Copolymers of acrylonitrile with some furans and their Diels–Alder adducts

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Copolymers of acrylonitrile with furan, 2-methylfuran and with 2,5-dimethyl furan have been prepared by free radical copolymerizations, and their ^{13}C spectra examined for evidence of the three types of structure that formed, according to previous studies. We have characterized the Diels–Alder adducts of acrylonitrile with furan and with 2-methylfuran, and have found that they may also copolymerize with acrylonitrile by addition at their double bonds. The enchained adducts were most readily recognized in the ^{1}H spectrum by shifts at 4.8 and 4.6 ppm respectively from protons at the oxygen bridgehead. The ^{13}C spectra of these various polymers have been assigned with the aid of model compounds. Below $\delta = 60$ ppm the nitrile shift was dispersed over a larger range of shifts than is found in PAN itself, and was joined by the shifts of unsaturated carbon atoms and of carbon atoms linked to the oxygen atoms within these structures. Above 60 ppm the shifts of carbons in acrylonitrile units were found to be perturbed systematically from their normal places by the presence of neighbouring structures formed from the different furan-containing molecules. In both the ^{1}H and ^{13}C spectra shifts characteristic of the end groups from the AIBN initiator were noted. Fine structure in the spectra was attributed to monomer sequence effects and to the tactic structure of the polymer. Chiral centres appeared to be created from the furan rings at random, at least when protonated carbons were the site of initial attachment, but the mode of addition to the ring—whether *cis*, *trans* or both, was not certain. Assignments were made of bands in the i.r. spectra to modes of vibration of the units formed from the furan monomers.

INTRODUCTION

The furan ring has an aromatic–diene duality[1]. Of the 5-membered heterocycles it is the least aromatic in terms of resonance stabilization and shows the greater tendency to participate as a diene in Diels–Alder reactions. For a short period the capacity of the furan ring to function as a diene in a free-radical copolymerization was so doubted that it was suggested that the polymers that formed from mixtures of maleic anhydride and furan were produced by the homopolymerization of their Diels–Alder adduct[2], but it is now well established that the copolymers are 1:1 alternating copolymers[3]. In them, and in the similar copolymers produced by the free-radical copolymerization reaction with α-cyanomethacrylate[4] the predominant structure formed from the furan ring is that produced by 2,5-substitution. The formation of these copolymers of furan was doubtless promoted by the presence of two strongly electron-withdrawing groups in each comonomer. Perhaps through the formation of a charge-transfer complex they thus have the ability to overcome another characteristic feature noted for furan-containing molecules—their tendency to behave as retarders in radical polymerizations, and even to provide strong generalized inhibition[1].

We have indicated that the three types of structure were recognized by [1]H n.m.r. spectroscopy as being produced from furan rings during copolymerizations with acrylonitrile that had been initiated with azobisisobutyronitrile,

AIBN[5]. As acrylonitrile is capable of homopolymerization, the structures were spaced out along the chain by acrylonitrile units, the number of which depended upon the feed. Circumstantial evidence showed that the furan ring might participate twice in addition reactions to give type III structures by way of type II structures[5].
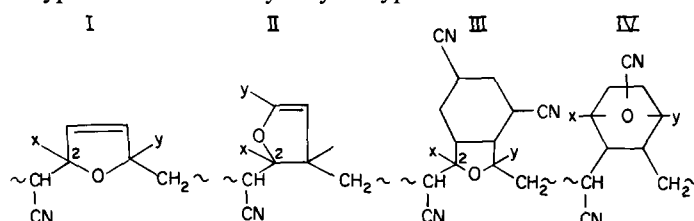

This case was supported by the observation that 2,3-dihydrofuran formed copolymers with acrylonitrile that had a higher 'furan' content and yield than did copolymers of the three furan ring monomers under similar conditions[6]. Moreover, ring-closure by attack on the C_4 site of the type II precursor of structure III would be promoted by the proximity of that site to the attacking radical, and by the stabilization induced in the resultant non-conjugated radical on C_5 by the adjacent electrowithdrawing oxygen atom at position 1.

