurements was equivalent to 40 kHz.

RESULTS AND DISCUSSION

^{13}C solution n.m.r. studies

The solution ^{13}C n.m.r. spectrum of cotton linters obtained using the *N*-methylmorpholine-*N*-oxide/DMSO mixture is shown in *Figure 1* and the shifts tabulated in *Table 1*. The solvent mixture exhibits a strong signal at the position where we would have anticipated observing the C–6 resonance. With the exception of this resonance, all the other cellulose signals can be clearly seen, although they are comparatively weak. The observed shifts agree with those reported previously[10] to within 2 ppm. *Figure 2* shows the spectrum obtained from a cellulose acetate of *DOS* equal to 0.48. This spectrum clearly shows the presence of both substituted and unsubstituted cellulose material, *Table 1*.

It was found that the spectra for the samples with *DOS*'s greater than 0.5 were identical irrespective of whether the *N*-methylmorpholine-*N*-oxide was present and had the form shown in *Figure 3*. This spectrum was obtained using DMSO as solvent. It is immediately clear that irrespective of the degree of substitution the spectrum that was obtained is that of the cellulose triacetate and there is no evidence for partially substituted or unsubstituted cellulose, despite the fact that chemical analysis clearly shows that acetylation is far from complete. Apart from a difference in the methyl signals in the 0.75 *DOS* sample, and minor differences in the intensities and shifts of individual peaks, the spectra above a *DOS* of 0.48 are identical and are those of a fully substituted cellulose triacetate.

Wu has studied the substitution of the hydroxyl groups in cellulose by the nitrate ester group[13] and has shown that this results in distinct changes in the ^{13}C spectra of the product. In contrast the proton n.m.r. spectra gave little useful information on the nature of the changes which were occurring in the system. On the basis of peak areas and positions, Wu characterized the distribution of the nitrate group in the bulk sample, basing his analysis on the assumption that the nuclear Overhauser enhancement (NOE) factors for carbons in the anhydroglucose unit were approximately equal. Clark *et al.*[14] expanded the work of Wu to an examination of the substitution pattern obtained as a result of nitration and denitration of cellulose in different nitration/denitration mixtures and

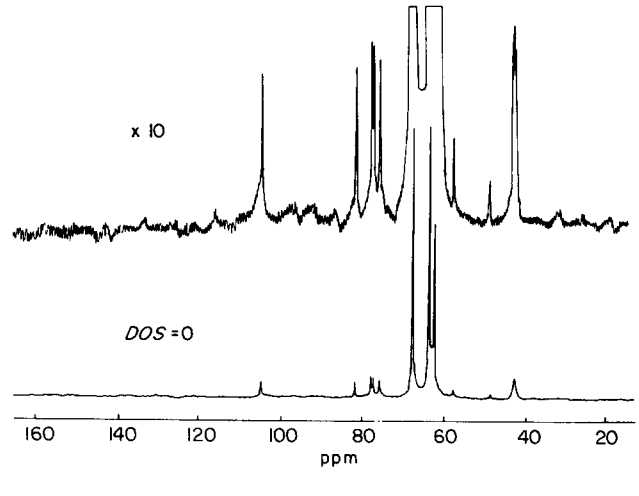

Figure 1 Solution ^{13}C n.m.r. spectrum of cellulose obtained in *N*-methylmorpholine-*N*-oxide/DMSO mixture using proton decoupling

Table 1 Solution state ^{13}C chemical shifts[a]

DOS[b]	C-1	C-2	C-3	C-4	C-5	C-6	CO	CH_3
0	103.9	74.5	75.3	79.3	76.7		—	—
0.48	103.4, 100.5	74.8, 73.3	76.2	80.7	76.8		171	21.3, 21.0
0.75	99.6	72.7, 72.3, 72.0[c]		76.1	—[c]	62.5	169.5	20.9
1.09	99.6	72.7, 72.3, 72.0		76.1	—	62.5	171.5, 170.5, 170	20.9
1.5	100.4	73.4, 73.0, 72.6		76.9	—	63.3	171.5, 170.6, 170.2	21.4, 21.1
1.74	100.4	73.4, 73.0, 72.6		76.8	—	63.2	171.5, 170.6, 170.2	21.4, 21.1
2.56	100.4	73.4, 72.8, 72.5		76.7	—	63.1	171.5, 170.6, 170.2	21.4, 21.1
2.93	100.4	73.6, 73.2, 72.9		77.0	—	63.4	171.3, 170.4, 170.1	21.2, 20.9
2.5[d]	102.6, 99.6	72.8, 72.4, 72.0		80.2, 76.2, 75.5, 75.2	—	62.6, 59.4	171.3, 170.4, 170.1	20.4, 20.1

