BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 3, pp. 479-485, 1995

0032-3861/95/$10.00+0.00

^{13}C nuclear magnetic resonance studies of cellulose ester derivatives in solution, powder and membranes

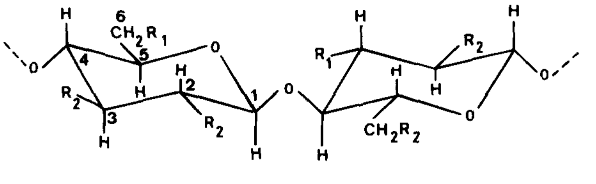
Teresa Nunes*, Hugh D. Burrows†, Manuela Bastos†, Gabriel Feio and M. Helena Gil†
ICTPOL, Av.Prof.Gama Pinto 2, 1699 Lisboa Codex, Portugal
†Departamentos de Química e Bioquímica da Universidade de Coimbra, 3049 Coimbra, Portugal
(Received 6 July 1994)

A ^{13}C nuclear magnetic resonance study (with cross polarization and magic angle spinning) is presented of commercially available cellulose acetate and cellulose propionate as powder samples and also in different membranes. Some physical properties of the films are interpreted in the light of data obtained for the principal components of the shielding tensor of ^{13}C nuclei on carbonyl groups. In particular, it is shown that the shielding asymmetry factor, measured on samples with a regular shape and with a fixed orientation in the rotor, is a sensitive probe to ordered domains in the polymers.

(Keywords: cellulose esters; ^{13}C n.m.r.; chemical shift anisotropy)

INTRODUCTION

During the investigation of suitable polymers to act as host materials in optically switchable new devices, cellulose acetate (CA) and cellulose propionate (CPR) were chosen as good candidates for the preparation of films by solvent evaporation.



CA: R_1=-OH, R_2=-O_2CCH_3
CPR: R_1=-OH, R_2=-$O_2CCH_2CH_3$

However, during preparation of the films, different physical properties were observed, depending on the solvent, the concentration of the starting solution and the temperature selected for the evaporation of the solvent. For example, a white membrane was obtained when using acetone at low concentrations of CPR and room temperature; to prepare transparent films the first two conditions were maintained but a higher temperature (~40°C) was needed. In other solvents, such as tetrahydrofuran and dioxan, the films were always transparent, possibly due to differences in boiling points or other solvent properties.

For optical studies involving these materials, it is essential to explain these features. In principle, formation of transparent films is connected with the degree of polymeric ordered domains in each membrane, which is strongly dependent on the amount of water present, as has been reported for cellulose[1]. The degree of crystallinity is normally estimated by differential scanning calorimetry (d.s.c.) or by X-ray diffraction; however, it is shown here that the shielding anisotropy of the carbon atom in the carbonyl groups obtained from ^{13}C nuclear magnetic resonance (n.m.r.) measurements, using cross polarization (CP) for proton enhancement and magic angle spinning (MAS), can be used as a sensitive probe to compare the crystallinity of these polymers. As far as we know, this is the first time that this method has been applied to cellulose derivatives, but this technique has already proved to be a powerful tool in the study of cellulose. The studies reported by Atalla *et al.*[2] and also by Earl and VanderHart[3] have clearly shown that it is possible to estimate the degree of crystallinity of this polymer from such measurements. More recently, solid state ^{13}C n.m.r. evidence was reported on ordered and amorphous regions of cellulose acetate[4].

It should be pointed out here that when comparing the degree of order in cellulose and cellulose derivatives, the term crystallinity is often used, however, for polymers which can present different morphologies, it is difficult to separate the concepts of crystallinity and morphology. In fact, to define the crystalline structure, not only the degree of order along the polymer chain must be considered but also the degree of lateral order or the chain packing. This difficulty has already been mentioned by several authors (e.g. ref. 3).

---

*To whom correspondence should be addressed

EXPERIMENTAL

Cellulose acetate and cellulose propionate (Eastman Chemical Company) were used to prepare acetone solutions in the concentration range 5–20% w/w. The solvent was allowed to evaporate at 40°C (5 and 20%, films 1 and 2) or at room temperature (5%, film 3, and 20%). For n.m.r. studies, the films were cut into small pieces ($\approx 4\,mm^2$) with no regular shape ('random' film) or with similar sheet patterns (4 mm × 15 mm, 'oriented film'); the thickness of the membranes was about 0.1 mm.

Differential scanning calorimetry measurements were made on 2–3 mg samples of films on a Polymer Laboratories PL-DSC apparatus in a nitrogen atmosphere using heating rates of 10°C min^{-1}. For thermogravimetric analysis (t.g.a.), 20–25 mg samples of films were used in a Polymer Laboratories PL-TG thermobalance with a heating rate of 10°C min^{-1}. Scanning electron microscopic (SEM) examination of films was carried out at the Department of Colour Chemistry, University of Leeds, UK. Experimental details of the equipment and material used are described elsewhere[5].

