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Novel cellulosic ethers with low degrees of substitution—II. Magic angle spinning NMR study

G. Torri[a], C. Cosentino[a], F. Delben[b,*], R. Simonutti[c], P. Sozzani[c]

[a]*Istituto di Chimica e Biochimica G. Ronzoni, Via G. Colombo 81, I-20133 Milan, Italy*
[b]*Dipartimento di Biochimica, Biofisica e Chimica delle Macromolecole, Università degli Studi di Trieste, Via L. Giorgieri 1, I-34127 Trieste, Italy*
[c]*Dipartimento di Scienza dei Materiali, Università di Milano, Via Emanueli 15, I-20126 Milan, Italy*

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Abstract

Magic angle spinning and cross polarisation magic angle spinning solid state ^{13}C NMR were used to study cellulose ethers with low degrees of substitution prepared in alkaline suspension using 1-iodo- or 1-bromoalkane as the alkylating reagent, and also the parent cellulose. The spectra, recorded under high resolution conditions, revealed both the amount and the type of crystallinity in the carbohydrate and aliphatic sequences. The cellulose crystallinity appeared to be modified more by the length of the alkaline treatment and the presence of water in the solid than by the number of side chains. The relaxation time measurements clearly revealed alkyl chain interactions and gave a rough indication of the dimension of the homogeneous hydrocarbon phase domains.

Keywords: Magic angle spinning; Degree of substitution; Cellulose; Modified celluloses

1. Introduction

Cellulose and modified celluloses can be employed as fillers for improving the properties of polymeric materials, and in recent years cellulose fibre has been widely tested as a filler in thermoplastic composites. The matrix in such composites ranges from polyolefins (Klason & Kubat, 1986; Bataille, Ricard, & Sapieha, 1989; Fiebig, Kretzschmar, & Schulze, 1990; Zang & Sapieha, 1991; Maldas & Kokta, 1992a; Chen & Porter, 1994) to other thermoplastic (Gatenholm, Felix, Kalson, & Kubat, 1992; Garcia-Ramirez, Cavailli, Dupeyre, & Piguy, 1994) and elastomeric polymers (Yano, Hirose, Hatakeyama, Westerlind, & Rigdahl, 1990; Yano, Stenberg, & Flink, 1992) and includes natural polymers (Flink & Stenberg, 1990a,b; Gatenholm et al., 1992; Gatenholm & Mathiasson, 1994) and even ceramics (Kurosawa, Ohmori, & Sato, 1994).

Attempts were made to understand the compatibility of cellulose fibre and matrix (Dickinson, Chu, Yang, & Chien, 1987a; Flink & Stenberg, 1990b; Felix & Gatenholm, 1991–1993; Gatenholm, Bertilsson, & Mathiasson, 1993) and to enhance it (Dalvaeg, Klason, & Stromvall, 1985; Raj & Kokta, 1991; Quillin, Caulfield, & Koutsky, 1992; Sain, Katka, & Maldas, 1993), compatibility being a major problem of these composites. The solutions proposed have, till now, been either too complicated and/or too expensive for industrial application. These composites remain however of great interest, as can be seen by the number of patents describing applications (e.g. Fiebig et al., 1990; Maldas & Kokta, 1992b–d; Hosokawa, Nishiyama, Kubo, & Yoshihara, 1990).

Long-chain alkyl substituents can improve cellulosic fibre and matrix compatibility. Moreover, such substituents can bring about marked changes in the physical properties of cellulose, even at low degrees of substitution (DS), i.e. the ratio between the mean number of aliphatic chains and the repeating glucose unit.

Ether substituted celluloses are of special interest because of their good stability, both in alkali and acid. Cellulose alkyl ethers can be successfully employed as fillers as the hydrocarbon chain interacts well with the matrix, especially in the case of the polyolefins.

Recently, novel cellulosic ethers with low DS were prepared, the derivatives being directly characterised by elemental analysis (EA) and Fourier transform IR spectroscopy (IR) (Blasutto, Delben, Milost, & Painter, 1995). These authors analysed samples degraded by acetolysis using a thin layer chromatography (TLC) and ^{1}H nuclear magnetic resonance (NMR) and applied gas–liquid chromatography and mass spectrometry to alditol acetates prepared from the acetolysates.

This article reports the solid state ^{13}C magic angle

* Corresponding author.

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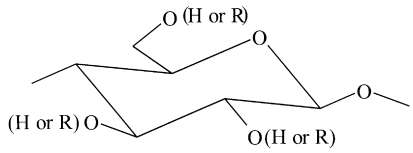


$R = -\underset{\omega}{CH_2}-(CH_2)_{n-3}-\underset{\alpha}{CH_2}-CH_3$

Fig. 1. Repeat unit of the cellulose derivatives.

spinning (SPE MAS) and cross polarisation (CP) MAS NMR characterization of some of these derivatives; Fig. 1 shows the general structure of both the derivatives and the parent cellulose.

2. Experimental

2.1. Materials

Cellulose fluff, prepared from hardwood by the acidic calcium sulfite method and bleached with chlorine and chlorine dioxide, was supplied in 1990 by Chimica del Friuli S.p.A. (Torviscosa, Italy). The cellulose derivatization reactions were carried out at room temperature, the cellulose being first suspended in either *iso*-propanol or dimethylsulfoxide (DMSO) and then activated by a strong base (sodium hydroxide or sodium hydride). The alkylating reagent was 1-iodo- or 1-bromoalkane with *n* carbon atoms (*n* ranged from 4 to 18). After quenching the reaction with distilled water, the derivatised cellulose was washed first with water acidified with acetic acid, then with pure water, ethanol and/or acetone, and finally air-dried. The characteristics of the starting cellulose and the derivatisation procedure have already been reported in detail (Blasutto et al., 1995).

In order to study the effect of alkali/*iso*-propanol or alkali/DMSO on the polysaccharide, a portion of the cellulose was swollen in each of them. These are the reference celluloses, respectively, referred to as RefCell1 and RefCell2.

A 500 mg portion of each derivative was measured out, the remaining portion being the ‘untreated’ sample. The 500 mg sample was suspended in 5 ml of $CHCl_3$ and filtered; this was done twice. The sample was then dried under reduced pressure at about 50°C, giving the ‘treated’ samples. This procedure dissolves higher alkyl-substituted cellulosic fragments and/or unreacted alkyl bromide. Furthermore, partial rearrangement of the cellulosic crystallites occurs due to the swelling caused by $CHCl_3$ and the following desiccation removes most of the water from the samples. The treated derivatives were stored in the presence of P_4O_{10} and were eventually re-hydrated by simply exposing them to the atmosphere at room temperature for a few days.

