Studies on copolymers of acrylonitrile with resins of furfuryl alcohol: 1. Preparation and thermal properties

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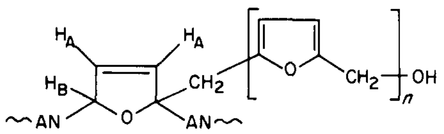
Copolymers of acrylonitrile with a furfuryl alcohol resin have been prepared by a free radical reaction, and have been characterized by n.m.r. and i.r. spectroscopy. Their t.g.a. has been performed in air and in a nitrogen atmosphere, to permit the recognition of a number of stages in the weight loss process. D.s.c., also in air and in nitrogen, has identified a number of exothermic and one endothermic process in the copolymers. Solid state cross-polarization/magic angle spinning ^{13}C n.m.r. spectroscopy and i.r. spectroscopy has been used to obtain some insight into the chemistry of the various chemical changes, which in air are completed by combustion and in nitrogen leave a carbon.

(Keywords: acrylonitrile; furfuryl alcohol oligomers; copolymers; thermogravimetric analysis; d.s.c.; cross-polarization/magic angle spinning ^{13}C n.m.r.; ^{1}H n.m.r.; i.r. spectroscopy; thermal decomposition; carbonization)

INTRODUCTION

Furan has very little free radical polymer chemistry[1], but the heterocyclic rings do form alternating copolymers with maleic anhydride[2], and furans and substituted furans may become entrained in polyacrylonitrile (PAN) chains. In this case they react in the normal manner of a free radical chain reaction addition polymerization to form residues of several types according to the manner in which the diene function behaves, as has been recognized by ^{1}H and ^{13}C n.m.r. studies[3–7]. In this paper we describe the preparation of copolymers of acrylonitrile with a furfuryl alcohol resin (FurCarb LP-270), and show the three main types of structure to be expected in these copolymers, I, II and III, on the basis of our earlier work. A number of features are of interest. One is the possibility that the furfurol resin residues on the acrylonitrile chain may provide a cross-linking effect when heated moderately, to render the acrylonitrile copolymer a thermoset in a new manner. Conversely, the acrylonitrile residues may modify the properties of the furfurol thermosetting resin. A third is whether and how a carbon forms during the rearrangement that takes place upon more intense heating. Acrylonitrile polymers and copolymers are an industrial precursor for carbon fibres[8–10] while furfuryl alcohol resins are a useful precursor to glassy carbons[11,12], both carbon forms being obtained by controlled heating. For the acrylonitrile–furfuryl alcohol copolymers, studies showed that furfurol residues might be > 50 wt% of the chain and the type II residues derived from furfurol monomer ($n = 0$) readily decompose on heating or on acid treatment in solution and in the solid state. Such residues have no capacity to cross-link the chains by the normal reaction, but reasonable quantities of a carbon were left following pyrolysis in nitrogen[6].



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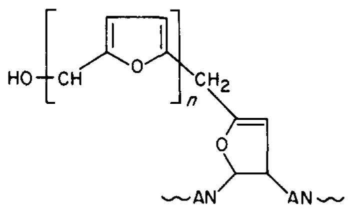

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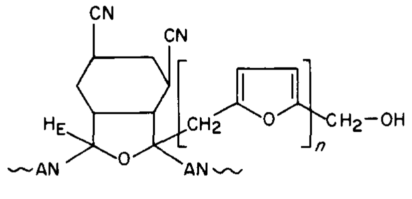

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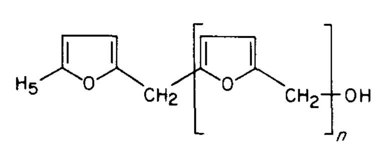
The normal sequence for converting PAN into carbon fibres commences with a stabilization phase, during which the fibre is partly oxidized in the temperature range 200–300°C and becomes infusible as a result of crosslinks that form, perhaps through the oxygenated sites as well as by the nitrile groups linking inter- and intramolecularly, in a process often referred to as 'cyclization', for it is believed to create six-membered rings along the acrylonitrile chain[8]. There then follows a pyrolysis at progressively higher temperatures up to 3000°C while an alignment is maintained by applying tension to the filament. During this stage nitrogen is expelled and the carbon framework rearranges to give the hexagonal structure of graphite, with six carbons per repeat unit. An equally thorough reorganization of the carbon framework is required before a thermoset furfurol resin, based on residues containing five carbons, expels oxygen and forms graphite at temperatures above 700°C (ref. 11). Each type of chemistry may be present with these copolymers in the separate components, the acrylonitrile and the furfurol oligomer residues. There is also the, perhaps naïve, possibility that the furfurol resin component may promote the 'cyclization' reaction involving the nitrile groups, or in some other manner replace the conventional preliminary slow oxidation stabilization step that cross-links the PAN chain backbones to make them tractable for carbonization.

The furfurol resin, a PAN and various copolymers were examined by t.g.a. and by d.s.c. in nitrogen and in air, to discover how a cure of the furfurol oligomers might be obtained by heat, how the 'cyclization' reaction of the nitrile groups takes place, and how the materials changed and degraded as the temperature was raised. Once the temperature ranges of the different processes had been identified and the thermochemistry examined, the chemistry involved was studied using ^{13}C n.m.r. and i.r. spectroscopy.

EXPERIMENTAL

Acrylonitrile and azobisisobutyronitrile (AIBN) were purified in the normal manner[3–7]. The FuroCarb resin (LP-270, lot Q832), was used as received from QO Chemicals. Its ^{13}C n.m.r. spectrum is not shown for it closely resembled the spectrum shown by Ddamba and Fawcett[13] in their Figure 4, the chief differences being smaller peaks from the terminal ether rings and larger peaks from the furfurol monomer that had been added to adjust the viscosity after the initial oligomer-forming reaction. In the ^{13}C n.m.r. spectrum signals from the methylene bridge, methylol group and ether bridge carbons were about 5:5:2 in intensity. The latter groups are thought to be required for the purposes of cross-linking the chains through the normal cure reaction (the ether links probably release formaldehyde)[14]. No methylfuran methyl carbon signals were seen at 14 ppm (ref. 13). In the ^{1}H n.m.r. spectrum the furan ring α and β protons were recognized in the ranges 7.5–7.7 and 6.0–6.5 ppm, respectively, the integrals of which give an estimate of the value of n as 1.3 in the representative formula IV. [An analysis of carbon, hydrogen and oxygen (by difference) gave the same result assuming formula IV.] By neglecting the small ether component in the oligomers and the presence of any oligomers which have lost their methylol groups[13], the n.m.r. value of n is an underestimate of the mean number of rings in the oligomers.



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One copolymerization (AS67a) was performed at 68°C in a Carius tube sealed under vacuum after two freeze–pump–thaw cycles[3,4]. The remaining preparations were performed at 60°C in a 1 litre flask that was purged with nitrogen before and while the polymerization continued within the feed of FurCarb, acrylonitrile and AIBN (summarized in *Table 1*). The polymers were purified by reprecipitation into methanol from a solvent (dimethylsulphoxide for copolymers with acrylonitrile residues >42 wt%, acetone for the others), until powdery solids were obtained after filtration and vacuum drying. Samples of polymers for the solid state ^{13}C cross-polarization/magic angle spinning (CP/MAS) n.m.r. spectra were placed in a glass tube and heated at 5–10°C min^{-1} in a furnace in a slow stream of nitrogen until the required temperature was reached, and held there for ~10 min before cooling[6].