All ^{13}C CP/MAS spectra were obtained at 75.5 MHz in 7 mm or 4 mm ZrO_2 rotors normally at spinning rates of 1000 ± 3 Hz or 8000 ± 5 Hz, respectively (when other values were selected these will be referred to in the text); an MSL 300 P Bruker spectrometer was used, and the n.m.r. data were obtained at the probe temperature (293 K). Al_2O_3, previously dried, was used as a spacer to completely fill the rotors. Chemical shifts are reported in parts per million from tetramethylsilane, taken as an internal or external reference for liquid or solid state n.m.r., respectively.

RESULTS AND DISCUSSION

Chemical and physical characterization of films

As noted in the Introduction, cellulose acetate and propionate films prepared at room temperature by evaporation of dilute solutions (5%) in acetone were white, whereas those obtained either at higher concentrations (20%), or at higher temperatures (40°C) were completely transparent. Observation of the white films by SEM showed a number of irregular pores of 0.2–1 μm. With CPR, the pores were round, slightly larger, and were surrounded by structured zones. The transparent films showed no evidence of pores up to the highest magnifications studied (5000 ×).

Analysis of the films by t.g.a. revealed a weight loss in the region of ~100°C, corresponding to loss of water. The onset of a second weight loss above 200°C corresponded to degradation of the cellulose esters. Values of the weight loss in the first step (~100°C) are presented in *Table 1*. The t.g.a. data suggest the presence of water in all cases, with higher percentages in the CA films, in agreement with the lower hydrophobicity of these films relative to the CPR films. However, there were no significant differences in water content between the white and transparent films.

D.s.c. studies on the same films showed a broad, endothermic peak at ~100°C. With CA, a second, fairly sharp, endothermic transition was observed in the range 200–230°C. The thermograms of the CA films are shown in *Figure 1* and the d.s.c. results for all the membranes are presented in *Table 1*. In agreement with previous studies[6], the transition at ~230°C is assigned to melting of the crystalline regions of CA. While a wide variation has been observed for the enthalpy of this transition, the ΔH values for the transparent films are close to those observed with several commercial CA membranes[6]. It is noteworthy that both the transition temperature and enthalpy change for this transition are higher in the white CA films than in the transparent ones; this strongly suggests a larger degree of crystallinity in the white film.

With CPR, melting is not observed over the temperature range studied. However, a weak transition is observed at ~160°C, which may be due to the glass transition (T_g).

For CA films, the relative order of ΔH values for the transition at ~100°C closely follows the order of weight

Table 1 Thermal analysis data on cellulose acetate and cellulose propionate films

Polymer	Film no.	Preparation conditions	T.g.a. weight loss at 100°C (%)	D.s.c. data Transition temperature (°C)	 ΔH ($J\,g^{-1}$)
Cellulose acetate	1	5% solution,	3.95	116	61.1
		40°C,		223	13.1
	2	20% solution,	4.63	113	89.2
		40°C,		225	7.2
	3	5% solution,	4.35	115	76.4
		room temperature		230	17.7
Cellulose propionate	1	5% solution,	2.24	109	20.4
		40°C		158	–[b]
	2	20% solution,	2.16	106	49.1
		40°C		161	–[b]
	3	5% solution,	2.51	109	55.4
		room temperature		158	[b]