We have prepared and characterized by n.m.r. spectroscopy the Diels–Alder adducts of furan and of methylfuran with acrylonitrile, (1) and (2), for two purposes: (a) to discover whether they can copolymerize with acrylonitrile, and how the presence of the resulting structures, IV, can be recognized and distinguished from structures of type I, II and III, and (b) for model compounds of

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structures of type I, with which to understand the fine structure in the ^{13}C n.m.r. spectra of the copolymers at low field. The ^{13}C shifts of the molecules (3) to (7) have been obtained for the same purpose. The ^{13}C spectrum of
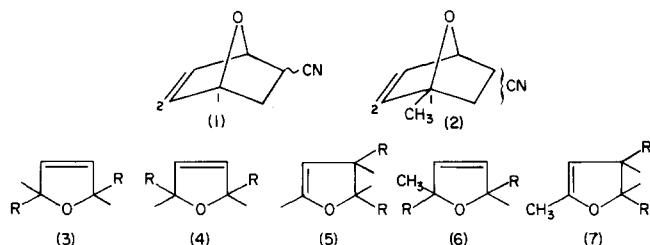
the copolymers has been examined, to show how the normal shifts of the repeat unit of acrylonitrile (CH_2 at 33 ppm and CH at 27.4 ppm) are modified by the proximity of a furan-derived unit. As the copolymers typically have low molecular weights, the shifts of the endgroups have also been identified. Finally we show infra-red spectra of the three copolymers.

EXPERIMENTAL

Preparation of model compounds

A mixture of the *exo* and *endo* Diels–Alder adducts of acrylonitrile and furan was prepared by standing an equimolar mixture at room temperature for three weeks. Unreacted material was removed on a rotavapour, and the pure *exo* adduct isolated by column chromatography. The pure endo adduct formed as a solid when the reactants were left at $-20°C$. A mixture of methylfuran adducts was similarly prepared, in which all four were almost equally present. After elution down a column, a second mixture with a clear order in composition was obtained, according to the ^{13}C spectrum.

Di-2-cyanopropyl adducts of furan and of 2-methylfuran were prepared as by Gandini[7]. Elution chromatography was used to provide fractions rich in each molecule, from which the ^{13}C spectra were obtained.

Preparation of polymers

Before use in polymerization reactions the furan-containing monomers were dried over calcium chloride, fractionally distilled under nitrogen, and stored over activated molecular sieves at $-20°C$ until required. The inhibitor was removed from commercial acrylonitrile before it was treated similarly. Polymers were prepared in thick-walled glass tubes from feeds of the comonomers, with AIBN as initiator, on occasions the solvents dimethyl formamide, ethylene carbonate or propylene car-

bonate being used as well. Oxygen was removed by at least two freeze–pump–thaw cycles before sealing off the tube, for otherwise oxygen inhibited the copolymerization. The initiator was decomposed by heat at 78°C or by u.v. irradiation. When two reactions were done simultaneously, to ensure each sample had an equal exposure they were rotated before the lamp in a special holder. Polymerization conditions typically used are given in *Table 1*.

Copolymers of high acrylonitrile content precipitated as they formed, unless a solvent was present, whereas those with a relatively high furan content remained soluble in the feed. To complete precipitation all products were poured into slightly-acidified methanol. Unreacted Diels–Alder adducts were removed from those copolymers by Soxlet extraction with methanol.

^{13}C spectra were obtained on a Bruker WM250 or a Varian SC-300 spectrometer, usually with 20% w/v solutions in dmso-d_6. In only one case, when a quaternary end-group shift was assigned, was the Nuclear Overhauser Enhancement suppressed. The composition of the copolymers, where reported, was obtained from the ^1H spectrum recorded on a Brucker WH90[5]. Infra-red spectra were recorded with a Perkin–Elmer 598 Spectrophotometer, using samples in KBr disks.