^{1}H n.m.r. spectra, such as in *Figure 1*, were obtained at 300 MHz on a General Electric QE 300 MHz FT

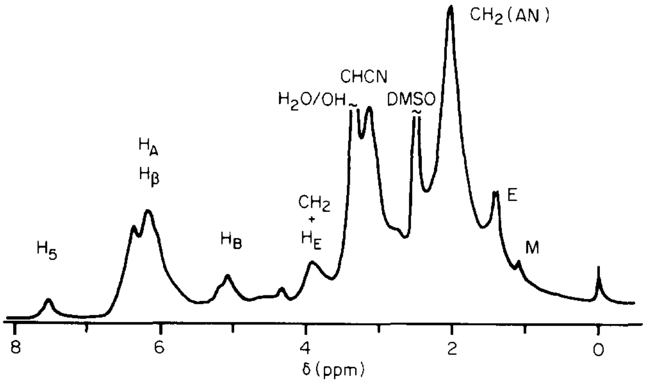

Figure 1 ^{1}H n.m.r. spectrum at 300 MHz of copolymer AS134 in $CDCl_3$. The copolymer has 34 wt% acrylonitrile residues

Table 1 Preparation and compositions of the copolymers of acrylonitrile (AN) and furfuryl alcohol resin[a]

Code	AN (ml)	FurCarb[b] (g)	Yield (g)	AIBN (g)	Time (h)	AN (wt%)[c]
AS67a	20	50	13.9	3.5	24	20
AS135	360	360	72	8	19	29
AS134	450	360	84	8	26	34
AS132	500	250	97	8	7.5	42
AS166	240	40	21.2	3	11	52
AS169	400	50	26.3	4.5	5.25	67
AS170	400	40	57.1	4.5	3.5	76
AS199	400	10	54.6	6	0.67	89
AS200	200	2.5	16.2	3	1.75	95
AS8	100[d]	–	21.3	0.2	6	100

[a] Temperature was 60°C, except for AS67a, which was prepared at 68°C

[b] FurCarb LP-270, from lot no. Q832

[c] From the N/C elemental ratio, except for samples AS200 and AS199 whose composition was determined from the ^{1}H n.m.r. spectrum

[d] In 500 ml of *n*-butyl ether; the molecular weight by viscometry was 30 000 (ref. 7)

spectrometer from samples in solution. The solid state ^{13}C CP/MAS spectra were obtained at 75.4 MHz on a Varian VXR 300 spectrometer at ambient temperature. The rotation frequency of the sample spinning at the magic angle was sufficiently high that spinning sidebands were substantially less intrusive than in the earlier study[6]. For i.r. spectra samples were dispersed in a KBr disc, and spectra were recorded on a Perkin-Elmer 938 instrument.

Thermogravimetric analyses were performed with a DuPont 951 thermal analyser that also provided first derivative curves (using 4–13 mg sample); d.s.c. measurements were performed with a DuPont 910 instrument that had been calibrated with an indium sample. For two copolymers measured in air, AS170 and AS166, replicate measurements were made and it was found that peak temperatures were accurate to within 2°C and peak areas were reproducible to within 5%. The areas of the peaks were evaluated for the heat of the reaction per unit initial mass using the software of the equipment to draw a curved base line.

RESULTS AND DISCUSSION

Characterization of the copolymers

The copolymers were creamy white solids if the acrylonitrile proportion was high, turning to a light orange as the proportion of the furfurol resin was increased. The substance that gives a dark red colour to FurCarb was thus not incorporated in the copolymer.

The composition of the copolymers was estimated by elemental analysis for C, H and N, the nitrogen content being a direct measure of the acrylonitrile residues, and the carbon content, after allowance for the appropriate amount of carbon in the acrylonitrile residues, being a measure of residues derived from the furfuryl alcohol oligomers. For calculating the composition values in *Table 1* it was assumed that the residues had the same carbon content as the oligomers (68.0%, though by doing this we may have slightly underestimated the value of n as is described next, and we may thus have slightly underestimated the oligomer content). The proportion of acrylonitrile residues to one (ideal) furfurol residue ranged from about 1 (AS67a), through 4 (AS166) to 64 (AS200).

A typical ^{1}H n.m.r. spectrum is shown in *Figure 1*, for polymer AS134, that had 34 wt% acrylonitrile residues, according to the elemental analysis. Since the relative reactivities of 2-methylfuran, furfurol and 2,5-dimethylfuran (at 78°C) are 0.46, 0.23 and 0.08, respectively[7], we suppose that the furfuryl alcohol component of the FurCarb reacted less readily than the left hand ring of typical oligomer IV, and that the other rings, particularly the right hand ring of IV, rarely participated in the copolymerization reaction. The ^{1}H n.m.r. spectrum is consistent with this view, the main peaks below 3.6 ppm being readily assigned to particular protons in I, II and III as indicated, following the known shifts of entrained furan rings[3,5,7]. The small shift at 7.6 ppm is assigned to the H5 proton of a furfuryl ring that is pendent to the chain: the simplest origin is the H5 proton of one ring of a difurfuryl ether[13] that is entrained through the other ring. Methylene groups between two furan rings contribute to the peak[13] at 3.9 ppm, but if one of the rings has become enchained, it is probable that the signal from the group then moves upfield, as happens with the methyl shift of methylfuran (that goes ~0.35 ppm upfield when the adjacent α carbon reacts[3]), to be lost under the envelope shared by hydroxyl protons, the protons of the enchained furan rings and the acrylonitrile methine protons. The methine and methylene group signals from the acrylonitrile residues are seen at their normal places, and the peaks labelled E and M have been previously assigned to the methyl groups of the initiator AIBN and a minor acrylonitrile-derived methyl side chain, respectively[4]. From the area of the end group methyls we estimate that the molecular weight was in the order of 20 000, assuming that the termination reaction was a combination[7]. We reserve the discussion of the ^{13}C n.m.r. spectra to later, when we describe the features seen in the CP/MAS spectra before and at different stages during the pyrolysis.

The i.r. spectrum of the copolymer AS170 (76% acrylonitrile) is shown at the bottom of *Figure 2*. The

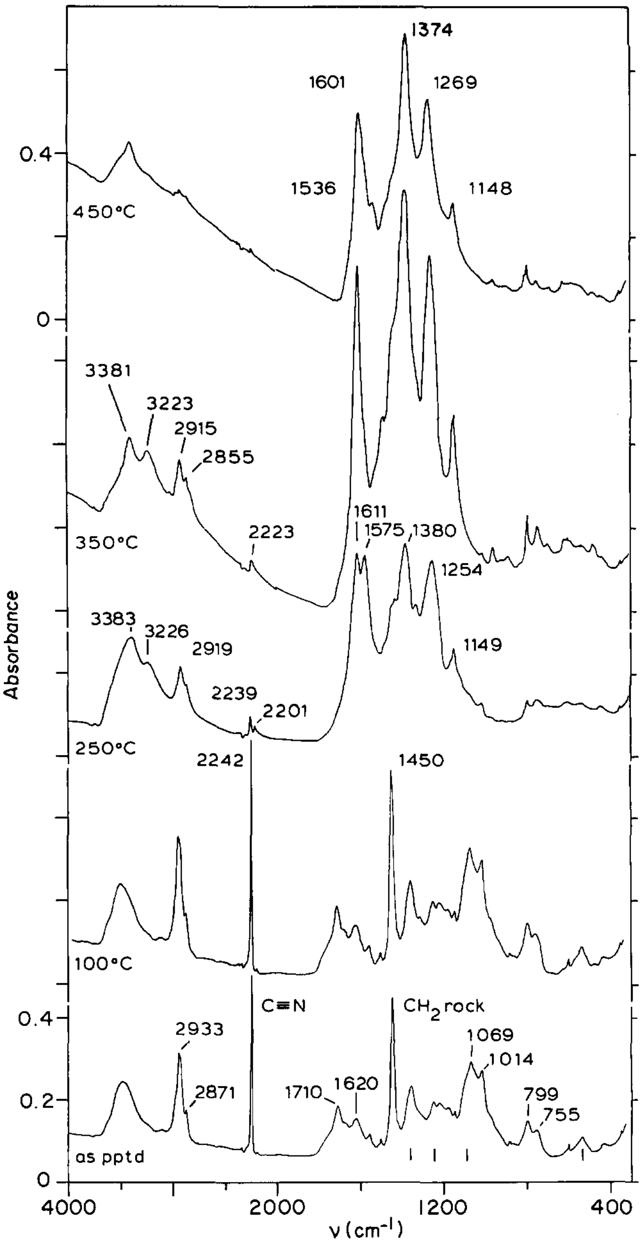

Figure 2 I.r. spectra of copolymer AS170 (76% acrylonitrile) measured for a sample as precipitated following purification and for samples prepared from that by heating in nitrogen to the temperatures indicated at the left of each trace. The absorbance scales are all identical

main peaks characteristic of the acrylonitrile residues[17] have either been labelled directly, as for the nitrile band at 2242 cm^{-1} and the CH_2 rock at 1450 cm^{-1}, or have been indicated by a bar where there is also a significant and masking contribution from the furfurol residues. We have given an i.r. spectrum of a copolymer of acrylonitrile and furfuryl alcohol in reference 5. The band at 1014 cm^{-1} may arise from a C–O–C stretching mode of the furan rings, there being a similar mode of the substituted furans active[4,5] near to 1070 cm^{-1} that is made more prominent in this spectrum by the presence near 1190 cm^{-1} of a band from acrylonitrile residues. We recognize several bands in an envelope above 1600 cm^{-1} that are assigned to vibrations of the C=C double bonds. The relative intensities differ from that in the resin, for bands from the I (1620 cm^{-1}) and II (1670 cm^{-1}) structures are also expected here[5]. There are two bands, at 799 and 755 cm^{-1}, that are out-of-plane C–H bending modes of the β and α positions on the furan rings[15]. The relative absorbances of these two bands fell from 1:1.5 for the resin to 1:0.75 ($\pm$ 0.05) upon copolymerization, confirming that the α position was the main point of attachment. The minor band at 3120 cm^{-1} is assigned to olefinic[5] and furan ring C–H stretch. We discuss the other spectra of this figure below.