[a] Taken as peak maximum

[b] Too small to determine accurately

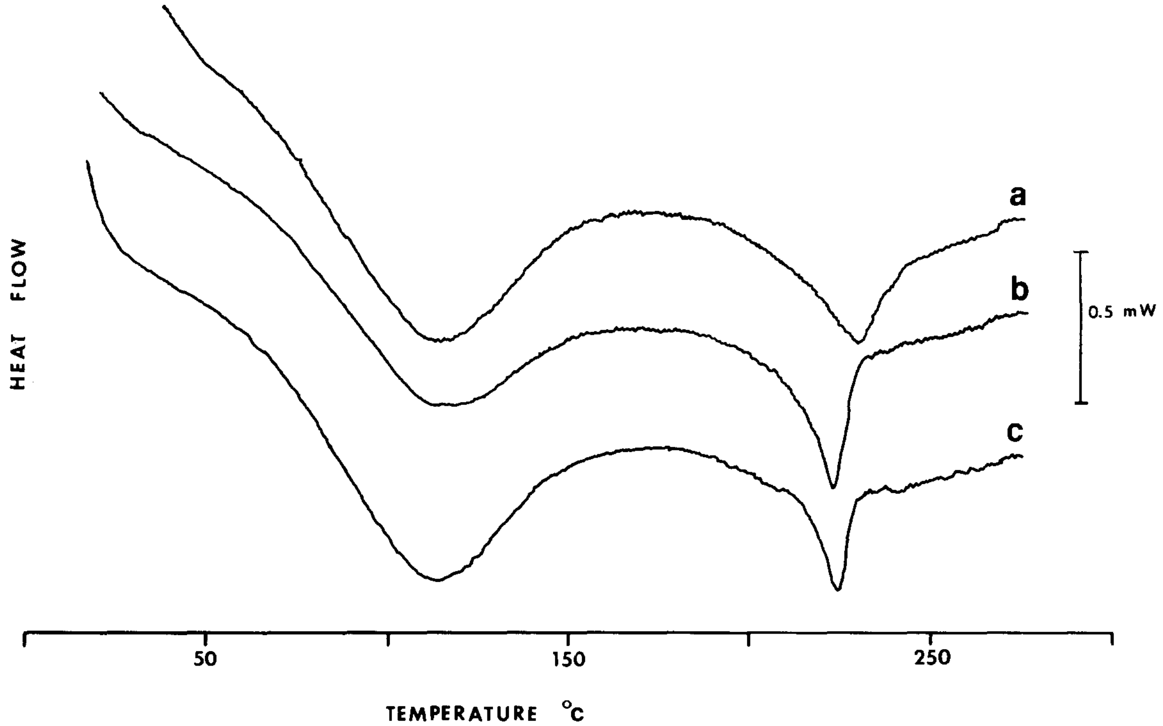


Figure 1 D.s.c. curves acquired on cellulose acetate films obtained from: (a) 5% solution at room temperature; (b) 5% solution at 40°C; (c) 20% solution at 40°C

loss in the t.g.a. experiments, suggesting that the enthalpy change here first reflects loss of water from the films. However, whilst the enthalpy changes in this temperature range for the CPR films are lower than those for CA, in agreement with the t.g.a. data, the value for the 5% film prepared at 40°C is considerably lower than that for the other films. Although large errors exist in the ΔH values for these rather broad peaks, it is possible that more than one transition is occurring over this temperature range.

Comparison of SEM, t.g.a. and d.s.c. data indicates that differences in the optical characterization of the various cellulose ester films are not due to differences in water content, but are associated with the presence of pores in the white films, close in size to the wavelength of visible light, acting as scattering centres. Associated with these pores, the white films show a higher degree of crystallinity than the transparent ones. This may be due to crystallization occurring in the final steps of the solvent evaporation process. This is favoured more at low temperatures, where both the polymer solubility and evaporation rate are lower.

Nuclear magnetic resonance studies

Cellulose acetate, obtained by hydrolysis of cellulose triacetate (CTA) or by direct esterification of cellulose, can be considered to be a copolymer consisting of eight different repeating units[7]. Recently, using compounds labelled at the carbonyl carbons with carbon-13, a detailed assignment was reported of the carbonyl resonances[7]. Experimental evidence of the involvement of C3 carbonyl group in hydrogen bonding was found for the monomers of the 3-monoacetyl, 2,3-diacetyl, 3,6-diacetyl and 3-triacetyl derivatives; a downfield shift of ~0.1 ppm was measured, taking the signal of the non-bonded carbon as the reference. Due to spectral overlapping, no lines could be assigned to hydrogen-bonded C2 and C6 carbonyl groups[7]. As in CA, eight monomers can be found in CPR; as far as we know, no detailed n.m.r. data on this polymer have been published.

To study the influence of the concentration of the starting solutions on the degree of ordered domains in the films, the n.m.r. spectra of their solutions were first measured. The ^{13}C spectra were recorded under the appropriate experimental conditions to be exploited for quantitative analysis (with ^{1}H decoupling but without nuclear Overhauser effect). The method of Miyamoto *et al.*[8] was used to find the relative degree of substitution of the cellulose derivatives under study, CA and CPR, which were, respectively: C_6, 0.71 and 0.72; C_3, 0.8(0)* and 0.7(3)*; C_2, 0.85 and 0.69. *Figures 2* and *3* illustrate the influence of solution concentration on carbonyl hydrogen bonding schemes: the carbon signals from the carbonyl groups can be observed for different CA and CPR concentrations (5% to 20%). The ^{13}C chemical shift of CO groups measured on CA and CPR spectra are assigned to the dominant monomers since, within the resolution of the spectrometer used in this study, it was not possible to obtain the parameters for each monomer. The resonances of carbonyl groups in the CPR are all downfield-shifted by ~3.3 ppm to the corresponding CA signals that appear at 171.0, 170.2 and 169.8 ppm (the carbonyl groups directly bonded to carbon 6, 3 and 2, respectively, also called carbonyl 6, 3 or 2 in the text). In *Figure 2*, the variation of the intensity of signal 3 is a clear indication of the contribution of resonances from hydrogen-bonded carbon 2 to this region of the spectra. For CPR, the differences observed in the line intensities between spectra (a) and (b) in *Figure 3* can be explained by the formation of additional hydrogen bonding