[a] Given in ppm with respect to the shift for tetramethylsilane, using the high-frequency-positive convention
[b] Degree of substitution
[c] The signals between 72 and 77 ppm arise from carbons 2, 3 and 5 but an absolute assignment is of limited reliability
[d] This sample is a commercially obtained acetate.

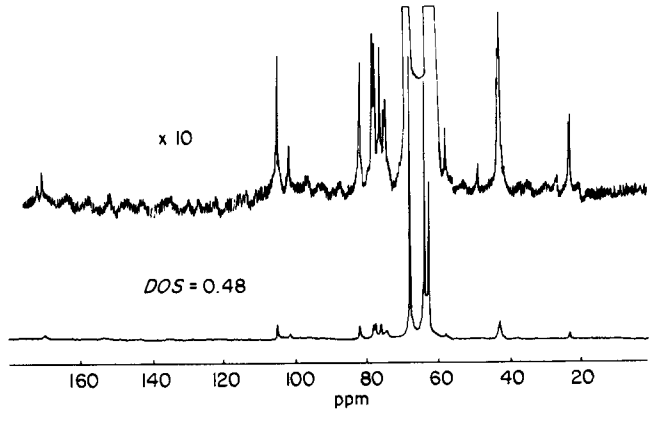

Figure 2 Solution ^{13}C n.m.r. spectra of cellulose acetate *DOS* of −0.48 obtained in *N*-methylmorpholine-*N*-oxide/DMSO mixture using proton decoupling

for various reaction times. These workers were able to show that the nitrate distribution was dependent upon the nitration/denitration time and the reaction mixture employed. The picture which emerges is very different for acetylation using the conditions indicated in this paper. It appears that the rates of acetylation are not controlled by the reactivity of the particular sites but rather by accessibility. The conditions used in nitration lead rapidly to the destruction of the organized regions of the cellulose and nitration proceeds as a pseudo-homogeneous process. In contrast, with the conditions used here, reaction appears to be limited by access to the cellulose molecules and, whilst we know that kinetic factors must be present, they are not sufficient to lead to the observation of partial substitution of the type seen in the nitrated materials.

As a comparison, the solution spectrum of a commercially produced cellulose acetate of *DOS* equal to 2.5 is presented in *Figure 4*. The lower spectrum shows the equivalent heterogeneously acetylated sample of equal *DOS*. The commercial sample will have been generated in conditions such that the basic cellulose structure has been destroyed and the observed *DOS* of 2.5 is achieved by subsequent hydrolysis of the triacetate. In the spectrum obtained from this material, both substituted and unsubstituted cellulose features are observed. At first sight the spectrum appears to correspond to the superposition of a cellulose and cellulose triacetate spectrum. However, careful examination of the C-4 region indicates a fine structure which can be attributed to the occurrence of a number of partially substituted cellulose rings. The integrals in the C-1, C-4 and C-6 regions in this sample indicate a ratio of acetate to cellulose carbons of approxi-