RESULTS AND DISCUSSION

The ^{13}C shifts of the Diels–Alder adducts

The *exo* and *endo* isomers of the furan adduct were distinguished using the coupling constants of the ^1H n.m.r. spectrum, J_{45} being 4.1 Hz in the *endo* form and $\leqslant 0.5$ Hz in the *exo* form. Such a small value was expected in view of the 80° dihedran angle between the C–H bonds of a model[9]. Following an off-resonance experiment, the ^{13}C spectrum of each isomer was straightforward to assign. As in PAN[10] the shift of the carbon in the methylene group was unaffected by a simple change in the configuration of the adjacent chiral centre. The pattern thus set helped with the assignment of the shifts of the four methylfuran adducts also entered in *Table 2*. The olefinic carbons suffered a γ_{CN} of about -4.3 ppm in the furan adducts, but in the methylfuran adducts this was altered, being only -2.4 ppm when the methyl group was β with respect to the CN, but rising to -6.5 ppm when the methyl group was γ with respect to the CN. Moreover changing the chiral centre from *exo* to *endo* caused γ olefins to move upfield by about 0.8 ppm and δ olefins to move downfield by about 0.4 ppm. When methylfuran adducts and furan adducts with the same stereochemistry were compared, the olefin shift suffered a β_{Me} effect of

Table 1 Typical copolymerization reactions of acrylonitrile

Furan molecule	Feed mole ratio F:AN	Volume (ml)	AZBN (g)	Time	Temp. (°C)	Yield (g)	Figure part
methyl furan	10:1	50	0.30	24 h	78	0.5	8(c)
methyl furan	3:1	50	0.30	1 h	78	4.0	3(b), 8(b)
methyl furan	1:3	50	0.30	10 min	78	1.1	8(a)
furan	1:2	41ᵃ	0.30	1 h	0	1.2	4, 5, 6(a)
furan	3:2	35ᵃ	0.31	30 min	78	2.5	4, 5(b)
furan	4.6:1	22ᵇ	0.014	17 h	78	0.29	4, 5(d)

ᵃ 7.6 ml of ethylene carbonate also added
ᵇ 10 ml of dimethylformamide also added

Table 2 Proton and carbon n.m.r. shifts of the acrylonitrile Diels–Alder adducts with furan and methyl furan (measured in $CDCl_3$ in ppm relative to TMS)

Molecule	Shift	Atom 1	2	3	4	5	6	Me	CN
(1) *exo*	C^{13}	77.99	137.32	133.68	81.30	27.43	31.46		122.38
	H^1	5.17	6.27	6.27	5.17	2.45	1.98 1.76[a]		
(1) *endo*	C^{13}	78.64	137.84	132.90	78.83	26.00	31.46		120.82
	H^1	5.15	6.46	6.46	5.15	2.87	2.19 1.43[a]		
(2) 6-*exo*[b]	C^{13}	86.87	136.84	138.05	78.02	34.52	32.33	16.27	120.74 [c]
(2) 6-*endo*	C^{13}	87.34	135.98	138.35	78.76	34.52	32.23	17.30	120.66
(2) 5-*exo*	C^{13}	86.26 [c]	140.16	134.34	81.47	30.17	37.37	17.82	122.40
(2) 5-*endo*	C^{13}	87.00	140.68	133.47	78.88	28.83	37.37	17.82	122.10

[a] endo hydrogen
[b] the nitrile group is in the 6-*exo* position
[c] the shifts above and below this might be exchanged

Table 3 Proton and carbon n.m.r. shifts of some di-2-cyanopropyl adducts of furan and methyl furan[a]

Molecule	Shift	Solvent	Position 2	3	4	5	2-Me
(3)	^1H	dmso-d_6	4.80	6.34			
	^{13}C		94.4	129.4			
	^{13}C	$CDCl_3$	91.9	129.5			
(4)	^1H	dmso-d_6	4.66	6.30			
	^{13}C	$CDCl_3$	90.2	129.8			
(5)	^1H	dmso-d_6	6.79	5.08	3.00	4.39	
	^{13}C	dmso-d_6	148.0	99.7	52.2	85.3	
	^{13}C	$CDCl_3$	148.4	98.9	53.5	86.2	
(6)	^1H	dmso-d_6		6.06	6.08	4.69	1.57
	^{13}C	$CDCl_3$	–	133.8	127.6	92.2	
(7)	^1H	$CDCl_3$		4.64	4.19	2.95	1.89
	^{13}C	$CDCl_3$	157.7	94.3	54.9	86.7	13.3

[a] The methyl groups of the 2-cyanopropyl group had proton shifts between 1.25 and 1.43 ppm, and carbon shifts of 22.1 to 24.0 ppm

+3.0 ppm, and a γ_{Me} effect of 0.6 ppm. When assignments of the nitrile carbon were unambiguous, the carbon had a lower shift in the *exo* form.