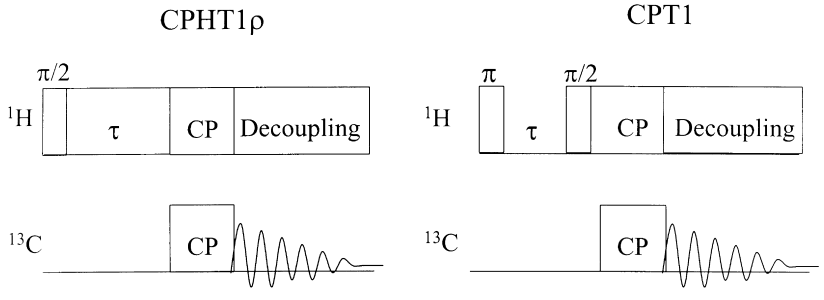
2.2. NMR experiments

MAS ^{13}C NMR analysis was performed using a Bruker CXP 300 spectrometer operating at 75.5 MHz. The samples (100–200 mg) were spun at room temperature in zirconia rotors at a rate of about 5000 Hz. The best CP contact time was found to be 2 ms for CP MAS spectra; a 90° pulse for carbon of 3.8 μs was used for the single pulse experiment magic angle spinning (SPE MAS) without cross-polarisation. In both cases (CP MAS and SPE MAS) a high power proton decoupling field of 15 G was applied. Delay between pulses was 4 s for CP MAS, and generally 9 s for SPE MAS. For each spectrum, 500–2000 transients were collected. The resolution was checked on glycine (width at half height = 26 Hz). Crystalline polyethylene was taken as an external reference at 33.63 ppm from tetramethylsilane.

The relative amount of crystalline and amorphous phases was estimated by the internal ratio of the areas of the signals assigned to C-4 and C-6, according to Horii, Hirai, and Kitamaru (1987).

^{13}C T_1 relaxation times were measured by Torchia sequence using CP T_1 experiments.

Rotating frame spin-lattice relaxation measurements ($T_{1\rho}$) in the hydrogen domain quantify the magnetisation propagation, a phenomenon known as spin-diffusion. The potential use of such phenomena in identifying separate phases in the polymer blend or, less frequently, in characterising the different polymeric domains has been highlighted by several authors (Dechter, 1985; Dickinson, Yang, Chu, Stein, & Chien, 1987b; VanderHart, 1990). The measurements were performed under high resolution conditions to identify single phases, where magnetisation



Scheme 1.

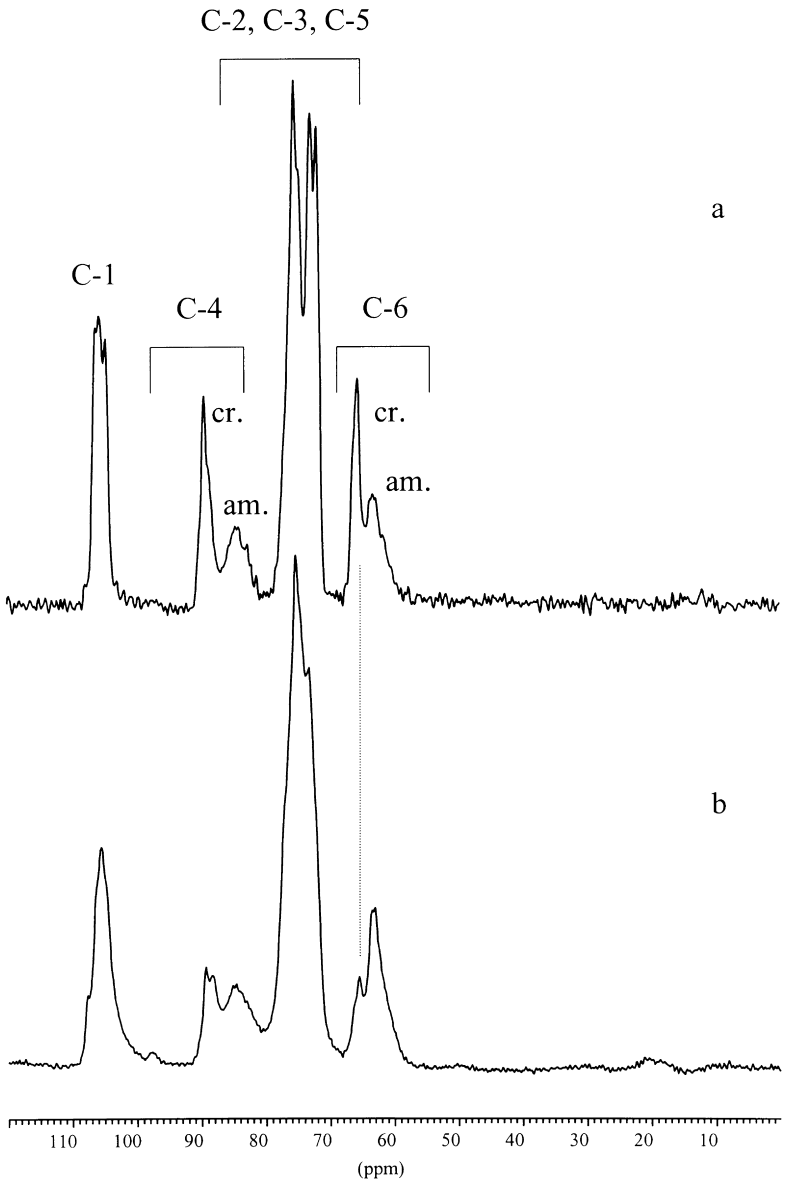


Fig. 2. (a) ^{13}C CP MAS NMR resolution enhanced spectrum of cellulose (LB = − 50 Hz; GB = 0.46; TD = 1 K; SI = 4 K). (b) ^{13}C CP MAS NMR spectrum of cellulose treated with *iso*-propanol and alkali, here referred to as RefCell1.

propagation occurred. Identification was possible by adopting pulse sequences revealed to be at high resolution, the relaxation sequence being ended by magnetization transfer from the abundant (^{1}H) to the rare spin (^{13}C) nuclei. The sequences (see Scheme 1 (Pulse sequence for the rotating frame spin-lattice relaxation time in the hydrogen domain ($T_{1\rho}$) and for ^{13}C cross polarized relaxation time (^{13}C T_1) measurements. τ values for $T_{1\rho}$: 100 and 400 μs and 1.5, 6, 10, 16, 19 and 22 ms; τ values for ^{13}C T_1: 100 ms and 1, 3, 8, 15, 20, 30 and 60 s. π: 8 μs; contact time: 2 ms)) are described elsewhere (Voelkel, 1988; Comotti, Simonutti, & Sozzani, 1996), as is our approach to the measurement of the phase domains (Comotti et al., 1996). The non-linear least-square regression analysis of the intensity of signals showed good correlation among the signals.

