Cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance spectra of acrylonitrile–furfuryl alcohol copolymers

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A copolymer consisting of nearly equal weights of residues from acrylonitrile and furfuryl alcohol has been subjected to heating to two different temperatures under nitrogen, and exposed to concentrated hydrochloric and sulphuric acids. The chemical changes thus caused have been monitored by cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance spectroscopy. Strong spinning sidebands from the nitrile carbons of the acrylonitrile residues and weaker spinning sidebands from the olefinic carbons of the furan residues were observed in the standard experiment. The structure of the material was completely altered by heating to 600°C, extensive aromatic structures being formed, but at 185°C only one type of furan residue was rearranged. This structure was also attacked by exposing the powdered copolymer to concentrated hydrochloric and sulphuric acids. The chemical changes within the copolymers were also characterized.

(Keywords: cross-polarization magic-angle spinning; nuclear magnetic resonance; acrylonitrile–furfuryl alcohol copolymers; chemical changes)

INTRODUCTION

Copolymers of acrylonitrile and various furan molecules have been formed by free-radical chain reactions in the bulk and in solution, and their structures have been characterized by means of solution ^{1}H and ^{13}C n.m.r. spectroscopy and by i.r. spectroscopy on the solid state[1–3]. It has been found that these acrylonitrile–furan copolymers decompose upon heating the solid, to yield carbonaceous materials[3]. Here we concentrate on one of those copolymers that contains furan residues with methylol groups. Such copolymers may be derived from furfuryl alcohol or 2,5-dihydroxymethyl furan, and when heated lose weight in two stages[3]. T.g.a. has shown the methylol group to be rather sensitive, for the low-temperature decomposition process found below 200°C was absent if the group itself was not present in the furan residues, or if it had first been protected by acetylation[3].

We chose to examine how the chemistry of these reactions might be followed by solid-state ^{13}C cross-polarization (CP) dipolar-decoupled magic-angle spinning (MAS) spectroscopy. Moreover, furfuryl alcohol and its oligomers[4] are a source of carbon, the reaction being promoted by heat and acid treatments, so acid-promoted reactions within the copolymer have also been studied. Infra-red spectra were recorded to provide a second guide to the chemistry. The CP–MAS technique has been applied to polyacrylonitrile[5] and to the curing reactions of furfuryl alcohol resins[6].

EXPERIMENTAL

Copolymer samples

A copolymer of furfuryl alcohol and acrylonitrile was prepared in a similar manner to but on a larger scale than that described before for sample B17[3]. Initiator (0.80 g of AIBN), freshly distilled (furfuryl alcohol (105 ml), acrylonitrile (21 ml) and pyridine (6 ml, to prevent any possible acid-catalysed condensation of the furfuryl alcohol) were added to a Cairus tube and subjected to two freeze–pump–thaw cycles before sealing under a vacuum. The tube was heated to 81°C for 24 h, during which time the contents became brown and viscous. The copolymer was precipitated by pouring the tube contents into ether, and was purified by reprecipitation twice from acetone before being vacuum-dried. According to the N/C ratio of the elemental analysis (*Table 1*), the furfuryl alcohol copolymer contained 34% of furan residues (48% by weight), a value in good agreement with the value determined by ^{1}H n.m.r., 35%[3], for the earlier preparation.

The light-yellow copolymer (12.5 g) was ground to give a fine powder before samples were subjected to the following thermal and chemical treatments: (A) heating in an atmosphere of argon to about 185°C, at which temperature the first weight-loss process is complete[3]; (B) heating in an atmosphere of argon to 600°C, the temperature at which the second weight-loss process is complete[3]; (C) treatment with concentrated hydrochloric acid; and (D) treatment with concentrated sulphuric acid, an oxidizing agent. The rate of heating for samples (A) and (B) was about 10°C min^{-1}, with a period of about

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10 min lapsing before the cooling started. Sample (A) (88% recovered) developed a darker colour (orange-yellow) and sample (B) (43% recovered) became black. The acid treatment involved covering about 1 g of the polymer with the acid for about 1 h, and stirring, before rinsing with distilled water and ethanol, and drying in a vacuum. Samples (C) and (D) were a dark-brown colour, the first being pliable before rinsing and the second being immediately friable.