Studies on the pyrolysis and the combustion of the copolymers

The furfurol resin, a PAN and various copolymers were examined by t.g.a. and by d.s.c. in nitrogen and in air, to discover how a cure of the furfurol oligomers might be obtained by heat, how the cyclization reaction of the nitrile groups takes place, and how the materials changed and degraded as the temperature was raised. Once the temperature ranges of the different processes had been identified and the thermochemistry examined, the chemistry involved was studied using ^{13}C n.m.r. and i.r. spectroscopy.

Thermogravimetric analysis. The traces of the t.g.a. conducted in nitrogen and in air are shown in *Figures 3* and *4*, respectively for a PAN, for several of the copolymers as prepared, and for the FurCarb resin. In air, as shown in *Figure 4*, only a small percentage of the initial weight was left at 800°C, the final combustion occurring near 600°C, but in nitrogen the main weight loss took place near 400°C and the residue averaged 46% of the initial weight, being at least 42% of the initial weight as shown in the legend to *Figure 3*. An exception was the resin sample itself, probably because there was not enough time for the cure. In air the PAN and the copolymers that had >60 wt% acrylonitrile units showed the sudden weight loss at temperatures above 250°C that has been associated with the thermal decomposition that accompanies the cyclization process of the nitrile groups[9]. The process was so sudden that the instrument was incapable of responding sufficiently quickly under the measurement conditions used; the onset fell from ~310°C to ~280°C as the furfurol component rose to 33%, but when the furfurol content rose above 50% two processes appeared, the second being ~100°C above the intermediate process of the resin.

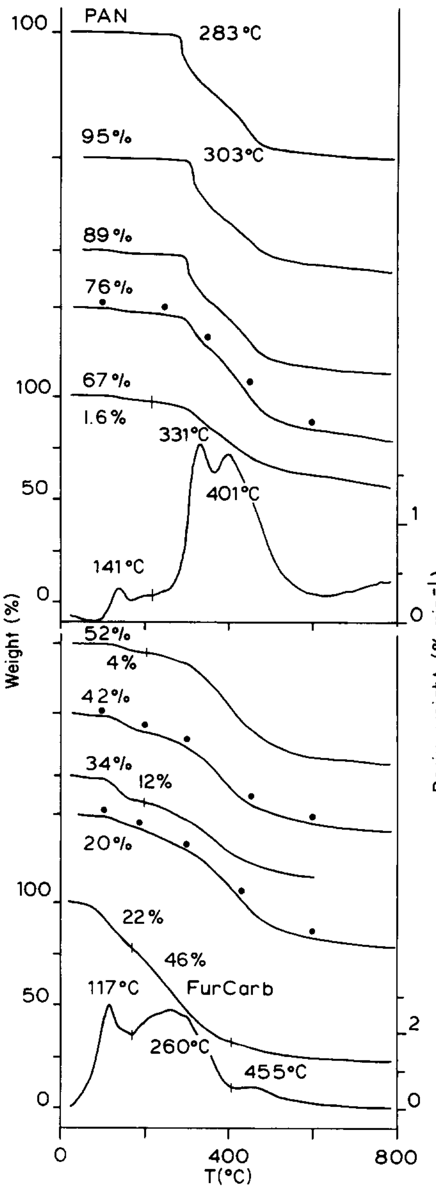

Figure 3 Thermogravimetric analysis in nitrogen of a PAN (AS8), several copolymers and the FurCarb resin itself. Heating rate 10°C min^{-1}. The composition of each copolymer is indicated as a percentage of acrylonitrile on the left-hand side; the samples in order of decreasing acrylonitrile content (and the weight fraction of residues left at 800°C) were: AS8(44%), AS200(48%), AS199(45%), AS170(40%), AS169(56%), AS166(46%), AS132(48%), AS134(42%), AS67a(42%) and the FurCarb resin (23%). The dots immediately above the curves for the 76%, 42% and 20% polymers indicate the temperatures to which samples were heated for the ^{13}C and i.r. spectra of *Figures 2* and *8–12*

The pure furfurol resin displayed a cure reaction at 110°C in air, the fall in weight being caused, we presume, by the expulsion of water. A similar cure was obtained by Chuang *et al.* at 100°C using an acid catalyst, to obtain a material without methylol and ether groups[16]. The derivative of the lower trace for FurCarb showed a sharp cure at 120°C in nitrogen, a broad decomposition centred upon 260°C (slightly higher than in air) with a minor process at 460°C. In air the final combustion took place above 500°C.

Evidence of a reaction at about the temperatures of the furfurol cure was prominent in derivative traces for the 20% and 52% AN samples at ~135°C in air, as well as in the weight curves themselves. The weight loss associated with this reaction was not proportional to the resin content, seeming to be a maximum at an acrylonitrile weight fraction of ~35% (for the resin the

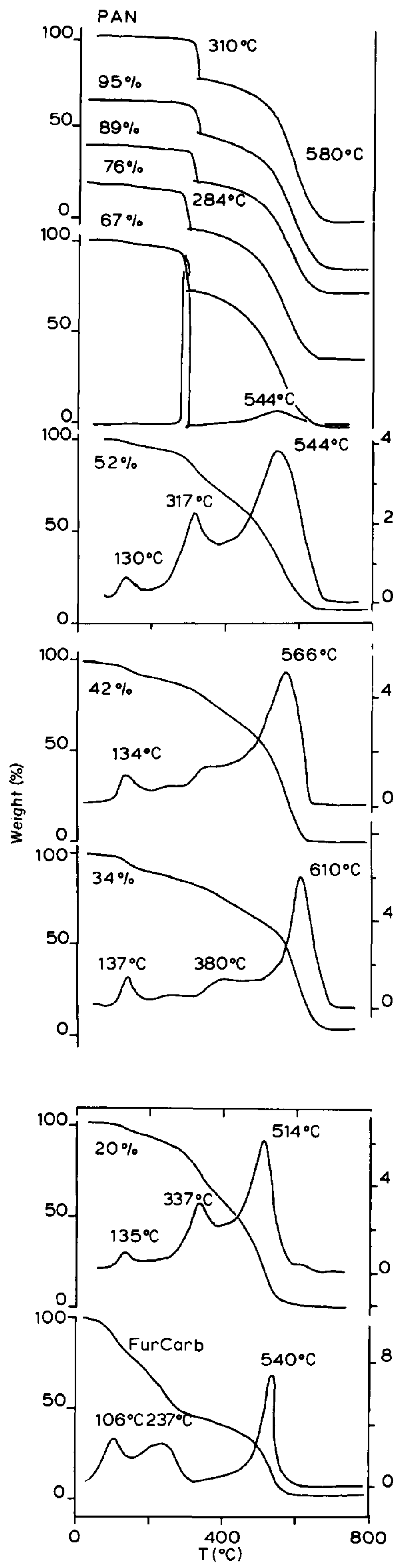

Figure 4 Thermogravimetric analysis of PAN, several copolymers and the FurCarb resin in air. Heating rate 10°C min^{-1}. The composition of each of the copolymers is indicated as a percentage of acrylonitrile on the left-hand side; the samples in order of decreasing acrylonitrile content were: AS8, AS200, AS199, AS170, AS169, AS166, AS132, AS134, AS67a, and the FurCarb resin

drop was ~22%, but for the 48% resin-containing copolymer it was only ~4%). In air as in nitrogen, the cure reaction had a lower weight loss for the copolymers than expected from the proportion of furfurol residues. It appeared to be over by the time the temperature had risen to ~180°C. The reaction was difficult to discern for the copolymers richer in acrylonitrile residues: it was not visible in the derivative plot for the 67% acrylonitrile sample heated in air because of the sharpness of the 'cyclization' process, but was visible in the plot performed in nitrogen at 141°C. We should note that some of the furfurol-derived residues may decompose and so cause a fall in weight, but not be capable of cross-linking[5]. We return to this topic again below, after the d.s.c. traces have been described.