3. Results and discussion

3.1. Parent celluloses

Raw untreated cellulose and cellulose after swelling with either alkaline *iso*-propanol or alkaline DMSO called, respectively, Cell, RefCell1 and RefCell2, were characterised.

Fig. 2 shows the ^{13}C CP MAS NMR spectra of both Cell and RefCell1. The main features of the Cell spectrum (Fig. 2(a)) are:

(a) C-4 and C-6 give sharp, well defined peaks, at 90 and 66 ppm, respectively, assigned to the crystalline phase and, at about 85 and 65 ppm, broad resonances in

Table 1
DS of the cellulose derivatives and crystallinity of the derivatives and the parent celluloses

Sample	*n*	DS			% crystallinity
		EA[a]	IR[b]	NMR[c]	
Cell	0	–	–	–	55
RefCell1	0	–	–	–	48
RefCell2	0	–	–	–	< 25
S7	4	0.50	0.44	0.42	33
S12	14	0.27	0.21	0.14	41
S10	18	0.21	0.18	0.13	24
S13	18	0.08	0.09	0.07	50
S19	18	0.02	0.04	0.03	58

[a] By EA.
[b] By FT-IR.
[c] Evaluated by the CP MAS ^{13}C NMR spectra (see text).

a less ordered condition. The crystallinity was about 55%.

(b) The general pattern was typical of that of the cellulose *I* allomorph (Torri, Sozzani, & Focher, 1993).

(c) The anomeric signal (at about 108 ppm) was split into three resonances, the central one being assigned to I_α and the others to the I_β crystalline forms (Atalla, 1987; VanderHart, 1990). The I_β form prevailed, as it does in higher plant celluloses, e.g. in cotton and ramie (Atalla & VanderHart, 1984; Focher & Beltrame, 1994). The crystalline form ratio I_α to I_β was about 1–3.

Fig. 2(b) shows the crystalline phase in RefCell1 to be less than 25%. The crystalline signal due to C-6 corresponds to allomorph I_β and the splitting at C-4 confirms that the crystalline allomorph remaining in the sample after treatment was I_β (Atalla, 1987).

In the case of RefCell2 (unreported), the changes induced by the alkaline treatment followed the same trend as for RefCell1, but were less evident. Residual crystallinity was about 48%.

3.2. Cellulose derivatives

The ^{13}C SPE MAS and CP MAS spectra of a typical sample containing aliphatic chains of 18 carbon atoms, namely the S10 sample indicated in Table 1, are reported in Fig. 3. The aliphatic NMR signals occur at high fields, and are sufficiently separated from those of the saccharidic moieties. By analogy with assignments for synthetic polymers (VanderHart & Perez, 1986), the signals were attributed to: methyl groups (14.5 ppm), α-methylene groups (24.1 and 23.1 ppm) and internal methylenes (30.5 and 32.9 ppm, see Fig. 3).

Peaks at 30.5 and 32.9 ppm could be attributed to the amorphous (*gauche* conformer) and to a more ordered phase, respectively (a signal at 34.0 ppm was reported in synthetic polymers, by VanderHart and Perez (1986), as being characteristic of the polymethylene bonds arranged in the *trans* conformation). The signal at 32.9 ppm prevailed in the CP MAS spectra, CP MAS being sensitive to rigid structures. When the spectra were collected with a short recycle time (in our case 9 s) the main signal in the SPE MAS spectrum was due to the amorphous phase, i.e. the short relaxing component was evident. In fact, it is known that the relaxation time of the crystalline phase is much longer than in the amorphous phase, and in the order of tens of seconds. On comparing solid state and solution NMR spectra of analogous compounds, we expected to find the ω-methylene signal at about 72 ppm.

Our NMR data on the S10 derivative could be explained in terms of a dynamic equilibrium between aliphatic chains in a somehow ordered *trans* conformation and in a less ordered *gauche* conformation, the former conformer prevailing. We therefore subjected the samples to chloroform extraction at room temperature.

The DS, determined by both Fourier transform IR spectroscopy and EA, was seen to decrease from 0.24 to 0.21, due to the dissolving of higher substituted cellulosic fragments and/or the presence of unreacted alkyl bromide. Fig. 4(a) and (b) shows the CP MAS spectrum of the *treated* S10 sample and the same derivative after re-hydration. The marked increase in the intensity of the peak at 30.5 ppm indicates that the solvent treatment transformed the methylene ordered *trans* phase of the alkyl chains to the amorphous *gauche* one. Natural re-hydration of the sample led to the partial recovery of the ordered phase, evidenced by the increased intensity of the peak at 32.9 ppm (Fig. 4(b)). If the moisture of the re-hydrated sample is increased by water addition up to about 30% w/w, also in the SPE MAS experiment (not shown) an inversion of the two methylene signals was observed, with a significant decrease in the disordered *gauche* phase signal (30.5 ppm). This behaviour suggests that the ordered *trans* phase partially depends on the sample's water content. Instead, re-hydration had little effect on the ratio of the aliphatic signal integral (15–40 ppm) to the saccharidic (60–110 ppm).

In the CP MAS spectrum (Fig. 3(b)) the crystalline signals of the cellulose part of S10 corresponded to those of the reference sample RefCell1 (Fig. 2(b)). Thus the cellulose structure was not affected, not even by a DS as high as 0.2, indicating that the change in the cellulose structure was due mainly to the alkaline treatment.

Similar to the S10 derivative, the S13 and S19 samples contain 18 carbon atoms in the side chain, but the values of the DS are lower (Table 1). Figs. 5 and 6, respectively, show the ^{13}C CP MAS NMR spectra of samples S13 and S19. The reference cellulose for these derivatives is RefCell2, which shows the same general signal pattern.