In the crude products obtained by decomposing AIBN in the presence of furan, the proportion of the isomers *trans*-2,5- (3): *cis*-2,5- (4): 2,5- (5) was approximately 2:1:2. The *cis* and *trans* isomers were assigned by analogy with phthalalan, where the protons of the carbons next to the oxygen absorbed at a lower field in the *trans* form[11]. The ^1H and ^{13}C shifts are entered in *Table 3*. In the 250 MHz spectrum we found only one 2,3-isomer of (5), in contrast to others[7]. In view of Batterhams's comments we did not utilise the value of $J_{23} = 3.6$ Hz in deducing the pattern of substitution[12]. However stereochemical considerations suggest that only *trans* addition is facile.

Features near $\delta = 1.3$ ppm in the ^1H spectra of the copolymers

A number of small sharp peaks were observed in the proton spectra of copolymers between 1.1 and 1.45 ppm in dmso-d_6, the region of the methyl groups of the 2-cyanopropyl end groups[7]. In the spectra of a series of homopolymers of acrylonitrile that had been prepared with a decreasing proportion of AIBN in the feed, peaks at 1.44 and 1.40 ppm were reduced in intensity by a factor of 2 relative to the area of the methylene and methine
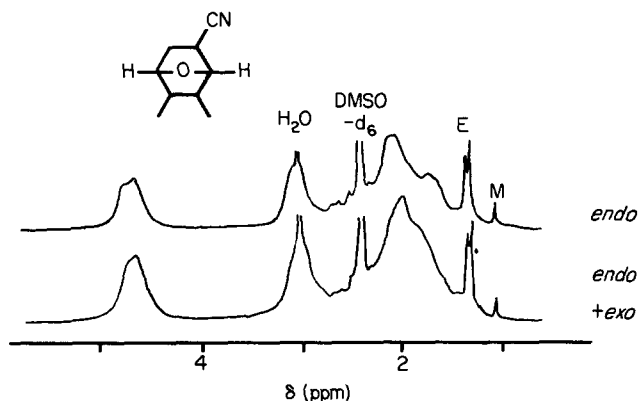

Figure 1 ^1H spectrum at 250 MHz of copolymers of acrylonitrile and the Diels–Alder adduct of furan, measured in dmso-d_6 at 70°C. The upper spectrum was from a polymer prepared with the pure *endo* adduct, but the lower spectrum was from a polymer prepared with a mixture of *exo* and *endo* adducts (see *Table 4*)

protons of the polymer, but the peak at 1.15 ppm was unaffected to within 5%. (The peaks are labelled E, for endgroup, and M in *Figure 1*.) The copolymer prepared from a feed rich in furan had extra peaks or shoulders at 1.26, 1.33 and 1.37 ppm that we assigned to the methyl groups of initiator radicals that had then become attached to furan molecules, in agreement with the shifts we

observed for the models (3), (4) and (5) in dmso-d_6. The peak at $\delta = 1.15$ ppm may have had its origin in a methyl group produced by the reverse addition of an acrylonitrile monomer followed by an H atom shift. Consistent with the suggested structure, ($\sim CH_2$–$CHCN$–$C(CH_3)CN$–CN_2–$CHCN \sim$) for which i.r. evidence has been advanced[8], was the absence of proton coupling, which, if present, would have been resolved, for the width at half height in one spectrum was only 5.7 Hz.

Copolymerization reactions of the Diels–Alder adducts

The possibility has been explored that the Diels–Alder adducts of furan and acrylonitrile might copolymerize. When acrylonitrile was heated at 78°C with AIBN and a mixture of *exo* and *endo* adducts, the polymeric product had a prominent ^1H peak at $\delta = 4.8$ ppm, from the bridgehead protons, X and Y of structure **IV**, together with traces of the low-field peaks that we have associated with 2,3- and 2,5- addition polymerization of furan[5]. This had been released by adduct dissociation, and then entrained in the chain with the adduct, whose olefin bond had entered into the free radical reaction. At 0°C and using u.v. light to decompose the AIBN, the copolymer thus prepared had only the peak at 4.8 ppm: in the time scale of that reaction (24 h) furan release had not occurred. To discover whether both *exo* and *endo* adducts might copolymerize, the pure *endo* adduct and a mixture of the two were separately copolymerized under the same conditions at 28°C (see *Table 4*). *Figure 1* shows that peaks at 4.8 ppm were present in the spectra of both copolymers. From the areas of these bridgehead protons and the area of the rest of the spectra, (omitting E and M), that had contributions from acrylonitrile units (3 protons) and the rest of the Diels–Alder adduct frame (5 protons), copolymer compositions were found to be independent of the ratio *exo*/*endo* of the feed. $\overline{DP}_n$, calculated using the areas of the end groups[5] and the yield were greater when the *endo* adduct was partially replaced by the *exo* adduct: the radical of the latter may not so readily participate in chain termination.