Spectroscopy

High-resolution solid-state ^{13}C spectra were obtained with cross-polarization on a Varian VXR 300 spectrometer operating at 75.4 MHz at ambient temperature. Chemical shifts were reported relative to the position of the methylene carbon of adamantane (38.9 ppm) run prior to the measurement, and are considered accurate to within 0.3 ppm. Samples were ground to a fine powder and spun at a rate between 4210 and 2900 Hz in a sapphire rotor. To permit a comparison of the normal spectra, the spectrometer settings for each spectrum were essentially the same, the details of these being recorded within the captions to the figures we show. Certain spectra shown were also obtained with resolution enhancement, the free induction decay (FID) being multiplied by an increasing exponential function and a Gaussian apodization function before the Fourier transform was performed. Total suppression of sidebands (TOSS) spectra were obtained with the pulse sequence described by Dixon *et al.*[7], and for one sample the signals from protonated carbon atoms were suppressed by having a delay of 40 μs without proton decoupling, before the start of collection of the FID[8].

Table 1 Characteristics of the copolymers studied

Sample	Elements present (%)[a]				A_{CN}/A_{CH}[b]
	C	H	N	S, Cl	
B17/DC	58.5	5.8	10.53	–	1.02
A, 185	61.19	5.86	11.25	–	1.00
B, 600	78.47	3.22	8.78	–	–
C, HCl	54.24	5.97	8.90	5.0 (Cl)	0.75
D, H_2SO_4	46.3	5.75	6.21	5.3 (S)	0.13

[a] WO_3 was used in the combustion process
[b] Absorption at 2250 cm^{-1} divided by absorption at 2930 cm^{-1}; these were the bands from the nitrile and C–H stretches, respectively

I.r. spectra were recorded on a Perkin–Elmer 598 instrument, the samples being dispersed in KBr discs.

RESULTS

Preliminary observations

The CP–MAS spectrum shown in *Figure 1* (trace A) does have bands at the positions to be expected for this copolymer, following the study of the solution ^{13}C spectrum[3], but there are also prominent extra features. Before dealing in detail with the assignments of shifts, we first consider the resolution obtained with these solid-state spectra, and attend to the issue that arises from the anisotropic nature of the unsaturated groups, the nitrile and olefinic carbons. Certain of the lines in the spectra, e.g. those at 58 and 94 ppm in *Figure 1*, appeared to have only one component when the resolution enhancement procedure was applied. These, the narrowest lines in the spectra, have in the normal spectrum a width at half height of about 3 ppm, which is a measure of the resolution possible. Most of the bands are therefore the envelopes of the sum of a number of lines whose shift positions differ by less than this spacing, and which were not resolved. Thus there was no evidence for ^{14}N dipolar splittings, and little of the fine structure that might be observed in a solution spectrum[2,3].

The spectrum of *Figure 1* (trace A) was obtained in the standard manner, and shows prominent peaks below 140 ppm that were not seen in the solution spectrum[3]. These extra peaks were spinning side bands (SSB), those marked with an asterisk being separated by a simple