In samples characterised by side chains having the same *n*, the cellulose crystallinity increased from S10 to S13 and S19 preparations (Figs. 3(b), 5(a) and 6(a)), shown mainly by the signals at about 66 and 90 ppm due to C-6 and C-4, respectively. The increase in crystallinity is also observable in the corresponding *treated* samples (see Figs. 4(a), 5(b)

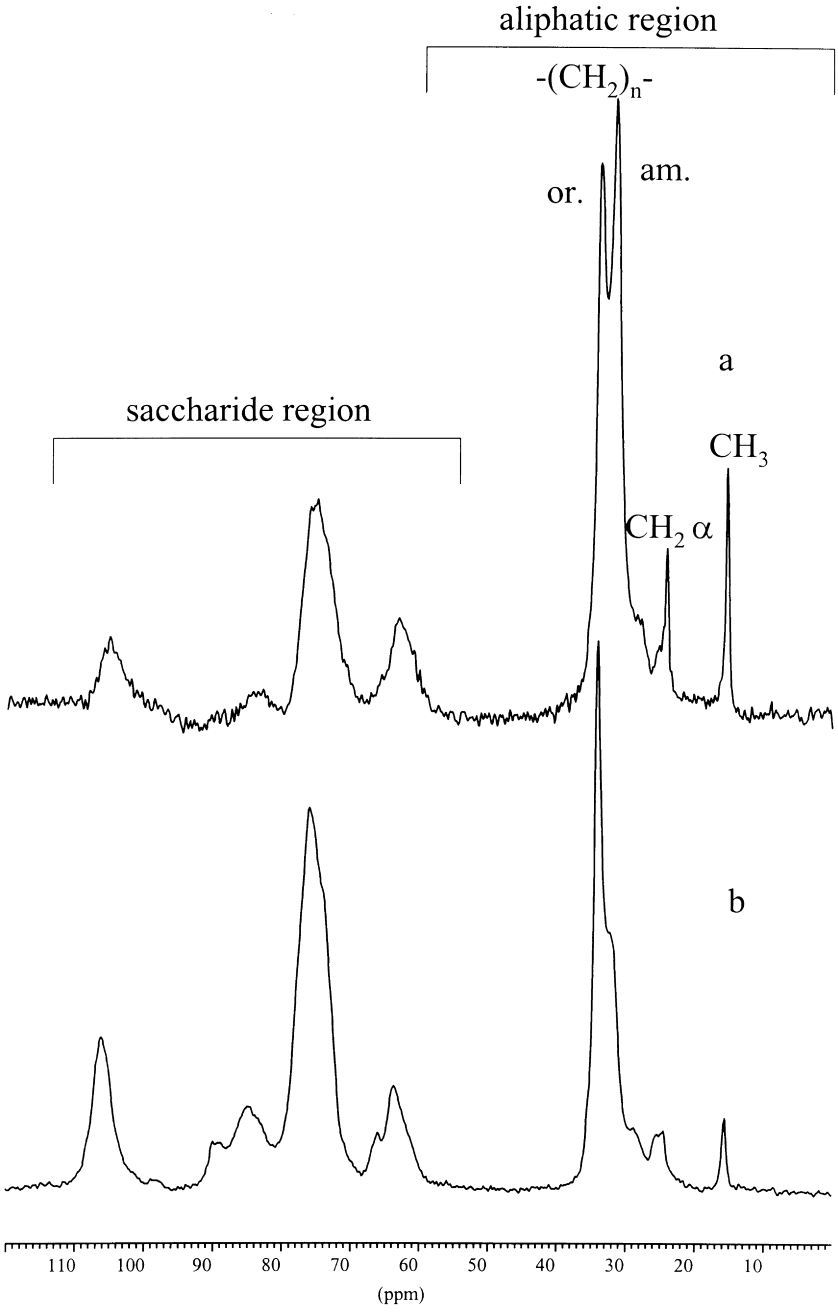


Fig. 3. (a) ^{13}C SPE MAS and (b) ^{13}C CP MAS NMR spectra of the derivative S10. Spectra were obtained with 2000 scans over the same sample; the absolute intensity refers to spectrum b, while the intensity of SPE MAS spectrum was multiplied by a factor of 4.3 to obtain the equivalence of the intensity of the methylene signals in the ordered phase.

and 6(b)) and is inversely proportional to the DS values (see Table 1). This effect could be explained by the different reaction conditions. Apparently, polysaccharide crystallinity is lowered mainly by alkaline treatment, as already discussed.

Figs. 5(b) and 6(b) show the spectra after dehydrating the derivative (see Section 2). The general broadening of the signals is probably due to the chemical shift dispersion. The conformations are no longer averaged as in a hydrated sample. The methyl and α-methylene signals, at about 16 and 24 ppm, respectively, show an even more dramatic broadening. Also the peaks of the side chain methylenes (30.5–32.9 ppm) broadened, and the signal corresponding to the amorphous phase increases quite noticeably. This overall broadening of the spectra is attributable to the transformation of the alkyl chains from the ordered *trans* to the amorphous *gauche* phase, a result of the dehydration treatment.

The SPE MAS spectra of the S10 and S19 samples were recorded without the dipolar decoupling needed for solid