In the ^{13}C spectrum of the copolymer prepared from the pure *endo* adduct (*Figure 2*) the nitrile carbon shift at 120.3 ppm nearly coincided with the normal shift of that group in PAN (119.8 ppm), but the spectrum of the copolymer prepared from both adducts had an extra peak at 120.0 ppm, confirming the idea, produced by the small differences between the proton spectra of *Figure 1*, that the *exo* adduct did copolymerize. For the adducts themselves the nitrile carbon had a greater shift in the *exo* adduct than in the *endo* adduct. The oxygen-bridgehead carbons behaved similarly, a minor peak from the enchained *exo* adduct being seen at 80.8 ppm, downfield of the main peak at 78.8 ppm, and a minor peak at 76.7 ppm being associated with the *endo* adduct. In each case the

Table 4 Copolymerization of furan-acrylonitrile Diels–Alder adducts with acrylonitrile

Monomers	Feed (moles)	AZBN (g)	Yield (g)	$\overline{M}_n$	x_{DA}
AN Endo	0.077 0.109	1.52	1.52	3,700	0.32 ($\pm$0.02)
AN Endo (54%) Exo (46%)	0.077 0.115	1.51	2.12	5,500	0.30 ($\pm$0.02)

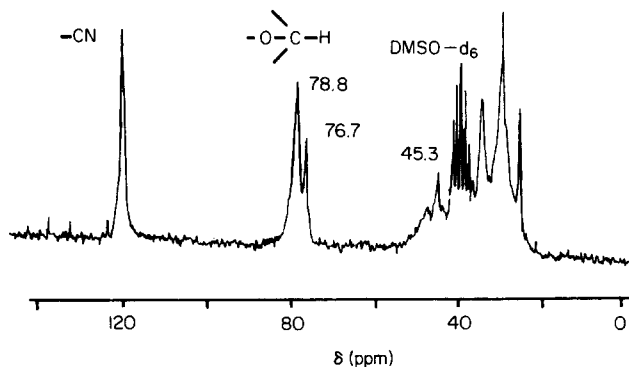**Figure 2** ^{13}C spectrum at 22.63 MHz of the copolymer of acrylonitrile with the pure *endo* Diels–Alder adduct, measured at 78°C in dmso-d_6: pulse width 11 μs, acquisition time 0.68 s, 10 000 scans, line broadening 1 Hz

Table 5 Proportion of structures derived from methylfuran in the acrylonitrile copolymers of *Figure 8*

Feed composition MeF:AN	Mole fractions of structures present				Figure 8 part
	x_F	I	II	III	
1:3	0.10	0.03	0.02	0.05	(a)
3:1	0.24	0.07	0.09	0.08	(b)
10:1	0.35	0.15	0.17	0.04	(c)

minor peak was probably from one carbon of one of a number of possible stereochemical forms. While the region above 60 ppm was too confused for analytical use, we note that the shifts between 40 and 50 ppm probably arose from highly-substituted carbon atoms such as those—formely olefinic—to which acrylonitrile units had become attached.

The copolymer prepared from a mixture of the Diels–Alder adducts of 2-methylfuran at 28°C showed an isolated proton shift at 4.6 ppm, that we associated with the single bridgehead proton of **IV** (X,Y = H,Me). Peak areas indicated a **IV** to acrylonitrile ratio of about 1:5. The four adducts may have reacted since three methyl peaks and a shoulder were seen at $\delta \simeq 1.5$ ppm. The spectrum of the copolymer prepared at 78°C showed evidence of structures **I**, **II** and **III** as well as **IV** (**I:III:IV** = 1:1:2), so again the adduct had dissociated at the elevated temperature. Acrylonitrile sequences predominated in this polymer chain: $x_{AN} \simeq 0.84$. The ^{13}C spectrum of this copolymer showed a shift at 49 ppm with a broad shoulder to 55 ppm that we attributed to carbons that had been C_2 and C_3 in the adduct (2).