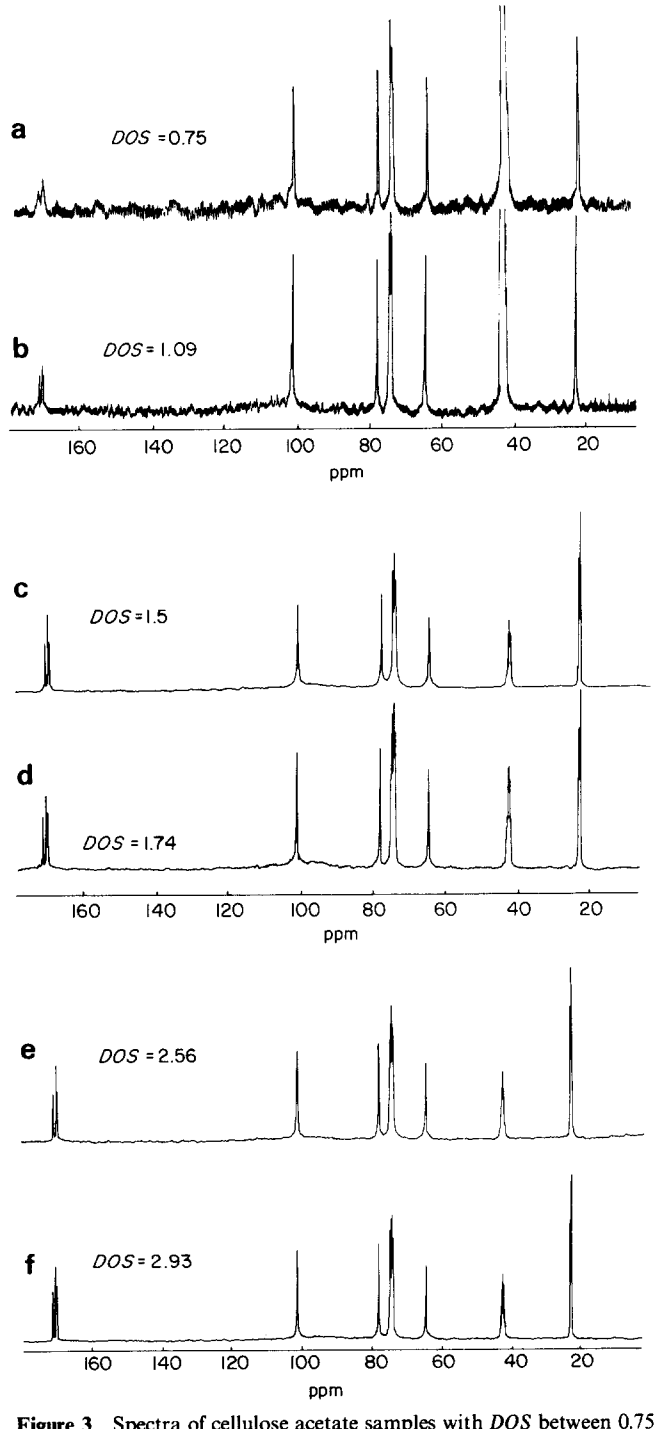

Figure 3 Spectra of cellulose acetate samples with *DOS* between 0.75 and 2.93 obtained in DMSO as solvent using proton decoupling

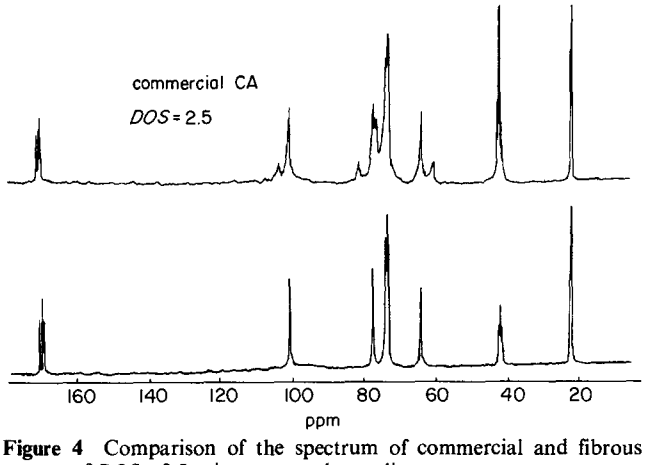

Figure 4 Comparison of the spectrum of commercial and fibrous acetate of $DOS = 2.5$ using proton decoupling

mately 5 to 1, in good agreement with the *DOS* determined by chemical analysis.

A possible interpretation of these observations is that the initial acetylation occurs in disordered accessible surfaces of ordered regions. Once this has been completed, further acetylation occurs in the ordered regions, and occurs without these regions losing their integrity. The solutions subsequently obtained really contain dispersions of these ordered regions and hence the spectra correspond to the solubilized part of the cellulose structures only. An important implication is that contrary to common belief *N*-methylmorpholine-*N*-oxide/DMSO mixtures may not be true solvents for cellulose but rather are capable of achieving dispersions of the ordered regions. It is thus possible that such ordered regions survive to a large extent in fibrous cellulose acetate and that the solution spectra correspond to solubilized surface groups which occur in disorganized areas.