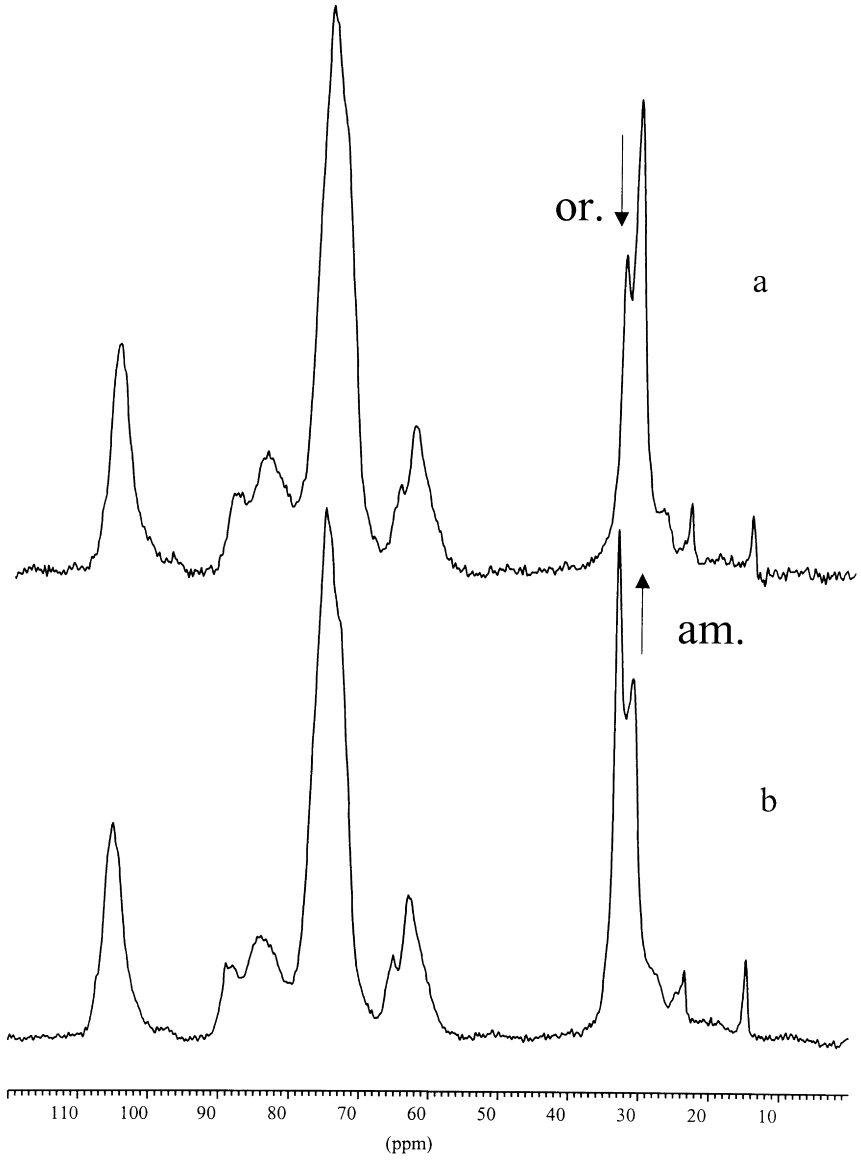


Fig. 4. ^{13}C CP MAS NMR spectra of the derivative S10, (a) after dehydration and (b) after subsequent re-hydration.

compounds, but using the typical decoupling power needed to obtain solution spectra. In these conditions only structures with high molecular mobility can be detected. In fact our spectra (not shown) showed only aliphatic signals that were relatively weak despite the very high number of scans used, compared to the normal SPE MAS experiment. The fact that the alkyl signal is visible confirms the high mobility of at least some of the aliphatic chains i.e. highlighting a liquid-like behaviour.

Behaviour like that of the S13 was shown by the sample S12 (unreported) that had a shorter side chain. In the case of the untreated S7, which had the highest DS and the shortest side chain, the CP MAS spectrum (Fig. 7) showed a cellulose crystallinity similar to that of the parent cellulose (Fig. 2(a)).

Table 1 shows the DS values of the treated cellulose derivatives obtained by EA and FT-IR spectroscopy, according to the methodology described by Blasutto et al. (1995). Also the crystallinity values of the derivatives and the celluloses Cell, RefCell1 and RefCell2 are reported.

The CP MAS NMR spectra were used to tentatively compute the DS of the derivatives as we suspected that a relationship existed between the peak areas. Thus, we calculated the ratio of the peak area corresponding to C-1 (around 106 ppm), or a third of that due to the three carbon atoms C-2, C-3 and C-5 (from 69 to 80 ppm), to the area, divided by $(n - 3)$, of the peak assigned to the internal methylenes centred around 32 ppm. If the area of these peaks were proportional to the number of C atoms involved in the resonance, then the value obtained was a clear indication of the DS of the derivative. Values obtained in this way

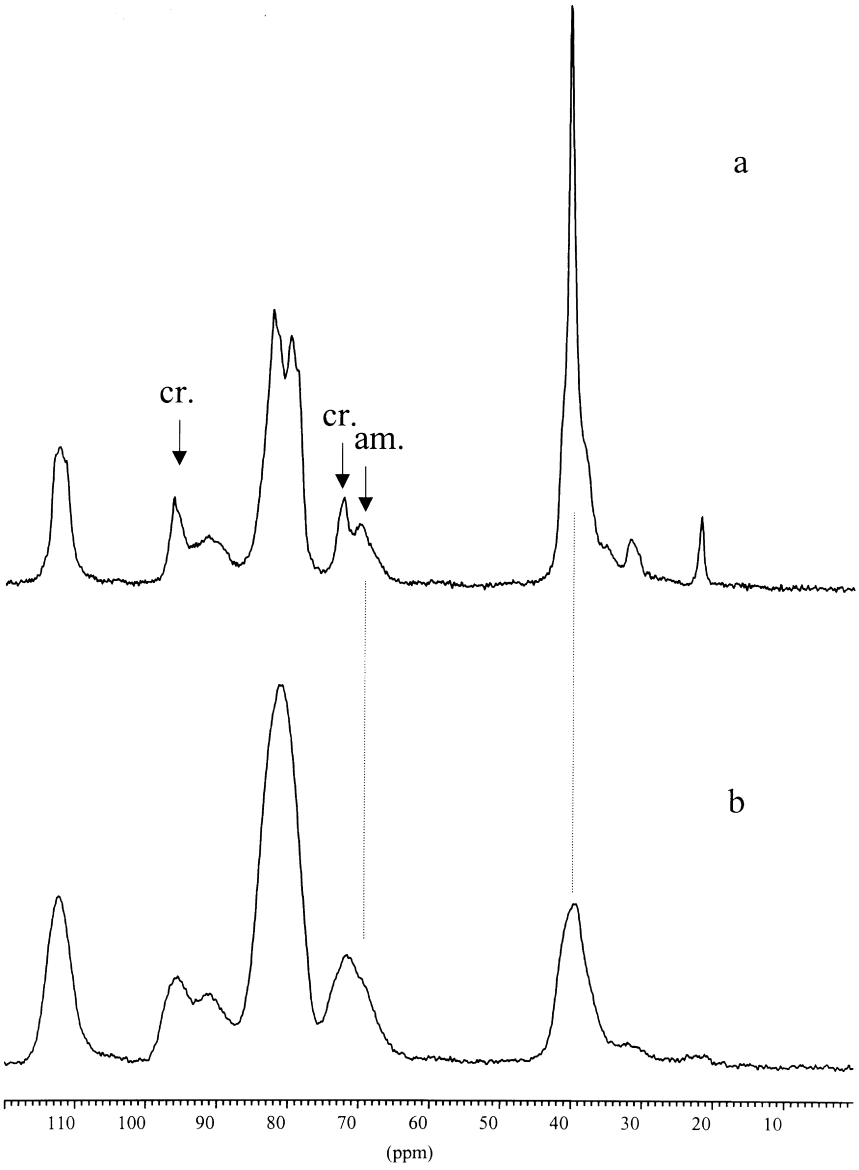


Fig. 5. ^{13}C CP MAS NMR spectra of the derivative S13, (a) before and (b) after treatment with chloroform.

are reported in Table 1; column NMR^c shows a trend that is, by and large, in agreement with the DS values obtained with other techniques.