Copolymer ^{13}C spectra at low field

As with the proton spectra of the copolymers of acrylonitrile with the furan molecules[5], the low field part of the ^{13}C spectrum was most readily understood. The most prominent feature in that part of the spectrum of the 2,5-dimethylfuran copolymer shown in *Figure 3a* was the triad pattern of the nitrile group in long acrylonitrile sequences. Between that and the small sharp peak at 124 ppm, from the carbon in the nitrile group of the initiator fragment, lay a multiplet ($\delta = 120.8$, 121.3, 121.6 and 121.9 ppm) that remained unaltered in an off-resonance experiment, and which we assigned to nitrile groups on carbon atoms attached directly to the furan structures **I** and the smaller proportion of **III**. The fine
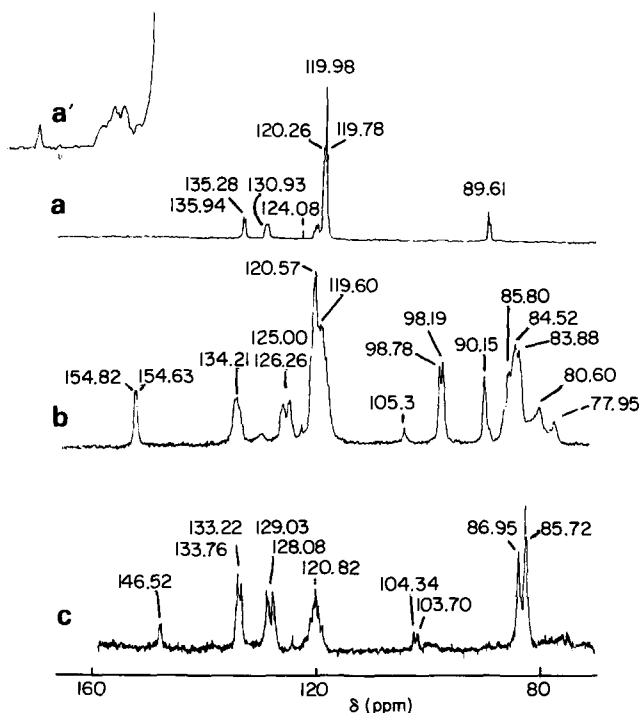
Figure 3 ^{13}C spectrum at 62.89 MHz of copolymers of acrylonitrile with (a) 2,5-dimethylfuran, (b) 2-methylfuran and (c) furan. The insert (a') shows an expansion of part (a) near 123 ppm. The upper spectra were measured in dmso-d_6 and the lower spectrum in acetone-d_6: pulse width 12 μs, acquisition time 0.67 s, line broadening 1 Hz (0.5 Hz for part (c)), number of scans 4627, 82 400 and 3040 respectively. The preparations of the polymers of parts (a) and (c) have been described, the latter from a 10:1 feed of furan to acrylonitrile[5]. The preparation of the copolymer of (b) is described here, and the fraction of units formed from the furan rings is given on the second line of *Table 5*

structure, shown expanded in *Figure 3a'* had a greater dispersion than that of the PAN homopolymer, which was attributed to the influence of the chirality of C_2 of I and III. There was little fine structure on the olefinic peaks C_3 and C_4 of I near 130 ppm nor on the quaternary carbon peak near 90 ppm from I. A broad featureless peak near 85 ppm in the spectra of copolymers containing a greater proportion of structure III is not detectable in the present spectrum. Occasionally spectra of other preparations of this copolymer contained small sharp peaks at 106.3 ppm and 149.7 ppm, that we attributed to atoms C_4 and C_5 of traces of structure II.