Solid state n.m.r.

Knowledge of ^1H T_1 and $T_{1\rho}$ relaxation parameters (i.e. spin-lattice relaxation in the laboratory and rotating frames respectively) is necessary in order to optimize the ^{13}C n.m.r. experiments on the materials when using cross-polarization from protons as a means of generating the ^{13}C n.m.r. signal. In addition ^1H n.m.r. studies have been shown to be useful in the characterization of the cellulose and cellulose acetate samples investigated in this project, but these results will be discussed elsewhere. The samples all exhibit single exponential T_1 behaviour (in the range 0.3 to 1.5 s), but the $T_{1\rho}$ process was found to be a superposition of two exponentials (in the ranges 3–5 ms and 15–25 ms). We believe that the short $T_{1\rho}$ value corresponds to disordered regions and the longer component to more rigid, ordered regions.

The ^{13}C CPMAS n.m.r. spectra of the samples are presented in *Figures 5* to *9* and their ^{13}C chemical shifts are summarized in *Table 2*. The ^{13}C spectra of the solids often show splittings not present in the corresponding ^{13}C solution spectra, and these may be related to the existence of non-equivalent sites in the solid state arising from conformational and crystallographic effects. As the degree of acetylation increases there is broadening of the spectral peaks, and hence the small crystallographic splittings can no longer be observed. This is probably indicative of loss of order in the structure, the broadening reflecting the presence of a range of isotropic chemical shifts for each carbon.

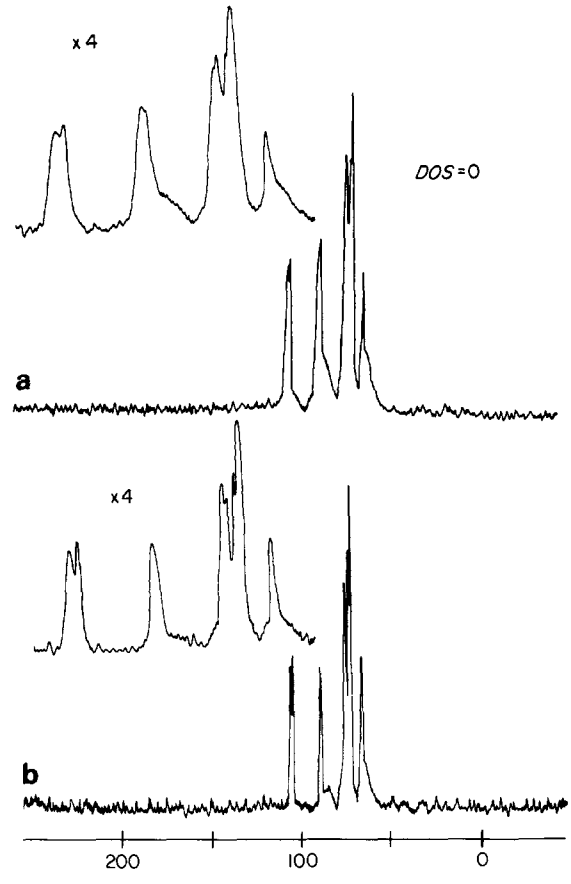

Figure 5 ^{13}C n.m.r. spectra of solid cellulose: (a) normal; (b) with a delay before contact of 25 ms