3.3. Relaxation time measurements and phase homogeneity

Table 2 shows the carbon spin-lattice relaxation time in the laboratory frame (^{13}C T_1) and the hydrogen relaxation time in the rotating frame (^1H $T_{1\rho}$) for samples RefCell1, treated S10 and treated S12, the relaxation values being reported for the most significant signals.

The ^{13}C T_1 relaxation times, associated to each carbon atom's mobility, fall into different groups. The relaxation of the cellulose crystalline part, measured on the C-4 crystalline component, was over 70 s for all the samples, i.e. it is compatible with a rigid crystal phase. Instead the more mobile component of C-4 presented relaxation times of 14–22 s.

The derivatives could be considered equivalent to the reference cellulose, indicating that the alkyl chains did not affect the relaxation property of either the "amorphous" or the crystalline cellulose phases. If the alkyl chains were randomly distributed within the phases, the relaxation times would be lower than that of the reference cellulose. This and the effect of the $CHCl_3$ treatment followed by re-hydration suggest that some short range interaction, possibly alkyl chain aggregation, takes place. We observed very low values for the relaxation time of the alkyl chains, indicating the complete absence of alkyl chain crystallinity. Note that the signals assigned to the side chain methylenes show relaxation times lower than 1 s, which is not compatible with any conventional hydrocarbon crystal

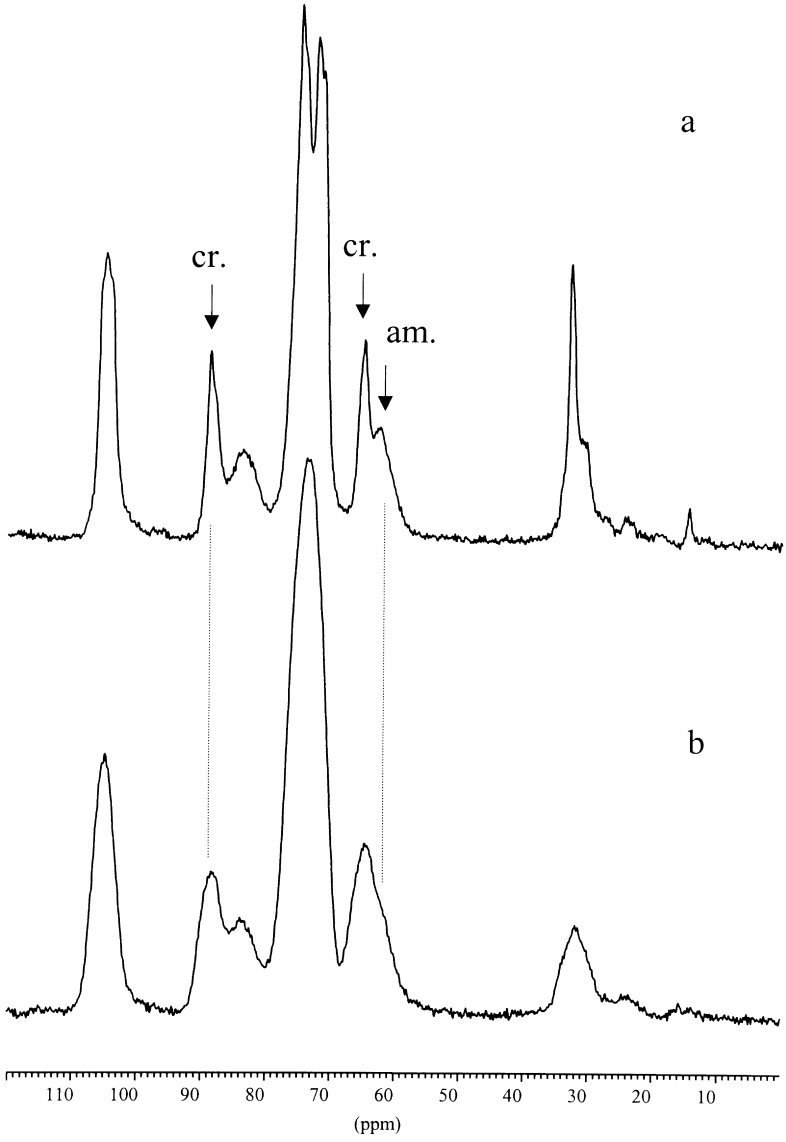


Fig. 6. ^{13}C CP MAS NMR spectra of the derivative S19, (a) before and (b) after treatment with chloroform.

structure. At room temperature the pure bulk hydrocarbon crystals show ^{13}C T_1 relaxation times in the order of tens of seconds (Moeller et al., 1986; VanderHart, 1990).

The methyl signals showed even longer relaxation times (1.7 and 3.4 s) than the methylenes, confirming our observation for treated S10 and treated S19, i.e. the mobility of the chain ends was such as to produce relaxation times in the liquid-like region of the theoretical ^{13}C T_1 curve (Abragam, 1961). Therefore the alkyl chains must behave like molecules in gels.

The experiment to measure $T_{1\rho}$ was based on magnetisation propagation within the hydrogen domain, such propagation being finally detected by the carbon atoms under high resolution conditions (see Section 2). This experiment allowed us to establish the homogeneity or heterogeneity of the system for a certain scale length. The treated S10 derivative and the reference cellulose showed the same values for all the carbon atoms in the 6–8 ms range. This means that the materials were homogeneous and that the hydrogen spin system was fully equilibrated within a few milliseconds. If the value of the diffusion coefficient equals that of the polyethylene ($D = 6.2 \times 10^{-16}\ m^2\ s^{-1}$) then the homogeneous phase in the material is no larger than about 5 nm (VanderHart, 1990).