---

* A very broad signal is assigned to the unsubstituted carbon 3

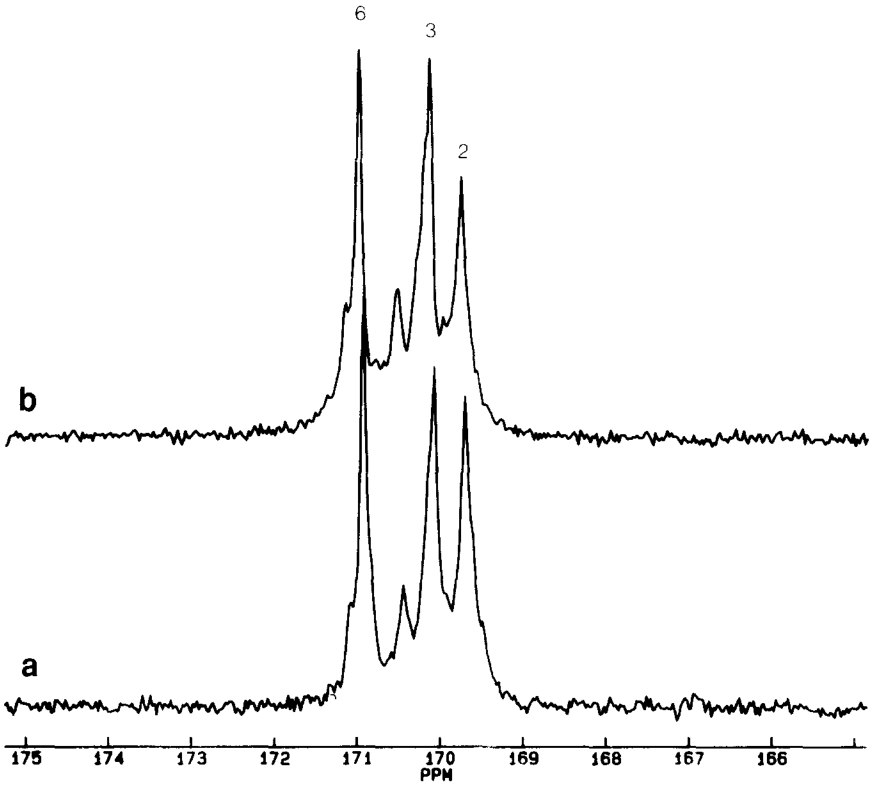


Figure 2 ^{13}C n.m.r. signals of carbonyl groups obtained from cellulose acetate in acetone-d_6 for sample concentrations 5% (a) and 20% (b)

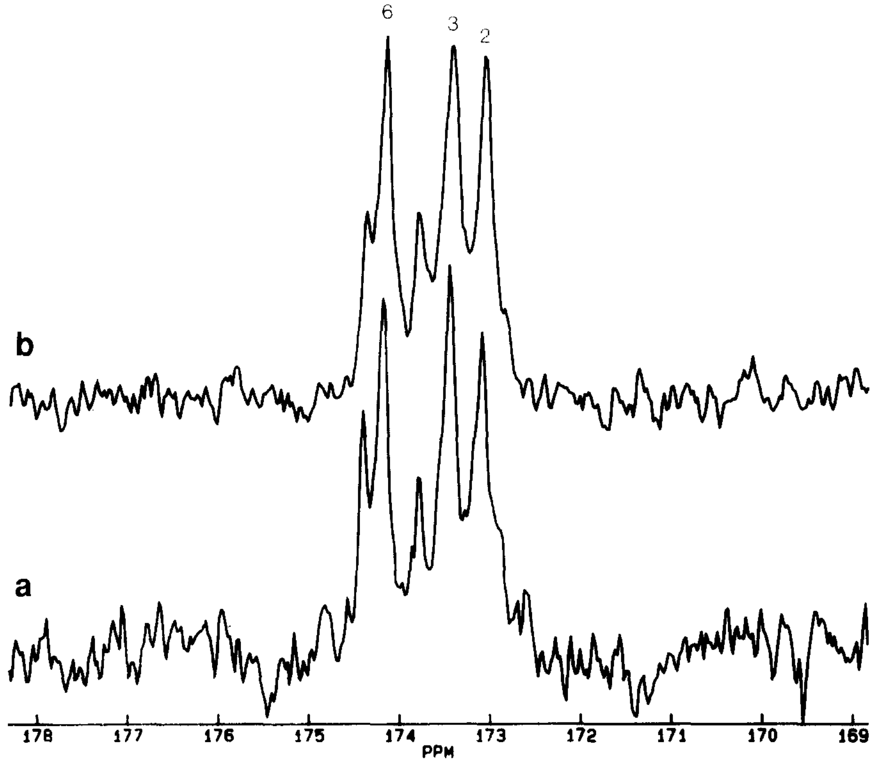


Figure 3 ^{13}C n.m.r. signals of carbonyl groups obtained from cellulose propionate in acetone-d_6 for sample concentrations 5% (a) and 20% (b)