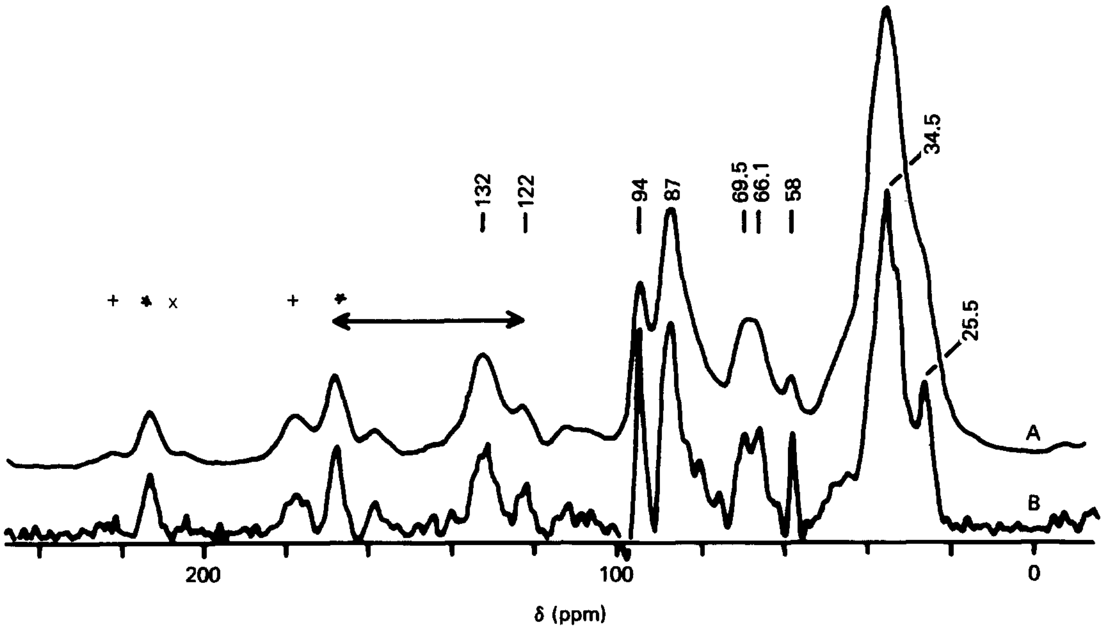
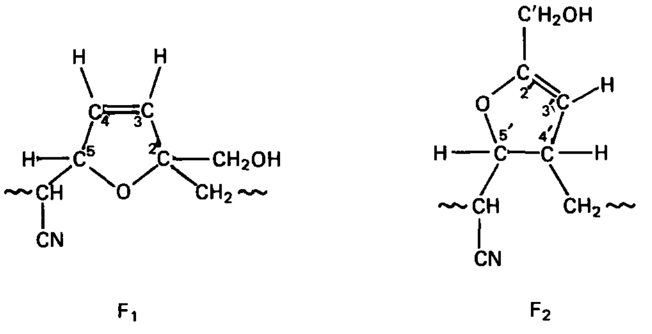


Figure 1 CP–MAS spectrum at 75 MHz of the furfuryl alcohol–acrylonitrile copolymer B17/DC at ambient temperature: spectral width 20 kHz, acquisition time 9.6 ms, relaxation delay 2.0 s, pulse width 90°, repetitions 2000, cross-polarization contact time 0.5 ms, spin rate 3.42 kHz. Trace A was plotted after a standard Fourier transform. Trace B was obtained after the same data had been modified to enhance the resolution. The arrow measures the 3.42 kHz sideband spacing. Spinning sidebands are marked * and + or x for –C–N and =C–H respectively

multiple of the spinning rate from the peak at 122 ppm of the carbon of the highly anisotropic C–N group, whose shift in solution also lies here[2,3]. To low field, the envelope of these resembles somewhat the pattern of a powder spectrum[9,10], leading one to expect peaks at the high-field side, too. It is thus possible that the shifts at 32.8 and at − 12 ppm in *Figure 2* (trace A) are also sidebands of the nitrile peak, though there is no strong evidence for a first upfield SSB at about 77 ppm. Two further experiments designed to aid shift assignment provided confirmation that the 122 ppm peak is from the nitrile carbons, as may be seen from the spectra in *Figure 2*. The first part of this (trace A) was obtained by acquiring data in such a manner that the signals from the protonated carbons were suppressed (see above), and the peak at 122 ppm persists, as would be expected of a nitrile carbon shift. It is also found in the TOSS spectrum of *Figure 2* (trace B), which lacks the sideband peaks in the low-field region. SSB were also seen in the low-field regions of the spectra of the remaining figures, the effect of different spinning rates being demonstrated in *Figure 3* (traces A and C). That the low-field sideband of the nitrile group is apparently greater in area than the central peak is probably associated with its axial symmetry, which causes the low-field SSB to be more intense than the upfield SSB[9], and might be reduced by using a greater spinning rate[10].