The treated sample S12 (Fig. 8) exhibited similar behaviour to treated S10 and RefCell1, except that the ordered phase signals showed higher relaxation times (11 and 13 ms). In this sample the crystallite dimensions (Comotti et al., 1996) appeared to be somewhat larger than 5 nm. All the three samples had relaxation times of 6–8 ms, thus it can be assumed that the alkyl chains were dispersed throughout the amorphous phase and had been expelled from the crystallites.

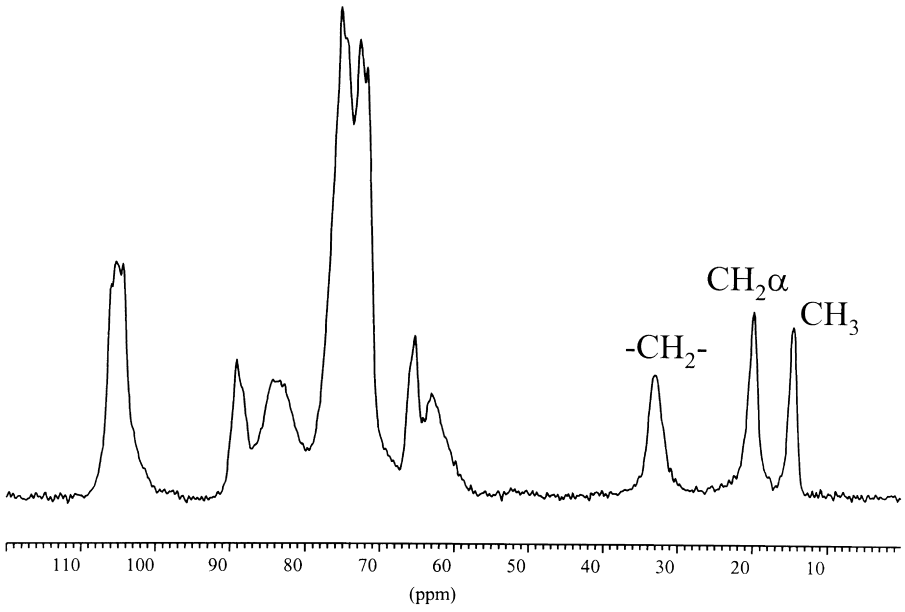


Fig. 7. ^{13}C CP MAS NMR spectrum of the derivative S7.

4. Conclusions

Characterisation of the ether derivatives of cellulose by ^{13}C SPE MAS and CP MAS NMR measurements in the solid state has provided a better insight into their DS, the arrangement of the side alkyl chains, and the morphological modifications of the substituted polysaccharide chains.

The parent cellulose was the cellulose I allomorph. After alkaline treatment, the crystallinity of the polymer significantly decreased, although the crystal structure still remained in form I. Moreover, the original ratio of I_α to I_β forms was retained, indicating that only some crystallites were attacked by the swelling agent and alkali. The derivatives showed a clear cut separation between the cellulose and aliphatic signals in both the MAS and the CP MAS spectra, permitting measurement of the DS, which was found to be essentially in agreement with the data obtained by other analytical techniques. A tentative description of the conformational arrangement of the chains with the S10 derivative containing most of the aliphatic chains in a ordered *trans* phase has also been given. The effect of the alkaline treatment and the presence of the aliphatic side-chains on the crystallinity of cellulose was investigated by the CP MAS technique, which is sensitive to rigid structures. Dehydration and subsequent re-hydration treatments indicated that the degree of crystallinity of the sample S10 decreased with decreasing the water content in the solid. The mobility and the aggregation of the alkyl chain on the cellulose surface was addressed by measuring the relaxation time. Experiments to measure the diffusion of the magnetization

Table 2
Relaxation times ^{13}C T_1 and $T_{1\rho}$ for celluloses. ((c) and (a) stand for crystalline and amorphous, respectively. (o) and (g) indicate the ordered phase and the *gauche* conformer, respectively)

Signal		^{13}C T_1 (s)			$T_{1\rho}$ (ms)		
Ppm		Ref Cell 1	S10	S12	Ref Cell 1	S10	S12
105	C-1	32	33	31			5; 11[a]
88	C-4(c)	76	79	75	↑	↑	13
84	C-4(a)	22	20	14	6 ÷ 8	6 ÷ 8	7
75	C-2, C-3, C-5	30	21	23	↓	↓	8
65	C-6(c)	–	–	37			11
63	C-6(a)	17	12	2			7
32	$-CH_2-$ (o)	–	0.9	0.5	–		6
30	$-CH_2-$ (g)	–	0.5	0.4	–		5
23	$\alpha-CH_2-$	–	0.9	0.9	–		8
15	$-CH_3$	–	1.7	3.4	–		7

[a] The reported values were in agreement with a mono-exponential and a bi-exponential fit, respectively.

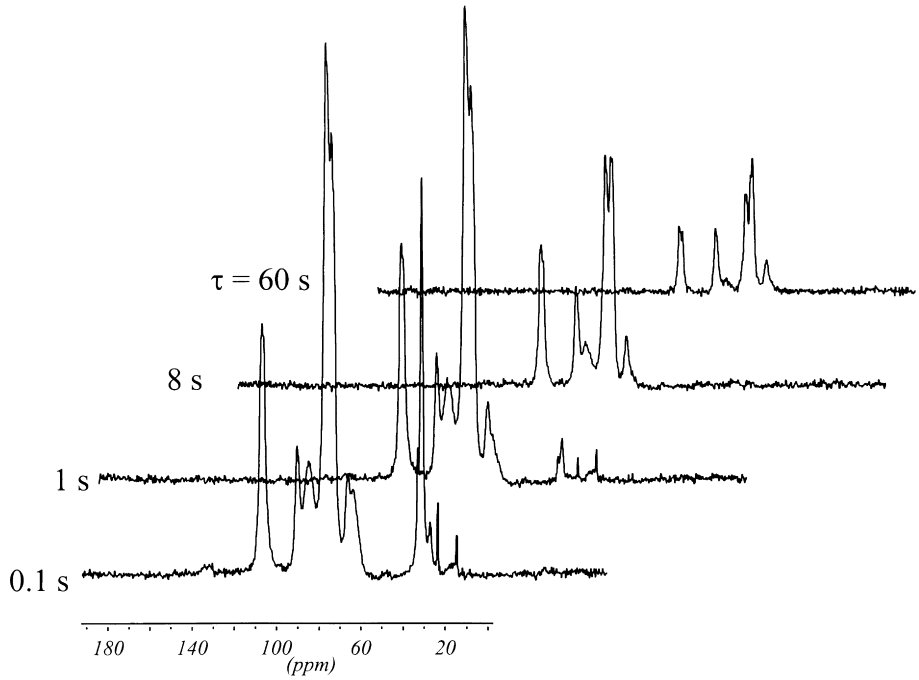


Fig. 8. Most significant ^{13}C CP MAS spin-lattice relaxation times in the laboratory frame frequency experiment (^{13}C T_1) NMR spectra of the derivative S12. The signals at lower fields have longer ^{13}C T_1 values than those of the high-field group, as shown by the time values (τ). The experiment was performed using the following τ values: 100 ms and 1, 3, 6, 15, 20, 30, 60 s.