involving CO groups 2 and 3. In both polymers, there is no clear indication for the involvement of carbonyl 6 in hydrogen bonding.

To characterize the polymers in the solid state, the ^{13}C signals from the powder samples were observed by CP/MAS technique. *Figures 4b* and *5b* show typical spectra of CA and CPR powders obtained with MAS rates of 5500±4 and 4990±4 Hz, respectively. The isotropic chemical shifts obtained for the carbon atoms on CA and CPR carbonyl groups were 171.1 and 173.4 ppm, respectively. Comparing these values with the chemical shifts measured in the spectra of the polymers

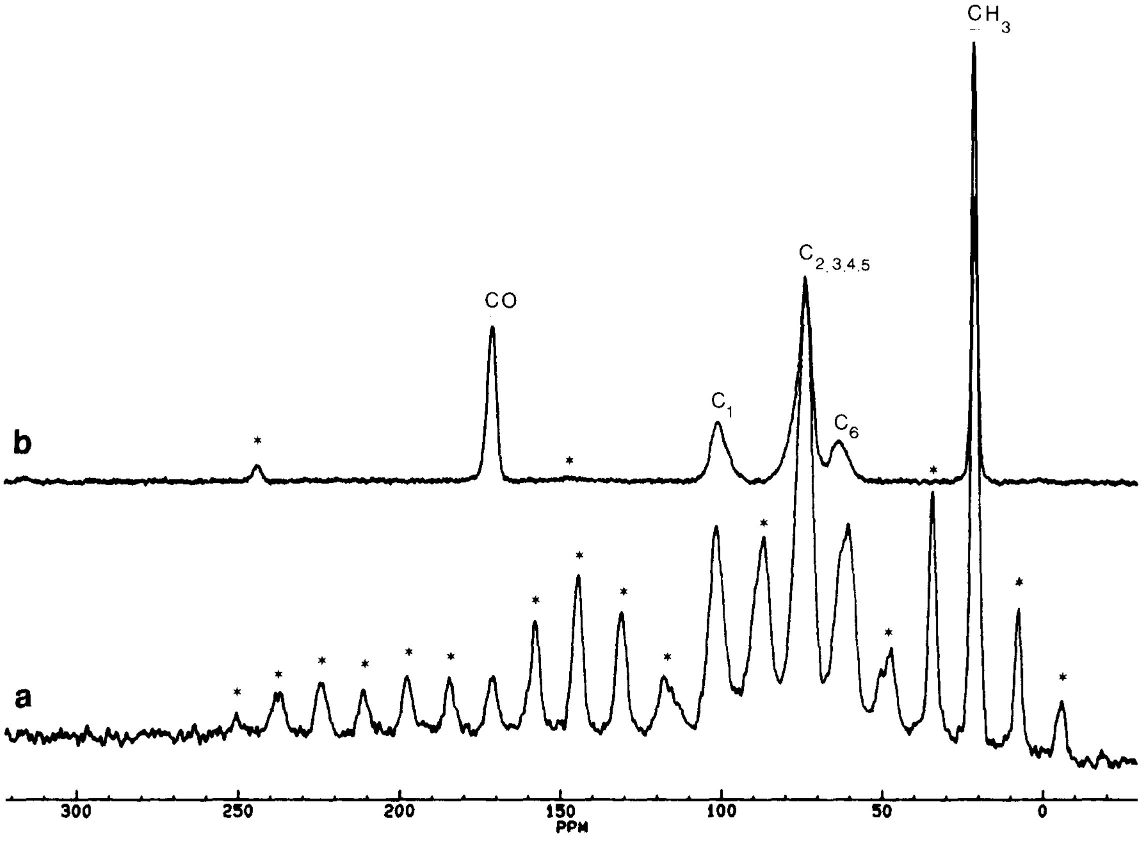


Figure 4 ^{13}C CP/MAS spectra of cellulose acetate powder and film 2 (sheets with a fixed orientation in the rotor), obtained with the following spinning rates: (a) 1000 ± 3 Hz; (b) 5500 ± 4 Hz (* = spinning sideband)