Furfuryl residues

Acrylonitrile–furfuryl alcohol copolymer spectra

Near to the nitrile shift at 122 ppm the solution spectrum leads us to expect two shifts at about 132 ppm from the olefinic carbons of the F_1 residues, comprising about 50% of the furan residues[3]. Only one band is resolved at 132 ppm, but it is clear that this too has sidebands to the left (+), though in contrast to the nitrile carbon pattern, their intensity is less than the central peak, and diminishes with distance. Assignments of other peaks in the spectrum may be made, with some reservation caused by possible interferences from the

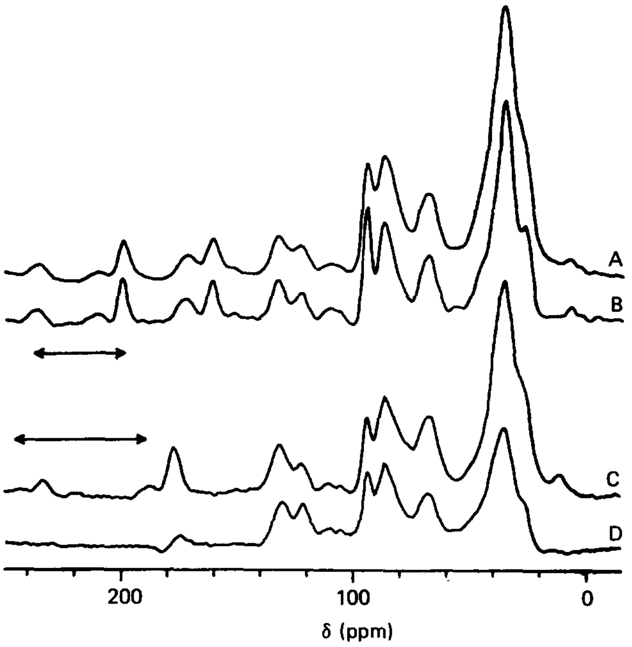


Figure 3 CP–MAS spectra of samples of the furfuryl alcohol–acrylonitrile copolymer after heating in argon to 185°C. Spectrometer settings as for *Figure 1*, except that the spinning rate was 2.90 kHz for traces A and B, and 4.21 kHz for C and D, which had an acquisition time of 28.8 ms. The arrows show the sideband spacing. Trace B is a resolution-enhanced version of A, and trace D is a TOSS spectrum[8]