relaxation time in the hydrogen domain showed the alkyl chains to be dispersed within the amorphous phase of the cellulose and outside the crystallites.

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References

Abragam, A. (1961). The principles of nuclear magnetism. Oxford: Oxford University Press.

Atalla, R. H. (1987). *ACS Symp. Series 340*. Washington, DC: American Chemical Society.

Atalla, R. H., & VanderHart, D. H. (1984). *Science*, *223*, 283–285.

Bataille, P., Ricard, L., & Sapieha, S. (1989). *Polym. Compos.*, *10*, 103–108.

Blasutto, M., Delben, F., Milost, R., & Painter, T. J. (1995). *Carbohydr. Polym.*, *27*, 53–62.

Chen, H. L., & Porter, R. S. (1994). *J. Appl. Polym. Sci.*, *54*, 1781–1783.

Comotti, A., Simonutti, R., & Sozzani, P. (1996). *Chem. Mater.*, *8*, 2341–2348.

Dalvaeg, H., Klason, C., & Stromvall, H. -E. (1985). *Int. J. Polym. Mater.*, *11*, 9–38.

Dechter, J. J. (1985). *J. Polym. Sci., Polym. Lett. Ed.*, *23*, 261–266.

Dickinson, L. C., Chu, C. W., Yang, H., & Chien, J. C. M. (1987). *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)*, *28*, 112–113.

Dickinson, L. C., Yang, H., Chu, C. W., Stein, R. S., & Chien, J. C. W. (1987). *Macromolecules*, *20*, 1757–1760.

Felix, J. M., & Gatenholm, P. (1991). *J. Appl. Polym. Sci.*, *42*, 609–620.

Felix, J. M., & Gatenholm, P. (1992). *Polym. Mater. Sci. Eng.*, *67*, 315–316.

Felix, J. M., & Gatenholm, P. (1993). *J. Appl. Polym. Sci.*, *50*, 699–708.

Fiebig, J., Kretzschmar, B., & Schulze, J. (1990). East Ger. Pat. 222890.

Flink, P., & Stenberg, B. (1990). *Br. Polym. J.*, *22*, 147–153.

Flink, P., & Stenberg, B. (1990). *Br. Polym. J.*, *22*, 193–199.

Focher, B., & Beltrame, P. (1994). *Chim. Ind.*, *76*, 637–645.

Garcia-Ramirez, M., Cavailli, J. Y., Dupeyre, D., & Piguy, A. (1994). *J. Polym. Sci., Polym. Phys.*, *32*, 1437–1448.

Gatenholm, P., Bertilsson, H., & Mathiasson, A. (1993). *J. Appl. Polym. Sci.*, *49*, 197–208.

Gatenholm, P., Felix, J., Kalson, C., & Kubat, J. (1992). *Contemp. Top. Polym. Sci.*, *7*, 75–82.

Gatenholm, P., & Mathiasson, A. (1994). *J. Appl. Polym. Sci.*, *51*, 1231–1237.

Horii, F., Hirai, A., & Kitamaru, R. (1987). *Macromolecules*, *20*, 2117–2120.

Hosokawa, J., Nishiyama, M., Kubo, T., & Yoshihara, K. (1990). Eur. Pat. Appl. EP 393,825.

Klason, C., & Kubat, J. (1986). *Mater. Sci. Monogr.*, *36*, 65–74.

Kurosawa, Y., Ohmori, Y., & Sato, T. (1994). In;Proceedings of 1994 Cellulose R&D, First Annual Meeting of the Cellulose Society of Japan.

Maldas, D., & Kokta, B. V. (1992). *Int. J. Polym. Mater.*, *17*, 205–214.

Maldas, D. & Kokta, B.V. (1992b). Can. Pan. Appl. CA 2,029,726.

Maldas, D. & Kokta, B.V. (1992c). Can. Pan. Appl. CA 2,029,727.

Maldas, D. & Kokta, B.V. (1992d). Can. Pan. Appl. CA 2,035,328.

Moeller, M., Cantow, H. -J., Drotloff, H., Emeis, D., Lee, K. S., & Wegner, G. (1986). *Makromol. Chem.*, *187*, 1237–1252.

Quillin, D. T., Caulfield, D. F., & Koutsky, J. A. (1992). *Int. J. Polym. Mater.*, *17*, 215–227.

Raj, R. G., & Kokta, B. V. (1991). *Angew. Makromol. Chem.*, *189*, 169–182.

Sain, M. M., Kotka, B. V., & Maldas, D. (1993). *J. Adhes. Sci. Technol.*, *7*, 49–61.

Torri, G., Sozzani, P., & Focher, B. (1993). Morphology and structure of cellulose materials as studied by SPE MAS NMR spectroscopy ch. 5. In

F. Morazzoni (Ed.), *From molecular materials to solids*, (pp. 71). Milan: PEC.

VanderHart, D. L. (1990). *Makromol. Chem., Macromol. Symp., 34*, 125–159.

VanderHart, D. L., & Perez, E. (1986). *Macromolecules*, *19*, 1902–1909.

Voelkel, R. (1988). *Angew. Chem., 100*, 1525–1540.

Yano, S., Hirose, S., Hatakeyama, H., Westerlind, B., & Rigdahl, M. (1990). *J. Appl. Polym. Sci., 40*, 657–667.

Yano, S., Stenberg, B., & Flink, P. (1992). *Nihon Reoroji Gakkaishi, 20*, 132–140.

Zang, Y. H., & Sapieha, S. (1991). *Polymer*, *32*, 489–492.