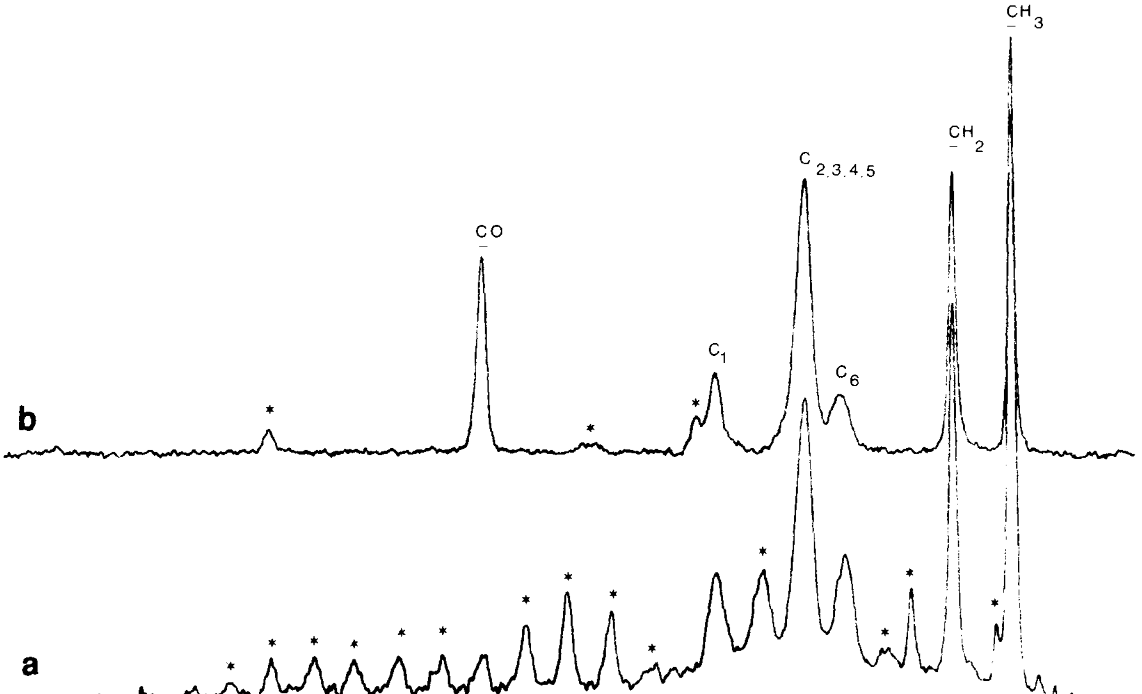
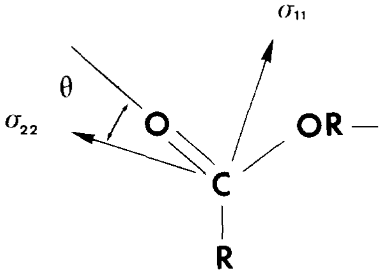


Figure 5 ^{13}C CP/MAS spectra of cellulose propionate powder and film 2 (sheets with a fixed orientation in the rotor), obtained with the following spinning rates: (a) 994 ± 3 Hz; (b) 4990 ± 4 Hz (* = spinning sideband)

dissolved in acetone (indicated above), it is clear that the CA signal is now shifted to higher frequency while for the CPR carbonyl resonance a similar value is found. We have already shown that in CA dissolved in acetone, a downfield shift of ~0.1 ppm was found for ^{13}C resonances of the carbonyl groups involved in hydrogen bonding to the hydroxyl groups; the strong deshielding of the CA carbonyl group in the solid state can therefore be explained by the formation of additional hydrogen bonds, probably involving sorbed water molecules[1].

From the spectra shown in *Figures 4b* and *5b* it is not possible to assign different resonances to the crystalline and amorphous regions in the polymers, as was done in the case of cellulose[2]; this makes these spectra useless if the main goal is the determination of the degree of crystallinity of the polymers. However, it is well known that the principal components of the tensor of the chemical shielding of carbon atoms can also be very informative; for example, the values obtained for σ_{11}, σ_{22} and σ_{33} in acetic acid and methyl acetate carbonyl groups are −81, 4, 78 ppm and −85, 22, 62 ppm, respectively[9]. In this particular case, the involvement of the hydroxyl group in hydrogen bonding affects mainly σ_{22} and σ_{33} (+18 and −16 ppm, for the ester), while σ_{11} only shows a 4 ppm variation; the difference between the ester and the acid carbonyl isotropic shifts is 6 ppm. In fact, the shielding anisotropy of ^{13}C in the CO group is strongly dependent on hydrogen bonding to the oxygen atom; as first suggested by Pines *et al.*[10], ^{13}C shielding tensors should provide a sensitive tool for the study of hydrogen-bonding schemes.