The PAN lost weight over a broad temperature range by combustion in air after the sudden weight loss near 300°C. This combustion generally occurred at lower temperatures as the furfurol resin content rose, the centre of the final weight loss process moving from ~580°C to below 550°C.

In nitrogen the traces were similar to those obtained in air, but differed in detail in the temperatures and the extents of each decomposition. The weight loss associated with cyclization took place in the copolymers rich in acrylonitrile residues, but was smaller in extent than in air: for the top three traces the sudden drop in nitrogen averaged ~8%, whereas in air it was ~18%, being greater for the pure PAN (23%) than for the other two traces (16%). This behaviour differs from that shown by other types of PAN, for which the fall in weight was often less in air than in nitrogen[17]. For the 76% and 67% acrylonitrile copolymers the process was not co-operative in nitrogen, extending over a temperature range of ~30°C, whereas it was so in air. The furan rings seemed to have an inhibiting effect in air and in nitrogen upon the 'cyclization' reaction, which, from the low reactivity of furan radicals in free radical reactions[1,7], suggests that the cyclization may be a free radical process. On the traces obtained in nitrogen and shown at the top of *Figure 3* there appeared to be a weight loss process immediately following and related to the sudden cyclization. This was followed above 350°C by a thermal decomposition that was generally complete by the time the temperature reached 600°C.

To explore the possibilities of effecting a cure by thermal treatment, the FurCarb resin, and copolymers AS135 (29% acrylonitrile) and AS169 (67% acrylonitrile) were heated to 200°C for 1 h under vacuum. The t.g.a. traces that were obtained in nitrogen and in air for these samples are shown in *Figure 5*. It may be seen that weight losses hardly occurred until 250°C had been exceeded, confirming that not only had the 141°C process been removed from the 67% acrylonitrile copolymer and the 117°C process removed from the FurCarb resin, but also that much of the 260°C process was eliminated from the resin. The first decomposition peak of the resin thus moved up to ~340°C in air and to 430°C in nitrogen. These measurements suggested that a cure was possible. The traces in air and in nitrogen differed for each of the three samples, principally in that the proportion of residues left at the high temperature was >45% in nitrogen and <12% in air, but also in the relative importance (and central temperature from the derivative plots) of the weight loss steps. The cured FurCarb resin, for example, had a preliminary weight loss at 340°C in

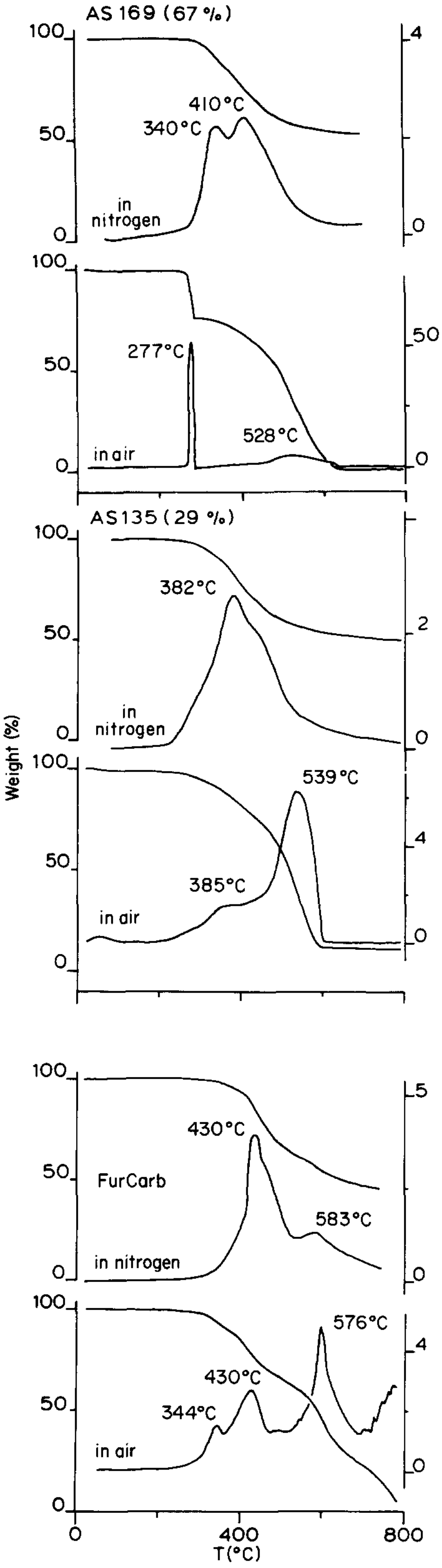

Figure 5 Thermogravimetric traces and derivative curves for copolymer AS169, copolymer AS135 and FurCarb resin after each had been cured at 200°C for 1 h. The atmosphere was nitrogen or air, as indicated, and the heating rate was 10°C min^{-1}

air from an oxidation reaction (that was absent in nitrogen), and a pyrolysis process at 430°C in both air and nitrogen that was probably accompanied by a rearrangement of the skeleton. In nitrogen there was a minor pyrolysis process at 580°C, at which temperature in air the material underwent a substantial combustion and the remaining 15% of the material burned off as 800°C was reached. The sample rich in acrylonitrile units, AS169 of *Figure 5*, displayed the sharp degradation starting near 270°C associated with the cyclization of nitrile units that was clearly stimulated by oxidation, as the process was lacking in nitrogen. The thermal degradation in nitrogen had two steps, at ~340 and 410°C, in which successively 15 and 32 wt% was lost. The second step probably involved acrylonitrile units, as it was less important in the degradation of the copolymer AS135 (29% acrylonitrile), being merely a shoulder on the main peak at 380°C, that left a remnant of 50 wt%. In air for that polymer, the cyclization reaction was no longer evident as a sharp feature, presumably because the nitrile groups were too dilute for a co-operative process to take place. The effect of the thermal pretreatment was most evident in the behaviour of the resin, the temperature at which half the weight was lost in air rising from ~280 to 600°C.

Differential scanning calorimetry. We show in *Figure 6* d.s.c. traces measured in nitrogen for seven copolymers, the homopolymer PAN and the furfurol resin. A very sharp exothermic process peaking at 273°C is shown for the PAN homopolymer sample in the upper plot, which otherwise was quite featureless, and as the furfurol resin component in the sample rose towards 70 wt% this peak broadened from ~20°C to range > ~100°C for sample AS135 (29% acrylonitrile) with corresponding falls in the maximum value of heat flow, before petering out when the acrylonitrile fraction was only ~20%, for then, presumably, the nitrile groups were too dilute to undergo the cyclization reaction. The enthalpy values are reported on the figure, and peak temperatures are also indicated. In nitrogen the enthalpy values are similar to the value of 280 ± 20 J g^{-1} that was previously found for PAN[18]. The enthalpy values did not fall quite in proportion to the AN content until that had dropped to ~30 wt%. In the acrylonitrile-rich copolymers the enthalpy was greater than expected on the basis of nitrile group content because the furfurol resin component either participated in the process or it facilitated the reaction between the nitrile groups, perhaps by permitting their movements.

A small fraction of furfurol resin units raised the temperature of the peak maximum (perhaps through furan being a free radical scavenger[2,7]) but then that temperature fell, and the initial temperature of the process fell from ~270°C for the PAN to ~230°C for the 52% acrylonitrile copolymer. The exotherm peaked at ~10–15°C below the start of the weight loss, indicating that the weight fell as a result of the release of heat. The final weight loss process, e.g. at 401°C for sample AS169 (67% acrylonitrile), had a barely noticeable exotherm.

The copolymers rich in furfurol resin, such as AS134, with only 34% acrylonitrile units, had a less stable baseline over the first 50°C, but clearly showed an endothermic process starting near 100°C and peaking at ~133°C. There may be an exothermic process starting at ~30°C, and coincident from ~80 to 120°C with the endotherm. The endothermic process was absent from the furfurol resin itself, and was difficult to recognize as a dip after a small exotherm (~60 J g^{-1}) in the trace from the sample containing 67% acrylonitrile residues – it was restricted to those copolymers with acrylonitrile residue contents near 35%, where there are about two acrylonitrile residues per furfurol unit. The weight loss peaked at ~140°C, just after the endotherm minimum.