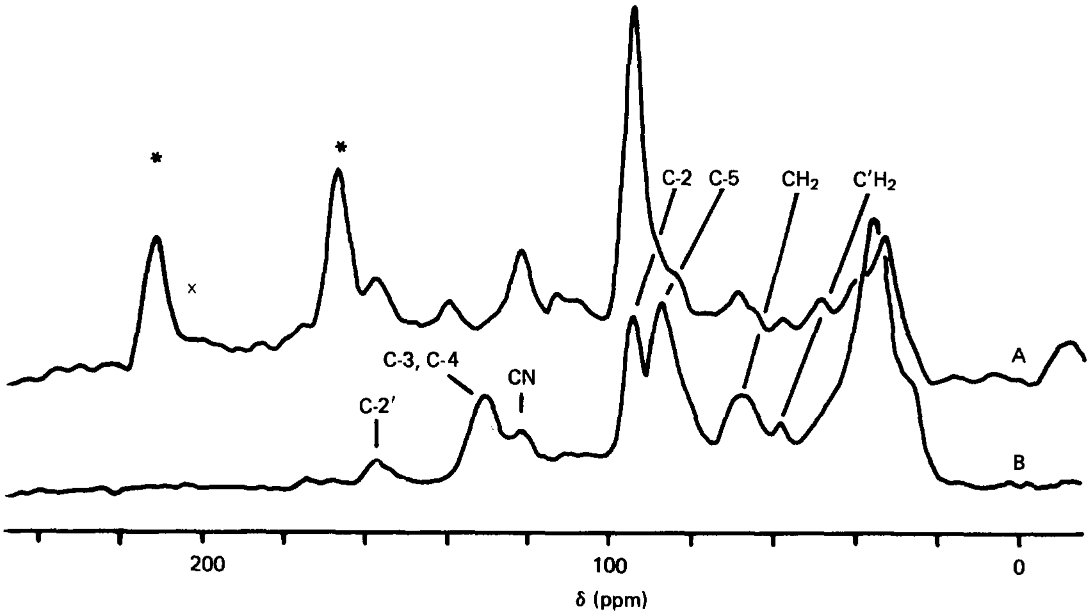


Figure 2 CP–MAS spectrum of the furfuryl alcohol–acrylonitrile copolymer. Trace A was obtained using a pulse sequence that suppressed the signals from protonated carbon atoms. Trace B was obtained with a sequence that suppressed sideband signals (TOSS[8]). Spinning sidebands are marked as in *Figure 1*

sidebands. The most prominent peak of *Figure 2* (trace A), which displays signals from non-protonated carbons, is at 94.4 ppm, and is assigned to the quaternary carbon C-2 of the F_1 structures. In the TOSS spectrum of *Figure 2* (trace B) the cross-polarization enhancement effect causes the protonated carbon C-5 to be relatively more prominent at 86.9 ppm, as it is also in *Figure 1*. The shoulder to the right of that peak in *Figure 1* (trace A) and the peaks resolved at 77.8, 80.3 and 83.4 ppm in trace B probably derive from carbon atoms linked to oxygen in structures that are present in minor proportions as a third type of furan residue (about 20 % of the furan residues[3,11]), and perhaps also as entrained Diels–Alder adducts[2,3]. The methylol shift of F_1 residues is seen at 68 ppm. Its resolution into two in *Figure 2* (trace B), with a shift difference of 3.5 ppm, may indicate either *cis* and *trans* addition in the F_1 structures, or the influence of the chirality of the nearest methine carbon of an acrylonitrile residue. This effect was not seen in the solution spectrum[3]. The proportion of F_2 structures (31 % of furan residues[3]) gives rise to the single sharp peak at 58 ppm (methylol group), the non-protonated olefin peak at 158 ppm (C-2, with a possible SSB (×)) and perhaps the peak near 106 ppm (C-3). Main-chain methylene and methine carbons of the acrylonitrile residues and certain carbons of the furan residues[2] contribute to the large envelope between 20 and 50 ppm, resolution in the solid state being insufficient to allow further assignment to all the sequence and chirality effects that might be seen in a solution spectrum[2]. The sharp feature resolved at 25.5 ppm in *Figure 1* (trace B), however, is probably caused by methyl groups and other carbon atoms of the end groups[2]. The assignments are tabulated in *Table 2*.

Spectra of heated samples of the copolymer

We show spectra from the sample (B) that had been heated to 185°C in *Figure 3*, the difference between traces (A,B) and (C,D) being the spinning rates for the sample, which cause major differences below 140 ppm. Peaks unaltered by changing the spinning rate are not sidebands, whose identification is also allowed by reference to trace D. It is clear from the spectra that the bands at 56 and 158 ppm we associated with the methylol and an olefinic carbon of the F_2 structure have vanished. The TOSS spectrum shown in trace D confirms the absence of these bands, and provides direct evidence that the weight loss previously recorded for such a copolymer[3] is the consequence of a change in the structure. The TOSS spectrum also shows a slightly out-of-phase peak at 175 ppm, where carbonyl or carboxyl carbons might be found[12]: such groups might well be formed by the rearrangement of the F_2 residues or by hydrolysis of the nitrile group. Maciel *et al.*[6] give 177 ppm as the shift of a substituted amide group carbon and 204 ppm as the shift of the carbonyl group of the unit formed from an opened furan ring: $-CO-CH_2-CH_2-CO-$; the latter is thus discounted. Only minor chemical changes have occurred, for the F_2 residues comprise only about 15 % by weight[3], but the technique is sensitive enough to detect the reaction of carbon atoms, which each comprise only about 2.4 % of the carbon mass. The AIBN-derived end-group shift remains at 26.2 ppm in the resolution-enhanced trace B. The apparently enhanced nitrile signal of *Figure 3* (trace C) (cf. *Figure 2* (trace B)) may indicate that chemical change at the F_2 residues has modified the CP process. The spectrum of the sample clearly differs in detail from that of the carbon fibre precursor, partially oxidized polyacrylonitrile (PAN) tow, that has four or five shifts within the region of 100 to 160 ppm[5].