σ_{33} (the most shielded element) is perpendicular to the nodal plane of the CO Π molecular orbital; angle θ will be zero if the CO double bond is of pure sp^2 character (as in benzophenone)[11], but a hydrogen bond to the carbonyl group should increase θ. Considering that the number and the type of hydrogen bonds involving the carbonyl group in a crystalline polymer might be different from those found in a less ordered state, a variation in the shielding anisotropy of the carbon atom should be detected between both states. The main goal of this study was to observe this variation (if any) in CA and in CPR membranes with different physical properties, i.e. refraction index and mechanical properties.

In the next step, three CA membranes were studied: films 1 and 3 show discontinuous change of transparency and refractive index (some white spots are observed in film 3), while brittle rupture occurs easily; in contrast, film 2 is completely transparent and not notably brittle (see Experimental for details and the previous section for chemical and physical characterization). Two different samples of each of the films were studied using the ^{13}C–^{1}H CP technique, with a low MAS rate of 1000 ± 3 Hz. The way in which the rotor was filled in depended on the shape of the sample: the sheets were stacked parallel to the rotation axis while the other films, with no regular shape, were randomly oriented. In the first case, the interaction between the static magnetic field and the electronic environment of carbon nuclei can be described using a statistical distribution accounting for the quasi-two-dimensional spatial orientation of the polymeric chains in the sheets; in the other case, a three-dimensional approach should be used. Thus, to compare different membranes, an increased sensitivity has to be expected when studying samples with the regular shape, since a factor of ordering is introduced.

Figure 4a shows a typical spectrum of CA sheets of film 2, with a fixed orientation in the rotor. In this spectrum , it is possible to identify ^{13}C isotropic signals as well as the corresponding spinning sidebands (SSBs), spaced at the spinning frequency. From the number of SSBs assigned to the different carbon nuclei it is easily observed that, while similar chemical shift anisotropies can be assigned to methyl groups and to the ring carbons, a much larger value should be found for carbon nuclei in the carbonyl groups. Using the areas of the SSBs as the input for the computer program MASFIT, based on the algorithm by Herzfeld and Berger[12] (much smaller experimental errors are thus expected by comparison with those that should be quoted if the so-called graphical method, proposed by the same authors, was used instead), it is possible to obtain the values of σ_{11}, σ_{22} and σ_{33} for carbonyl carbon nuclei in CA powder and in the different membranes, the shielding anisotropy ($\Delta\sigma = \sigma_{11} - 1/2(\sigma_{22} + \sigma_{33})$) and the asymmetry factor ($\eta = (\sigma_{22} - \sigma_{33})/\sigma_{11}$) (the following assignment of the principal values of the chemical shift tensor is used here: $\sigma_{33} > \sigma_{22} > \sigma_{11}$). The integrals of nine SSBs were used to make the input (±1, ±2, ±3, +4, +5 and +6. SSB-3 and those appearing at higher frequencies are considered to be single lines, since a contribution from other signals would be observed as a shoulder in the low frequency region, as observed for SSB-4; this signal strongly overlaps with high-frequency SSBs assigned to carbon nuclei $C_{2,3,4,5}$ and thus was not used in the present calculation). The data are shown in *Table 1*. To test the accuracy of this method, different MAS rates were selected; *Table 1* also shows the values obtained for CA powder when a MAS rate of 1.57 kHz was used, in which case the spectrum again clearly reveals that no overlapping lines were introduced in calculations (the following SSBs were used: ±1, ±2, +3 and +4). However, it should be pointed out here that the reliability of the results depends on the number of SSBs used in the calculation (five is the minimum reasonable number of SSBs that should be used, taking into account the degrees of freedom in the error analysis); for example, if 2.5 kHz is selected for the MAS rate, only three SSBs are identified in the spectrum (not shown), which precludes such calculations. These values are in very good agreement with those reported for related compounds[10]. From the data shown in *Table 2* for the 'random' samples it is not possible to find any correlation between that data and the physical properties of the membranes; however, on close inspection of the values obtained for the samples with a regular configuration, it is possible to observe that $|\sigma_{11}|$ and σ_{33} increase in the order: film 3 > film2 > film 1. For σ_{22}, the opposite is true. The largest variation occurs

Table 2 Values of the principal components of the chemical shielding tensor, the shielding anisotropy and the shielding asymmetry factor obtained for membranes and for cellulose acetate powder (the errors are estimated to be less than 1 ppm)