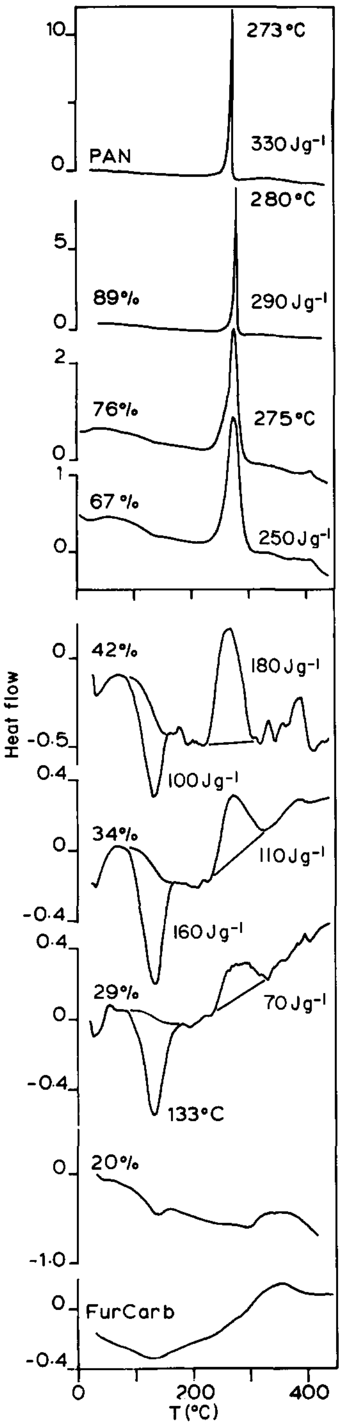

Figure 6 D.s.c. plots for PAN, seven copolymers and furfurol resin between ambient temperature and ~425°C measured for the sample in nitrogen. The heat flow values and the enthalpies obtained from the areas under the peaks have been calculated on the basis of the initial weight of the samples

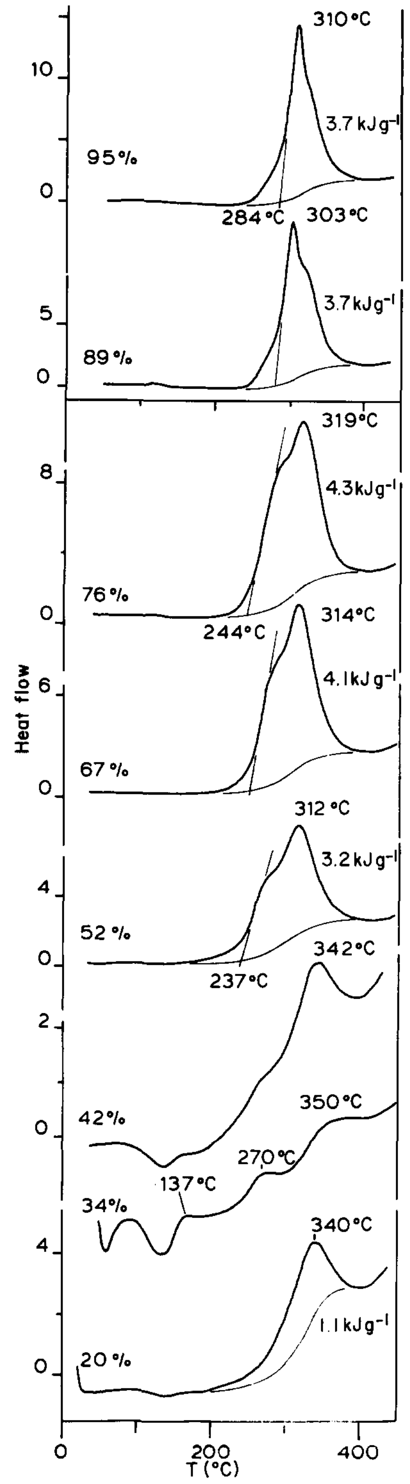

Figure 7 D.s.c. plots for PAN, seven copolymers and furfurol resin between ambient temperature and ~425°C measured for the sample in air. The heat flow values and the enthalpies obtained from the areas under the peaks have been calculated on the basis of the initial weight of the samples

Samples of these copolymers were cured at 120°C for 20 min in a vacuum oven before being examined by the d.s.c. technique. Though the endotherm was no longer apparent, the minor exotherm was still present centred on 80°C, as was the major cyclization exotherm that started once the temperature rose above 175°C.

Figure 7 shows d.s.c. traces measured in air at temperatures up to 400°C, before the combustion indicated in *Figure 4* had started. The trace for PAN is not shown, for the exothermic process that started at ~220°C became so rapid at 288°C that the instrument could not record and plot the data properly under the conditions employed. However, for the copolymer with 95% acrylonitrile the co-operative nature of the process was less pronounced, and the peak was spread over a wide temperature range. As the furfurol resin proportion rose in progression down the figure, the high temperature exotherm first broadened and then developed a shoulder on the high temperature side, which became the larger process as the furfurol resin component passed 80 wt%.

This suggested that the furfurol resin content was participating in the chemical changes once cyclization was stimulated. The magnitude of the heat evolved was at least one order greater than that found in nitrogen, indicating the importance of oxygen in stimulating the chemistry of the exotherm. The enhancement of the cyclization exotherm in air was observed some time ago[19]. The furfurol resin content was itself clearly incapable of stimulating the process in the same manner when nitrogen was used, but was involved in it. For example with sample AS169 (67% acrylonitrile) the exotherm in air was 4070 J g^{-1} and the major peak was at 314°C, as compared to 275 J g^{-1} and 275°C for the values in nitrogen. The exotherm started at 247°C in air and at 255°C in nitrogen, so oxygen only slightly brought forward the start of the process, but did prompt the process on the high temperature side. For sample AS134, with only 34% furfurol residues, the exotherm was in two distinct locations, at 270 and at 350°C, presumably related to the nitrile and the furan groups, respectively. At these temperatures the t.g.a. curves had corresponding weight loss processes (*Figure 4*). The low temperature exotherm noticed in nitrogen near 100°C and the endotherm at ~140°C were also found in the traces run on samples with high furfurol resin contents, but were less significant in air in comparison to the major exothermic feature.

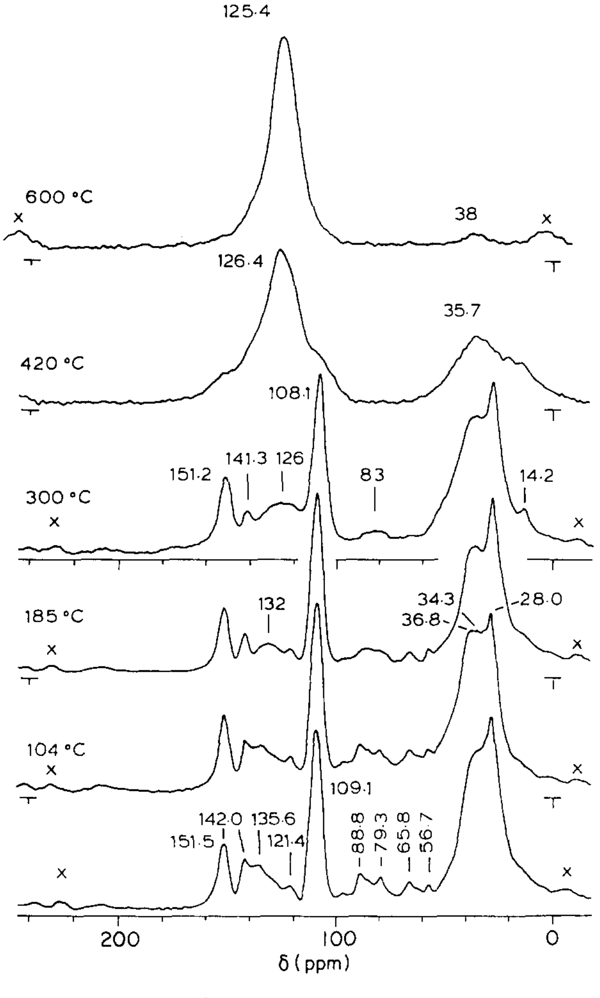

Figure 8 CP/MAS ^{13}C n.m.r. spectra of copolymer AS67a as prepared, with 20 wt% acrylonitrile residues, and after heating in nitrogen to the temperatures indicated on the left-hand side of each plot. Spectrometer settings: spectral width 40 kHz, acquisition time 9.6 ms, relaxation delay 2 s, 2000 repetitions, CP with flip back contact time 0.5 ms, apodization function time constant 2 ms, spinning rate 9000 Hz; spinning sidebands from the nitrile and graphitic carbons are marked by ×