Table 2 Shift assignments of the copolymer residues (in ppm relative to tetramethylsilane (TMS))

	Furan residue[a]					Acrylonitrile	
	C-2	C-3	C-4	C-5	CH_2OH	CH_2 and CH	CN
F_1	94.4	132.1	131.2	86.9	68.3	20–50	122
F_2	158	106			57.9		

[a] See structures in text for numbering system; F_3 structures were not distinguished, apart from possible peaks near 80 ppm in *Figure 1* (trace B) (see text)

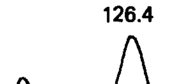


Figure 4 CP–MAS spectra of samples of the furfuryl alcohol–acrylonitrile copolymer after heating in argon to 600°C. Spectrometer settings as for *Figure 1*, except that the spinning rate was 3.40 kHz. The central peak is at 126 ppm, and the shoulder is at 20.5 ppm. The chemical structure of the material has been completely altered by heating to 600°C

A comparison of the spectra of *Figure 3* and *Figure 4* demonstrates that, on heating between 185 and 600°C, the chemical structure of the copolymer is completely altered: not only the F_1 residues but also the acrylonitrile residues have substantially changed their structure. The chemical analysis indicates that some of the carbon concerned is still protonated, so that there will be a cross-polarization effect. The value of the shift of the main peak (126 ppm) is close to that observed for the aromatic shift (125 ppm) in aromatic and bituminous coals[7,9]. We consider that most of the signal is associated with a new unsaturated or aromatized carbon shift, which has two SSB on each side, though there is a minor shoulder near 20 ppm from some remaining aliphatic type of carbon.

Spectra of acid-treated samples of the copolymer

We show in *Figure 5* spectra from the two samples produced by acid treatment: these clearly differ from the spectra of the starting material, but it is easier to observe that peaks have been lost through a reaction than to deduce what has formed. That acids could so readily influence the structure can be attributed to the methylol groups promoting proton penetration. The shift of the F_2 methylol carbon at 58 ppm has vanished from each spectrum, which shows that the reaction site first recognized as being sensitive to acid in solution[3] can also be affected in the solid state by an acid. When the peak from the methylol group of the F_1 residues is compared with the peak at 87 ppm, it is not significantly reduced in intensity by the HCl treatment, but may be a little reduced by the H_2SO_4 treatment. The position of maximum intensity in the carbon spectra, in the upfield region, is at 34.7 ppm in trace B but at 38.9 ppm in trace D, which compares with 34.5 ppm in the starting material. A measurement of sideband spacing suggested