Cellulose acetate	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	$\Delta\sigma$ (ppm)	η
Powder	−90	29	61	135	0.4
	−90[a]	29[a]	60[a]	134[a]	0.4[a]
Film 1					
random	−91	29	62	136	0.4
oriented	−89	30	59	134	0.3
Film 2					
random	−90	29	62	135	0.4
oriented	−91	28	63	136	0.4
Film 3					
random	−90	31	58	135	0.3
oriented	−92	28	65	139	0.4

[a] A spectrum obtained with a different magic angle spinning rate (1.57 kHz) was used for the calculation (see text for details)

Table 3 Values of the principal components of the chemical shielding tensor, the shielding anisotropy and the shielding asymmetry factor obtained for membranes and for cellulose propionate powder (the errors are estimated to be less than 1 ppm)

Cellulose propionate	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	$\Delta\sigma$ (ppm)	η
Powder	−89	33	56	133	0.3
Film 1					
random	−91	32	59	137	0.3
oriented	−89	33	57	134	0.3
Film 2					
random	−90	32	58	135	0.3
oriented	−90	32	57	134	0.3
Film 3					
random	−91	32	59	136	0.3
oriented	−89	28	62	134	0.4

on σ_{33} (6 ppm). The largest shielding anisotropy and asymmetry factor is found for the less transparent film (film 3), in agreement with a more ordered polymer.

A study, similar to those described above, was performed on CPR. *Figure 5a* shows a typical ^{13}C CP/MAS spectrum of CPR film, obtained with a MAS rate of 994 ± 3 Hz. All the membranes of CPR look homogeneous; films 1 and 2 are transparent while film 3 is completely white, but brittle rupture is more easily observed on film 2.

Comparing the data obtained for films 1 and 3, similar changes are observed on σ_{22} and σ_{33} (5 ppm); the variation on σ_{11} can be considered to be due only to experimental error (*Table 3*). The preparation of these films differs only in the temperature chosen for evaporation of the solvent; the role of sorbed water molecules is expected to be more important in film 3 (evaporated at room temperature)[1]. In the study of this polymer, similar shielding anisotropies are found but the asymmetry factor increases when going from the completely transparent film to the white film, as was also pointed out for CA.

CONCLUSIONS

In this report we have described a study of cellulose acetate and cellulose propionate by liquid and solid state n.m.r. techniques. Comparison of the spectra of several films with that obtained for the powder, using a similar spinning rate, suggest that a useful probe to study the polymeric ordered domains in films could be the values of the CO chemical shielding tensor. In particular, evidence has been presented for a correlation between the deviation of shielding tensor from an axial symmetry and the physical properties of the membranes. The sensitivity of this method could be improved by studying the films at higher temperatures; however, the data presented here can be considered as a reference for future work in this domain as well as in the extension of this study to other cellulose esters.

ACKNOWLEDGEMENTS

We are indebted to Dr J. T. Guthriy (University of Leads) for the SEM observation and to Professor M. T. Vieira (Centro de Materiais do Dept. de Eng. Mec., Univ. de Coimbra) for access to the t.g.a. apparatus. This work is part of the project ESPRIT no. 07238 (PROTIOS) sponsored by the Commission of the European Communities.

REFERENCES

1 Froix, M. F. and Nelson, R. *Macromolecules* 1975, **8**, 726
2 Atalla, R. H., Gast, J. C., Sindorf, D. W., Bartuska, V. J. and Maciel, G. E. *J. Am. Chem. Soc.* 1980, **102**, 3249
3 Earl, W. L. and VanderHart, D. L. *J. Am. Chem. Soc.* 1980, **102**, 3251
4 Doyle, S., Pethrick, R. A., Harris, R. K., Lane, J. M., Packer, K. J. and Heatley, F. *Polymer* 1986, **27**, 19
5 Ramos, M. C., Gil, M. H., Garcia, F. A. P., Cabral, J. M. S. and Guthriy, J. T. *Biocatalysis* 1992, **6**, 223
6 Kokta, B., Luner, P. and Suen, R. *Appl. Polym. Symp.* 1970, **13**, 169
7 Buchanan, C. M., Edgar, K. J., Hyatt, J. A. and Wilson, A. K. *Macromolecules* 1991, **24**, 3050
8 Miyamoto, T., Sato, Y., Shibata, T., Inagaki, H. and Tanahashi, M. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 2363
9 Pines, A., Gibby, M. G. and Waugh, J. S. *Chem. Phys. Lett.* 1972, **15**, 373
10 Pines, A., Chang, J. J. and Griffin, R. G. *J. Chem. Phys.* 1974, **61**, 1021
11 Kempf, J., Spiess, H. W., Haeberlen, W. and Zimmermann, H. *Chem. Phys. Lett.* 1972, **17**, 39
12 Herzfeld, J. and Berger, A. E. *J. Chem. Phys.* 1980, **73**, 6021