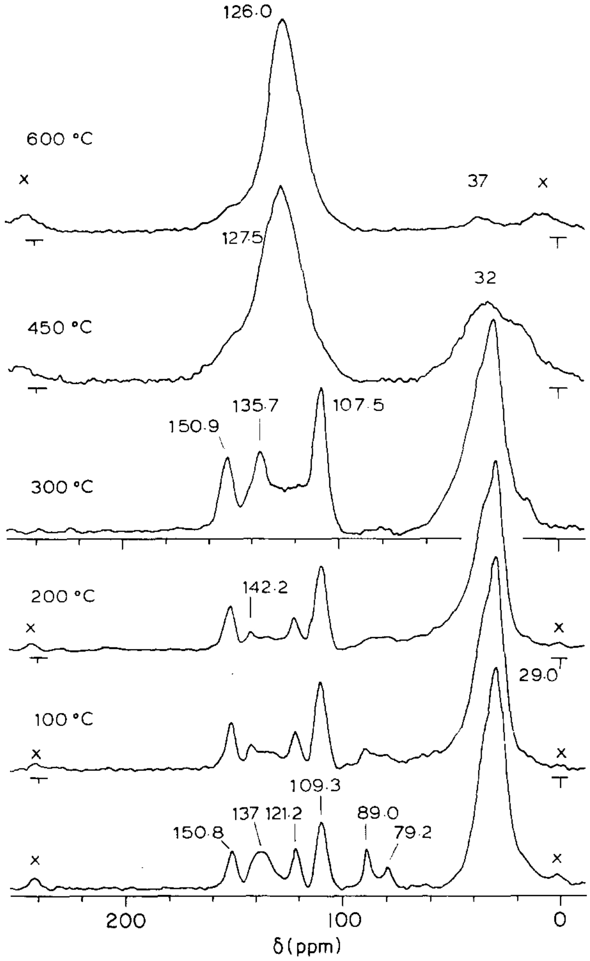

Figure 9 CP/MAS ^{13}C n.m.r. spectra of copolymer AS132 as prepared, with 42 wt% acrylonitrile residues, and after heating in nitrogen to the temperatures indicated on the left-hand side of each plot. Spectrometer settings as for *Figure 8*. Spinning sidebands from the nitrile and graphitic carbons are marked by ×

CP/MAS n.m.r. and i.r. spectra

The CP/MAS ^{13}C n.m.r. spectra of three of the copolymers and of samples obtained from them by heat treatments in nitrogen are shown in *Figures 8*, *9* and *10*, for copolymers with, respectively, 20, 42 and 76% acrylonitrile residues. The temperatures to which the samples were heated were spaced at intervals of 100–150°C, at values suggested by the t.g.a. traces of *Figure 3*, where the temperatures are indicated by dots. For the spectra of the polymers themselves that are shown at the bottom of each figure, the assignment of the carbon shifts in the prepared polymers is relatively straightforward in view of previous studies of furfuryl alcohol oligomers in solution[13] and in the solid state[16], our examination of acrylonitrile–furfurol copolymers in solution and in the solid state[5,6] and the assignment of the shifts of acrylonitrile–furan copolymers[4] in solution. These assignments are described first. The methylene and methine carbons of acrylonitrile residues contributed to the peak at ~30 ppm; its shape is sharp at 29.0 ppm, when the acrylonitrile residues predominate, as in *Figure 10* despite the shifts being quite distinct at 33 and 27 ppm, respectively, in solution. The peak is much

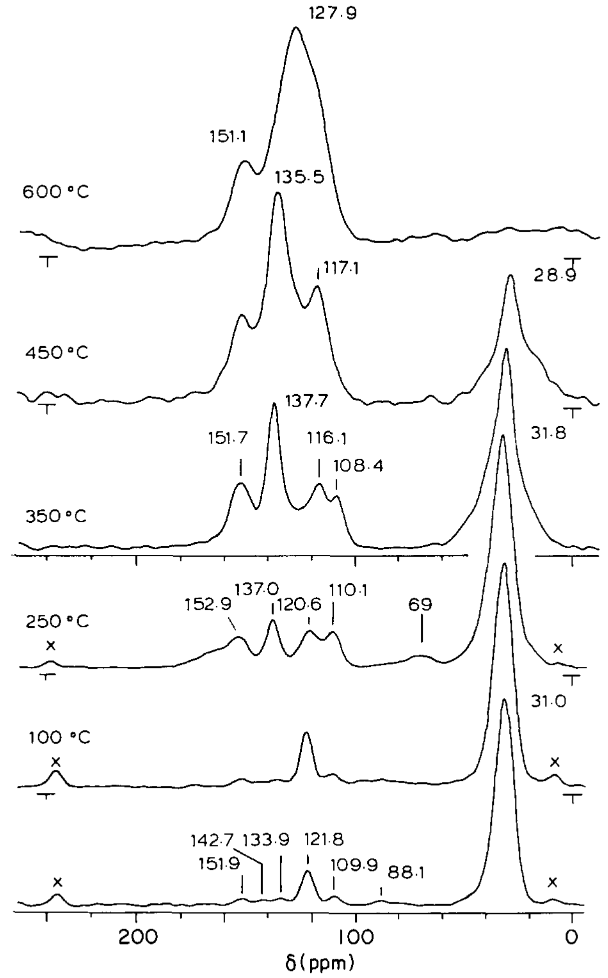

Figure 10 CP/MAS ^{13}C n.m.r. spectra of copolymer AS170 as prepared, with 76 wt% acrylonitrile residues, and after heating in nitrogen to the temperatures indicated on the left-hand side of each plot. Spectrometer settings as for *Figure 8*. Spinning sidebands from the nitrile and graphitic carbons are marked by ×

broader in *Figure 8*, for there are more residues in which the acrylonitrile carbon shifts are perturbed by the presence of adjacent furan residues[4] and the methylene shifts of the furfurol oligomers themselves are expected at 27 or 28 ppm[13,16]. The nitrile carbon is clearly seen at ~121 ppm in *Figure 10*, where the shifts of the furfurol residues are barely discerned. In that downfield region other shifts become more intense as the proportion of furfurol oligomers rises as shown in *Figures 8* and *9*. I.r. spectra for some of these samples are also shown in *Figures 2*, *11* and *12*, to provide complementary information on the chemical changes taking place.

The most obvious feature in the low field region of *Figure 8* is the peak at ~109 ppm from the β carbons of the intact furan rings in the side chains, but the small splitting observed by Maciel[16] and attributed to an orientation effect for the furan rings in solid furfurol oligomers themselves is not apparent here. The next peak in intensity in that region, at 152 ppm, was from the substituted α carbons. The peak from the protonated α carbons at 142 ppm was less intense, consistent with most of such shifts being depleted through that carbon being the site of attachment of the acrylonitrile units. The α carbon shifts tended to merge with the olefinic peaks of type I residues[4] in the region of 134–138 ppm. In contrast to the region below 125 ppm, the spectrum between 100 ppm and 50 ppm closely resembled that of the copolymers of furfurol with acrylonitrile[6]: the shifts at ~90 and 80 ppm are assigned to the protonated and quaternary alpha carbons of the enchained I furan ring and the peaks at 66 and 57 ppm are probably from methylol groups of I and II residues formed from the furfurol monomer in the

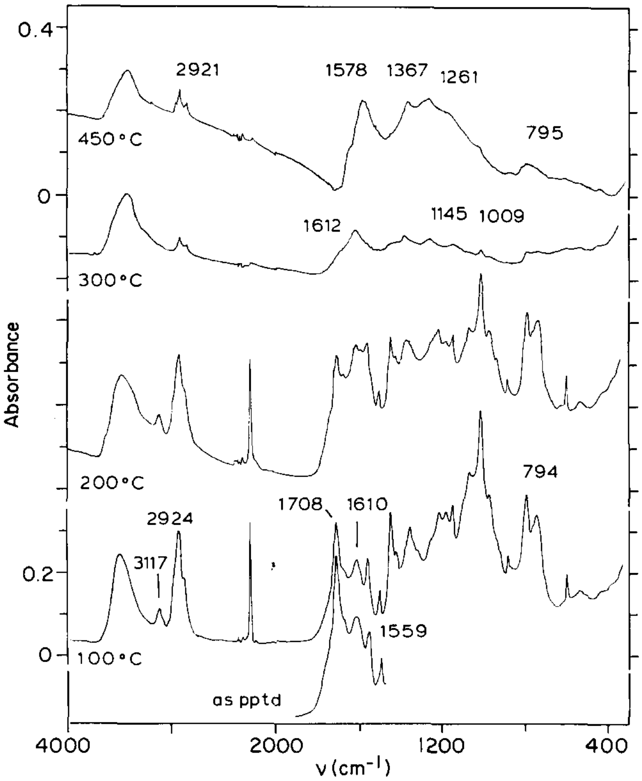

Figure 11 I.r. spectra of copolymer AS132 (42 wt% acrylonitrile) and samples obtained by heating it to the temperatures indicated on the left-hand side of each plot