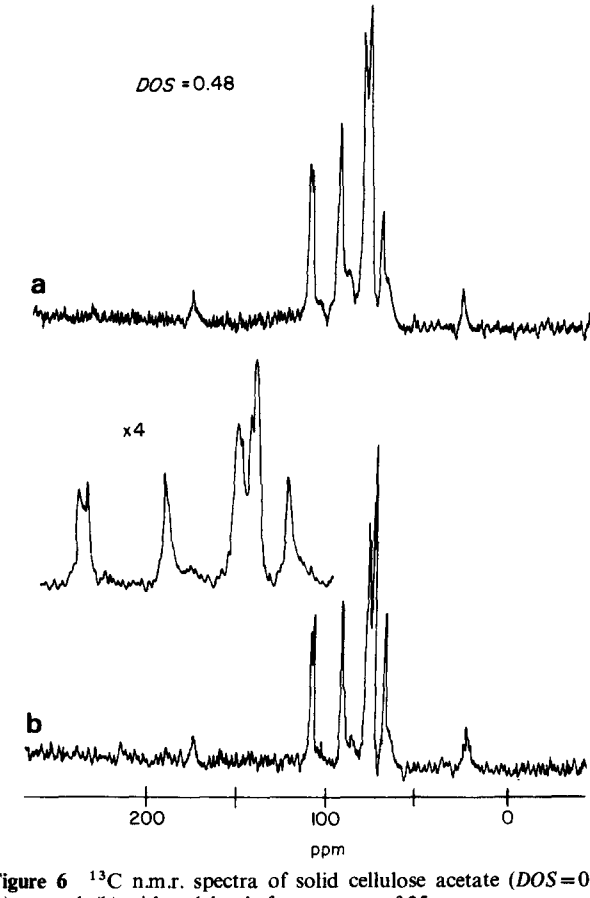

Figure 6 ^{13}C n.m.r. spectra of solid cellulose acetate ($DOS = 0.48$): (a) normal; (b) with a delay before contact of 25 ms

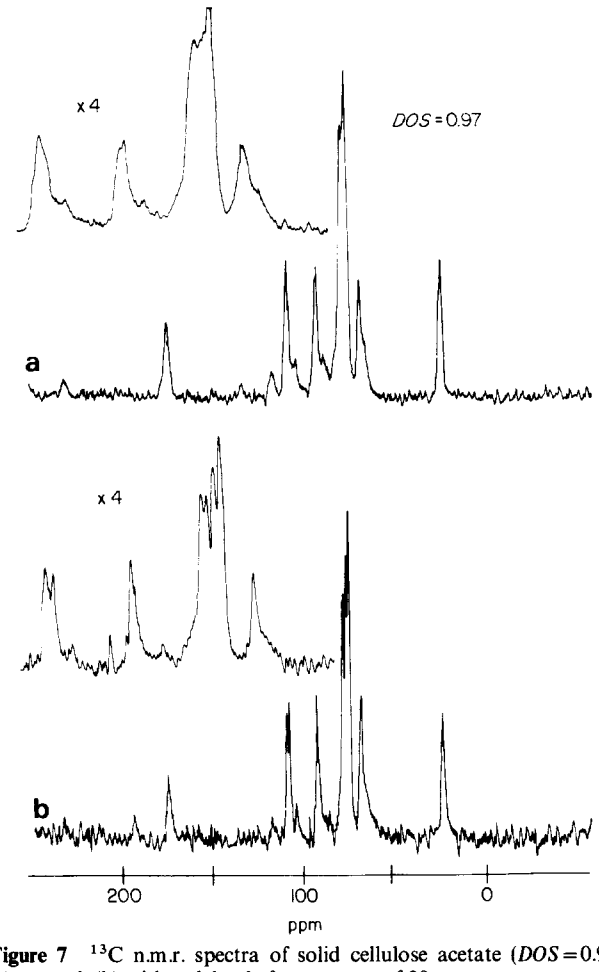

Figure 7 ^{13}C n.m.r. spectra of solid cellulose acetate ($DOS = 0.97$): (a) normal; (b) with a delay before contact of 20 ms