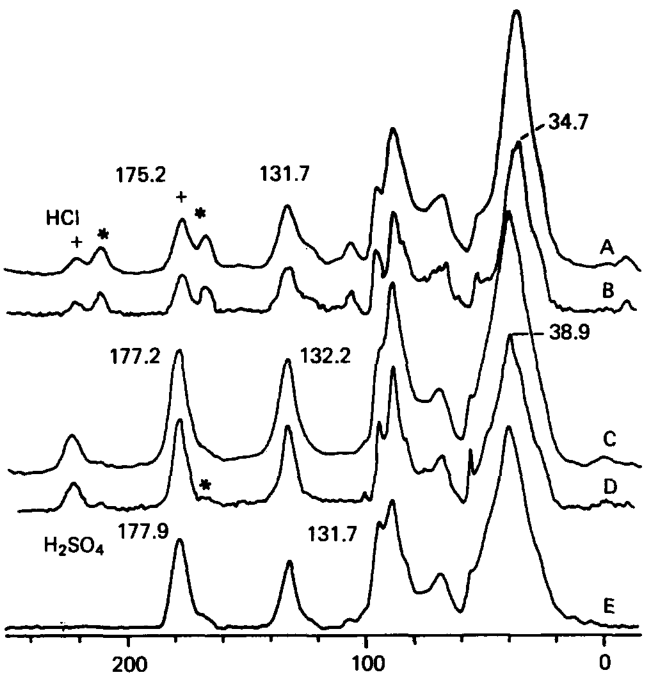


Figure 5 CP–MAS spectra of samples of the furfuryl alcohol–acrylonitrile copolymer after treatment with acid. The sample for traces A and B had been treated with concentrated HCl, as is indicated on the figure; the sample for the other spectra has been treated with concentrated sulphuric acid. The spectra of traces B and D were resolution-enhanced versions of the spectra of A and C respectively. The spectrometer settings were as for *Figure 1*, except that the spin rates were 3.30, 3.42 and 3.35 kHz for traces A and B, C and D, and E, respectively. Trace D is a TOSS spectrum

that this difference was probably a real effect, perhaps reflecting nitrile-group hydrolysis (see below), rather than the consequence of changes elsewhere in the spectrum that were transferred through the SSB pattern.

In the low-field region, the band from the nitrile carbon atom is much redued in the spectra (A and B) of the HCl-treated sample, again being much more apparent at the sites of the SSB (165 and 210 ppm) than at the central shift position. Evidence of the nitrile group is nearly lacking from the spectra (C–E) of the H_2SO_4-treated material. The infra-red spectra supported this view, when we compared the absorptions of the nitrile stretch and the C–H stretch bands, as may be seen from the entries in the final column of *Table 1*. The change suggests that the nitrile group has been hydrolysed. A clue to this question is provided by the TOSS spectrum of trace E, which also reveals that the prominent peak at 178 ppm in this (and therefore in the other spectra (C and D)) of the H_2SO_4-treated polymer was caused by a newly formed species. Its shift value is consistent with a group such as $-CO-NH_2$ or $-CO-OH$[12]. Some reduction in the N/C ratio is recorded in *Table 1*, which is indicative of some carboxylate formation. The shift at 178 ppm is well below the range found from the species present in oxidized PAN fibres[5].

There are a number of small peaks seen only in these spectra whose origin is at present unknown. They suggest the presence of a number of minor structures (53 and 71 ppm in *Figure 3* (trace B), and 56 and 101 ppm in trace D).

CONCLUSIONS

High-resolution ^{13}C MAS spectra have been observed and shift assignments made for a copolymer of furfuryl alcohol with acrylonitrile, and in materials derived from it by heating to two different temperatures and by treatment with two different acids. Spectra obtained under standard conditions were affected by the presence of spinning sidebands from carbon atoms in nitrile groups, from isolated olefinic units and from conjugated aromatic systems. By recording a small number of spectra run under similar conditions, it was possible to identify the sites of the reactions that occurred as a result of the four different treatments, even when the sites comprised only about 2% of the carbon atoms present.

In the solid state the methylol groups of the F_2 structures are found to be removed both by heating to 180°C and by treatment with concentrated hydrochloric or sulphuric acids, so that the F_2 structures have rearranged. Although the F_1 structures were little affected, the acid treatments caused the nitrile carbons to be removed, probably by hydrolysis, a process facilitated by the presence within the polymer of the hydrophilic methylol groups. The nitrile groups have almost completely reacted under the influence of the sulphuric acid but only partly under the influence of the hydrochloric acid. Upon heating the sample to 600°C the furan and acrylonitrile structures were destroyed and a simple and nearly completely aromatized structure remained.

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