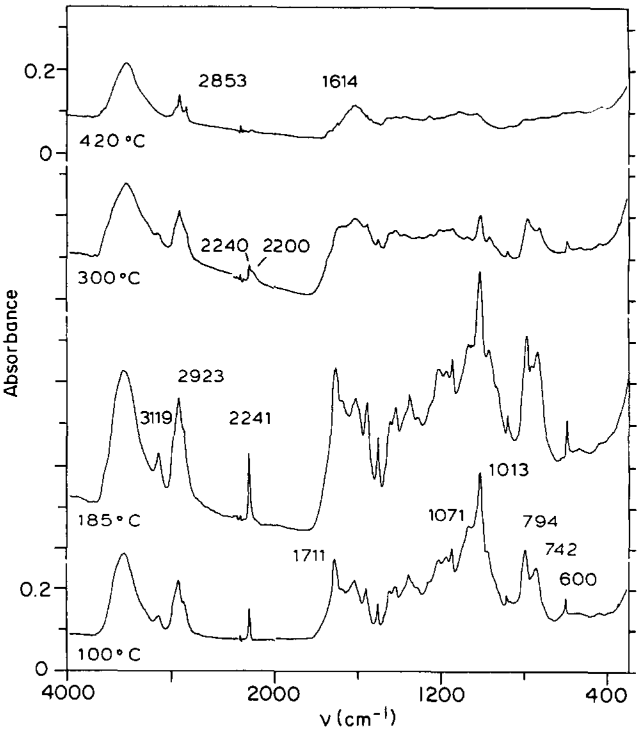

Figure 12 I.r. spectra of copolymer AS67a (20 wt% acrylonitrile) and samples obtained by heating it to the temperatures indicated on the left-hand side of each plot

FurCarb. Methylol groups of unreacted furan rings[13] are also expected at 57 ppm, and the methylene groups of ether links[14] are expected at 64 ppm.

As before[6], spinning sidebands from the cylindrically symmetrical nitrile carbons are clear, but this time they are more widely placed and less intense because of the higher rate of sample rotation, and there is little evidence for sidebands from the less symmetrically located olefinic carbons. The spinning sidebands decreased in intensity after the polymers had been heated, as the nitrile groups themselves reacted, thus providing an indication of the fate of the nitrile carbons when the main signal was obscured.

When each copolymer was heated in nitrogen to 600°C, the final product was a hard black mass that, according to the spectra of *Figures 8–10*, was predominantly carbon, for, as with the furfurol copolymer[6], the signal accumulated in the region around 126 ppm that is close to the aromatic carbon shift (125 ppm) shown by bituminous coals[20] characteristic of graphitic carbon. Only a trace remained near 38 ppm of aliphatic carbon shifts. Confirmation of this was provided by the elemental analyses, that found 4, 10 and 18% of nitrogen, respectively (though these values were only ~2% less than the values for the unheated polymers) and only ~2 wt% hydrogen in each case. It was noticeable that a peak downfield of the main aromatic carbon signal, itself rather wide because of a shoulder upfield, remained at 600°C for sample AS170 (*Figure 10*) an effect we attribute to the remnants of nitrogen in the char derived from that acrylonitrile-rich copolymer. Each of these copolymers was quite graphitized by heating to 600°C, in contrast to the findings of Eckert *et al.*[11] that furfurol oligomers should show the distinct shifts of alpha and beta carbons and bridging methylene groups in the ^{13}C CP/MAS n.m.r. spectrum even after the material had been heated to 650°C. The acrylonitrile residues thus facilitated the chemical changes in these copolymers at the furan rings that are induced by heat, causing them to take place at a significantly lower temperature. The synergistic effect may have derived from the catalytic influence of materials, such as ammonia, that are released from the acrylonitrile residues[9,21], or more simply from the proximity of the furan residues to structurally-changing acrylonitrile residues. The accumulation of the signal in the aromatic region proceeded in several stages, many new peaks formed in the region from 100 to 160 ppm before they eventually coalesced. The peak at ~30 ppm first broadened as structural variety developed and then diminished as the carbons changed their orbital hybridization from sp^3 to sp^2. All the spectra were obtained at the same spectrometer settings, so the observed changes reflected real chemical changes within the residues, though peak intensities may not be directly proportional to carbon numbers.

The spectra showed little change when the samples were first heated except that for sample AS132 (*Figure 9*) the broad peak at 137 ppm was diminished to leave a distinct signal at 142 ppm, and the shifts near 80 and 90 ppm also dropped in intensity. These changes suggest that the type I main chain structures were partially removed from that polymer. Similar changes were seen in the spectrum of AS67a (*Figure 8*) after heating it to 185°C: the backbone residues created by additions to the furan nucleus were thus the structures that were most sensitive to heat.

The nitrile carbon signal at 122 ppm and its spinning sidebands are clear at 185°C in *Figure 8*, at 200°C in *Figure 9* and perhaps at 121 ppm in *Figure 10* at 250°C, but after the next incremental heat treatment the peaks have gone from the spectrum of each polymer. The 121 ppm peak may not be from a nitrile carbon, for the i.r. nitrile band was no longer present (see *Figure 2*, and below). According to Usami *et al.*[21] the nitrile carbon shift moved from 122 to 153 ppm when the nitrile groups link in the cyclization process. Shifts at ~152 ppm from the non-protonated furan α carbons are present in the spectra of each of the low temperature polymers, and this process is thus obscured in the spectra of *Figures 8* and *9*, though apparently the nitrile shift vanished. In *Figure 10* the prominent nitrile signals of the lower two spectra are diminished in the third trace (250°C), as are the spinning sidebands, as the new peaks at 153, 137 and 110 ppm appear. A small broad hump at 70 ppm may indicate hydroxyl carbons forming on the main chain[22], the oxygen either having been released by the furfurol resin residues or coming from the trace present in the nitrogen. The latter idea is confirmed by the similarity of the carbon spectrum of the 250°C sample in *Figure 8* to that of a low oxygen content polymer that had been prepared in a nitrogen atmosphere[22]. As for Fochler *et al.*'s low oxygen polymer[22], the broad tail between 160 ppm and 180 ppm may represent a number of different carbonyl carbons formed either on the acrylonitrile residues by hydrolysis of the nitrile groups to acids or amides (though the sharp peak at 178 ppm from the amide group[5] is not seen), or in our copolymer such shifts could come from carbonyl carbons produced by a ring opening of the furans following a hydrolysis, in each case using water released by the step-growth reaction of the furfurol groups. Further heating at 350°C in nitrogen caused these latter features to vanish and enhanced the intensity of the signal at 138 ppm, that probably comes from backbone carbons in the olefinic form (either created by dehydrogenation, a loss of HCN[21] or a rearrangement of the unsaturation of the cycles[22], and caused the two peaks near 110 ppm to approach each other so that at 450°C they had merged. At 600°C the two remaining olefinic carbons have merged with the graphite peak, and the aliphatic carbons have gone.

For the copolymers richer in furfurol resins the peaks characteristic of the furan rings, the β carbons at ~109 ppm, and the non-protonated α carbons at 151 ppm survived the heat treatment in nitrogen until the temperature rose above 300°C, as seen in *Figures 8* and *9*. The peak observed at ~137 ppm in the acrylonitrile-rich copolymers of *Figure 10* was not prominent in the spectra of the samples derived from AS67A and AS132. The acrylonitrile residues of these polymers do not so readily lose hydrogen to become olefinic after the nitrile groups have linked together.