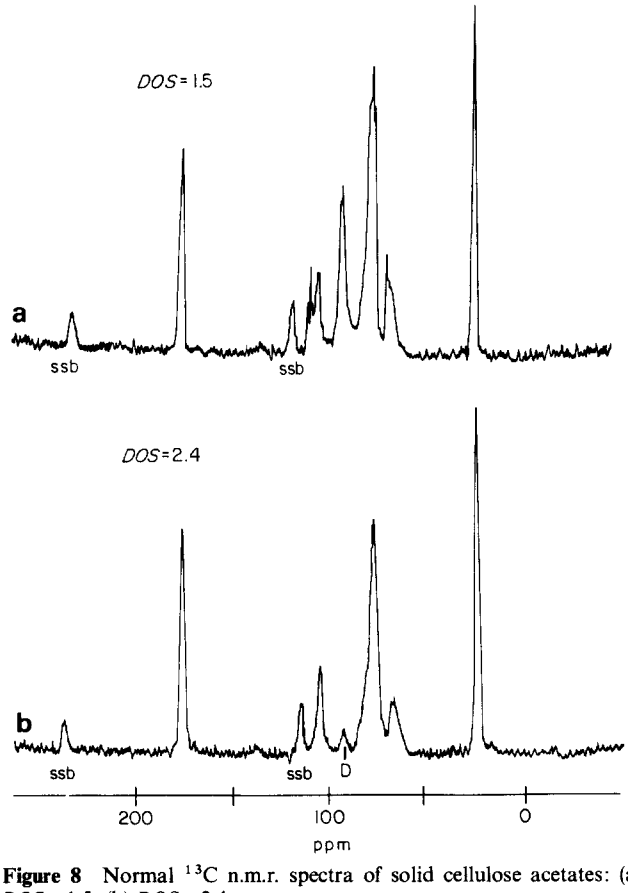

Figure 8 Normal ^{13}C n.m.r. spectra of solid cellulose acetates: (a) $DOS = 1.5$; (b) $DOS = 2.4$

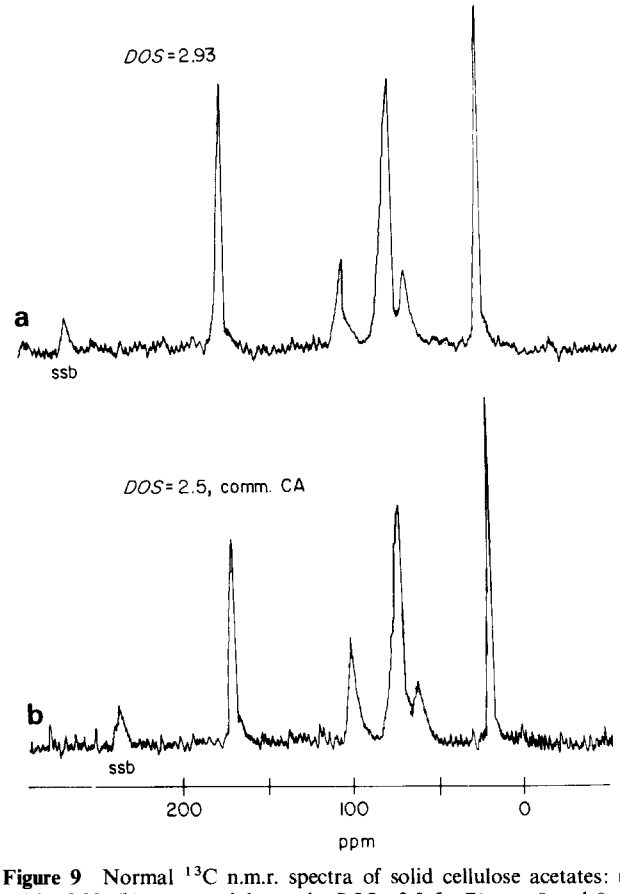

Figure 9 Normal ^{13}C n.m.r. spectra of solid cellulose acetates: (a) $DOS = 2.93$; (b) commercial sample, $DOS = 2.5$. In *Figures 8* and *9* ssb indicates a spinning side band and D indicates the resonance due to the Delrin rotor

The C–1 resonance region in cellulose (see *Figure 5*) is split into three peaks, indicating unit cell inequivalencies and possibly the existence of two crystalline forms in native cellulose, which have been designated as I_α and I_β[15].