We now consider the upfield regions. In *Figures 8* and *9* a methylfuran methyl signal was seen at 14 ppm in the spectrum of the sample obtained at 300°C, presumably from the rearrangement of the ether or methylol methylenes, whose signals have just vanished, in which formaldehyde has been released and has reduced a methylol group. Such a reaction has been recognized in the study of the furfurol oligomers that found the methyl group of 2-furfuryl-5-methyl-furan[13]. The upfield carbon signals were not greatly affected until the temperature rose above 250°C, when there was an accretion between

40 ppm and 50 ppm, suggesting that the degree of branching at these carbons had increased. It was when examining the furfurol resins in this region that Chuang *et al.* found evidence of cross-links formed by the addition of a methylol group to a bridging methylene group[16]. It is likely that the extra degree of substitution that takes place when the cyclization process occurs has a similar effect on the shifts of carbons of the acrylonitrile residues. Further heating to 350°C in nitrogen caused these latter features to vanish and enhanced the intensity of the signal at 138 ppm, that probably comes from backbone carbons in the olefinic form (created by dehydrogenation, a loss of HCN[21] or a rearrangement of the unsaturation of the cycles[22]), and caused the two peaks near 110 ppm to approach each other so that at 450°C they had merged. At 600°C the two remaining olefinic carbons have merged with the graphite peak and the aliphatic carbons have gone.

The i.r. spectra of the copolymers did not provide such detailed insight into the chemical changes that occurred, for the bands have not been so well assigned. We have observed the temperatures at which certain identifiable groups vanish and have related this information, as far as is possible, to the processes found by the thermal studies. We have recognized that copolymer AS170, with 76 wt% acrylonitrile content, gives products that closely resemble the material obtained by heating polyacrylonitrile in an atmosphere containing little oxygen[22,23], whereas the two other copolymers behave differently. In *Figures 2*, *11* and *12*, the i.r. spectra of the samples used in the ^{13}C n.m.r. study have been placed in ascending order of temperature, to display the changes caused by the heating.

In each set of spectra the prominent PAN nitrile stretch vibration[14] at 2240 cm^{-1} showed until the temperature reached 200–250°C, where the cyclization process took place. For sample AS170 (76%AN) the new small band that formed at 2201 cm^{-1} had the sloping shoulder that has been associated with a nitrile group that is conjugated to a variable number of olefins[19,21]: evidently the presence of the furfurol residues, spaced on average ~12 residues apart, is insufficient to interfere with this process. The acrylonitrile CH_2 rock band at 1450 cm^{-1} similarly survived until the nitrile band disappeared. Also seen in *Figure 2* are N–H stretch bands at 3223 and 3381 cm^{-1} that represent new NH and NH_2 groups[22,23] formed by the reaction of the nitrile groups, perhaps through the rearrangement of the hydrogens on the cyclic structures[22]. (There were no amide groups, as the 178 ppm shift[6] was absent from the carbon spectrum.) The olefinic C–H stretch band at ~3120 cm^{-1} survived until 200°C was reached: this band may have two sources, the olefin groups of the type II residues created when the furan rings become entrained[4] and the side chain (unsubstituted) furan rings. The band seems to have gone by 250°C.

The spectra of the samples of the acrylonitrile-rich polymer heated to 250°C and higher for *Figure 2* resemble the low oxygen pyrolysis samples obtained from PAN by Fochler *et al.*[22] and Rafalko[23], having two peaks at 1611 and 1575 cm^{-1} that have been assigned to C=N and C=C stretches, respectively, and which merged on further heating. There is little evidence for the survival of the furfurol residues, as a direct comparison of the 100 and 250°C spectra indicates, the strong bands at 1710, 1069, 800 and 755 cm^{-1} having vanished and the band at 1015 barely surviving that temperature change. This confirms the view provided by the ^{13}C n.m.r. spectrum that the furfurol residues largely decomposed at the time of the cyclization process; it is apparent that the products of the thermal decomposition of furfurol-rich copolymers such as AS67A show only a broad range of bands, as if from a number of similar structures, so it is not possible to identify the products of the pyrolysis of the furan-derived components and to conclude whether these have formed in sample AS1700 too, or have simply vanished, being the most readily decomposed structures in the acrylonitrile-rich copolymer.

Thermal treatment of the 42% acrylonitrile polymer (AS135) caused little change on heating to 100°C, as seen in *Figure 11*, except for a rise in the intensity of the 1610 and 1559 cm^{-1} bands that reflected the minor changes in the olefinic residues also observed in *Figure 9* near 135 ppm. Heating at 200°C further enhanced the intensity of the peaks near 1600 cm^{-1}, as the initial weight loss feature of *Figure 3* and the exotherm and endotherm of *Figure 6* were passed. Further heating caused the nitrile group bands to vanish between 200°C and 300°C, but this time no N–H stretches were obtained. The bands identified with furan residues were all also modified in appearance, only one peak remaining above 1600 cm^{-1} and the C–O–C stretch bands in the region of 1000–1100 cm^{-1} barely surviving.

For the third copolymer examined, AS67a with 20% acrylonitrile residues, the i.r. spectrum hardly changed on heating to 185°C, but the acrylonitrile CN band did substantially alter below 300°C. Though the bands at 1711 and 1013 cm^{-1} were reduced in intensity, the main effect of heating to 300°C was merely a smoothing of the envelope. The C–H stretch band at 3120 cm^{-1} and the out-of-plane bending modes near 770 cm^{-1} survived, indicating the presence of intact furan rings, as the carbon spectrum of *Figure 8* also suggested. Once the temperature rose to the next value, the envelope showed fewer features but retained the same pattern.

CONCLUSIONS

Acrylonitrile may be copolymerized with the oligomers of furfuryl alcohol by the free radical method to obtain tractable powdery copolymers with a wide range of compositions. The point of attachment of the oligomer to the chain was generally the terminal furfuryl ring, according to spectroscopic studies. The copolymers thus contained intact furan rings linked to residues in which the furan had behaved as a diene.

As in PAN, the copolymers rich in acrylonitrile had a sharp exotherm above 250°C followed by a weight loss when heated in nitrogen or in air, that is associated with the cyclization reaction of the nitrile groups. Much more heat was evolved and the weight loss was more sudden and greater in extent in air than in nitrogen. As the weight fraction of furfurol residues increased, the exotherm became dispersed over a broader temperature range, a nitrogen atmosphere favouring this. In air the exotherm was succeeded by a second process that we associated with the furan content and became separate when the AN content fell below 50 wt%.

If the weight per cent acrylonitrile was $\geqslant 76\%$, the cyclization in nitrogen produced a material very similar, according to the ^{13}C CP/MAS n.m.r. and the i.r. spectra to the products obtained by others in a nitrogen atmosphere from PAN itself. The fate of the furfurol residues was not clear, as no features associated with them could be perceived.

We now consider the question of whether the copolymers rich in furfurol residues became cross-linked through reactions within the furfurol resin components upon heating. A weight loss certainly took place at ~135°C, just a little above the temperature at which the furfurol oligomers themselves cured, and baking the copolymers to 200°C removed that process from the copolymers. The furan rings and the nitrile groups apparently survived to higher temperatures than these. The minor changes that took place in the spectra (in the carbon spectra of *Figure 9* near 135 and 90 ppm, and in the i.r. spectra of *Figure 11* near 1600 cm^{-1}), were consistent with rearrangements of the furan residues that had been created by addition polymerization. The copolymers exhibited a minor endotherm peaking at ~135°C, with a maximum heat flow when the acrylonitrile residues were ~30 wt%, and also showed indications of a minor exotherm preceding it. As the weight loss at ~135°C was larger when the acrylonitrile fraction was 34% than when it was 20 or 42%, the weight loss and the endotherm are probably associated, but the chemical changes are not clear. The copolymer with 34% acrylonitrile units had its final combustion at a higher temperature than any other. Whatever caused these effects, they may be a separate process from a cross-linking cure, which would involve other parts of the furfurol residues and affect parts of the spectra that are obscured. The clearest indication of a cure is given by the changes to the 20% acrylonitrile polymer spectrum near 60 ppm on heating above 185°C, where it is apparent that ether and methylol groups have gone.

The furan rings survived the acrylonitrile cyclization reactions, according to the studies on the 42 and 20% acrylonitrile content copolymers, but decomposed in the environment of 400°C in nitrogen, when the aliphatic carbons also diminished. In air the cyclization was more prominent and the final combustion process took place at temperatures over 500°C. As the proportion of acrylonitrile residues in the copolymers decreased, so did the proportion of nitrogen in the residual material, which was mainly sp^2 hybridized carbon.

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