The C–4 and C–6 resonance regions consist of fairly sharp peaks with broad low-frequency shoulders, representing the ordered and amorphous regions respectively. This is demonstrated by recording spectra using a delayed-contact cross-polarization pulse sequence which reduces the contribution from the short ^1H $T_{1\rho}$ regions. In the resulting spectra, for cellulose and the samples with low degrees of acetylation, there is a marked improvement in resolution and sharpening of the spectral peaks, together with a diminution in intensity of the broad low-frequency shoulders. Hence this confirms that these broad peaks represent the shorter ^1H $T_{1\rho}$ regions (see spectra labelled (b) in *Figures 5–7*). The broad resonances in cellulose have been attributed to chains on crystallite surfaces as well as chains in three-dimensionally disordered regions[15]. Comparison of the cellulose spectra labelled (a) and (b) shows that the central C–1 peak at 104.2 ppm, which has been attributed to the I_α crystalline form of native cellulose, decreases in intensity relative to the peaks at 105.1 ppm and 103.6 ppm which are said to correspond to the I_β form[15]. This suggests that if there are indeed two crystalline forms of native cellulose they have different ^1H relaxation properties.

The C–2, C–3, C–5 resonance region is split into several peaks but these have not been specifically assigned.

The C–1 and C–4 peaks show marked variations as a function of the degree of acetylation, which is strongly suggestive of a conformational change about the glyco-

Table 2 ^{13}C chemical shifts of cellulose and cellulose acetates in the solid state[a]

SAMPLE	C=0	C-1	C-4	C-2, -3, -5	C-6	CH_3
Cellulose		105.1 104.2 103.6	88.8 +low frequency shoulder (~84)	74.3 73.7 71.8 70.8	64.5 +low frequency shoulder (~62)	
CA *DOS*=0.48 Ac gps. per β-glucose unit	170.2	105.0 104.1 103.4	88.7 +low frequency shoulder	74.2 73.5 71.8 70.7	65.2 +low frequency shoulder	20.3
CA *DOS*=0.97	170.5 169.8	105.2 104.4 103.5 100.3	88.4 87.8 +low frequency shoulder	74.6 73.9 73.0 72.1 71.1	64.6 +low frequency shoulder	20.1
CA *DOS*=1.5	170.5 169.7	105.3 103.7 100.6 100.0	87.8 +low frequency shoulder	73.6 72.2 71.1	64.5 +low frequency shoulder	20.3 19.9
CA *DOS*=2.4	169.6	100.4	—	72.4	63.1	20.0
CA *DOS*=2.93	169.8	99.8	—	72.4	63.8	19.9
CA (commercial) *DOS*=2.5	170.3	102.0 101.2	—	73.6 72.7	62.8	20.4

[a] Given in ppm with respect to the shift for tetramethylsilane, using the high-frequency-positive convention. The shifts were measured by the replacement technique using solid adamantane (δ=37.7 ppm) as a secondary reference

sidic linkage. In the spectra of samples with *DOS* values of 2.4, 2.93 and 2.5 (commercial) the crystalline C-4 peak (δ=88–89 ppm) is no longer observed and the broad resonance is probably incorporated into the C-2, C-3, C-5 region. In the solution spectra a single C-4 resonance is observed at approximately 80 ppm; this suggests that only the amorphous regions are going into 'solution'. Acetylation leads to the generation of a new peak at about 100.5 ppm in the C-1 region which increases in intensity relative to the other C-1 peaks. Beyond a *DOS* of 2.4 only the broader peak at 100.5 ppm is present in the C-1 region of the spectra. In the solution spectra of all the samples of *DOS* greater than 0.48 the only peaks present are those of the triacetate. However in the solid state peaks corresponding to both the triacetate and unsubstituted cellulose can clearly be seen up to a *DOS* of 1.5. This again suggests that the solution spectra do not represent the total sample present.

A comparison of the spectra for low degrees of substitution with those for 2.4 substitution and above indicates that significant changes occur in the C-4 region of the spectrum. The initial acetylation occurs in the amorphous regions, and hence retention of a peak at 88 ppm is indicative of the existence of crystalline cellulose. The disappearance of this peak for acetylation of 2.4 or greater is consistent with acetylation occurring in the crystalline region with consequent changes at the molecular level in these regions, though apparently they do not lose their integrity sufficiently to be truly soluble.

CONCLUSIONS

A combination of the data obtained from solution and solid state studies indicates that in the cellulose acetate samples described in this paper there exist both ordered and disordered regions. The acetylation reaction in this case appears to be subject to morphological rather than chemical control. Unlike the nitrates, evidence for partially substituted ring systems is sparse. A more detailed analysis of the solid state n.m.r. will be presented later.

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