The furan copolymer, whose ^{13}C spectrum obtained in acetone-d_6 is given in *Figure 3c*, contained according to its ^{1}H spectrum in a 0.34 mole fraction of residues derived from furan[5], the major parts of this being in the form of type I units. Accordingly the pairs of peaks near 133 ppm and 129 ppm were assigned to the olefin carbons C_4 and C_5 of II. Near $\delta = 87$ ppm the two peaks were assigned to the oxygen bridgehead carbons of I, while upfield of this are traces of the bridgehead carbon shifts of the furan III structure.

In the spectrum of the methylfuran copolymer (*Figure 3b*) peaks below 95 ppm were similarly assigned: nitrile carbons at 120 ppm, the olefinic peaks of I(1) (X = H, Y = Me), C_3 and C_4 at 134 ppm, and the olefinic peaks of II(1)(X = H, Y = Me), C_4 and C_5 at 126 and 134 ppm. (The peak at 105.3 ppm, seen only in a few spectra we obtained of methylfuran copolymers, may have been C_4 in a type II(2) (X = Me, Y = H) structure, and was the only evidence found for this form.)

We identified two factors that influenced the shifts of C_3 and C_4 atoms in structures I of the three copolymers, when shifts in dmso-d_6 were compared: a γ_{CN} effect, on average -5.5 ppm, and a β_{Me} effect that was 3.7 ppm. (We have omitted a γ_{Me} effect, for the *gauche* conformation was not present.) With these parameters, whose values are similar to those obtained for the adducts (1) and (2) when the olefin shifts were considered, the olefin shifts of I(2) (X = Me, Y = H) were predicted from the shifts of I(1) to be C_3: 130.5 and C_4: 129.5 ppm. These were in good agreement with the shift of the small peak seen at 130 ppm. If both carbons contributed to that peak, then about 6% of the type I structures were the result of 2,5-addition to 2-methylfuran, a proportion sufficiently low for it to have been undetected in the proton spectrum[5]. That the shift of C_3 in II(1) of this copolymer was upfield of the furan-derived structure II was consistent with the negative β_{Me} effect noted for furan and 2-methylfuran[13].

Between 70 and 90 ppm the spectra of the furan and dimethylfuran copolymers did not show the strong multiple features that the methylfuran copolymer has in *Figure 3b*. According to the proton spectrum, this copolymer had a fraction of 0.24 units derived from the furan, in the rather similar proportions of 29:36:35, and with no clear evidence for IV. The peaks at 78 and 81 ppm, being absent from the spectrum of a copolymer lacking much structure III, were thus assigned to C_2 and C_5 of III respectively (X = H, Y = Me). Their broadness was ascribed to stereochemical variations in the upper ring of III. The height of the quaternary carbon peak at 90 ppm varied from one preparation to another with the other known II peaks, and thus was assigned to C_5 of II(1). The position of the three peaks marked near 84 ppm varied somewhat with the composition of the copolymer, so that the shifts of the carbons we assigned to this region, C_2 of I(1), were probably modified by the identity of neighbouring sequences.

The olefinic peaks we have assigned were resolved as doublets with splittings ranging from 0.2 to 1.0 ppm. This fine structure may have three possible origins: the mode of addition to the ring, which might be either *cis* or *trans*, the relative stereochemistries of the methine carbon atom of the acrylonitrile unit and the carbon of the furan unit to which it is bonded, and effects arising from the sequence of units. Furan copolymers of different compositions have been examined at 75 MHz, and the parts of their spectra shown in *Figure 4* were considered in terms of the following structures.
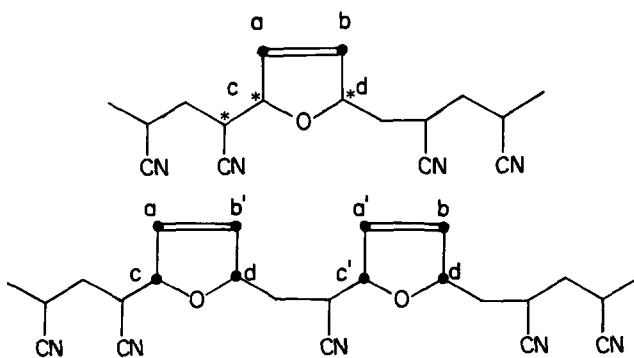
The a shifts were upfield of the b shifts by a margin of 5.1 ppm that was attributed to the α_{CN} effect. As the furan content rose, the four peaks (a_1, a_2, b_1, b_2) visible in the
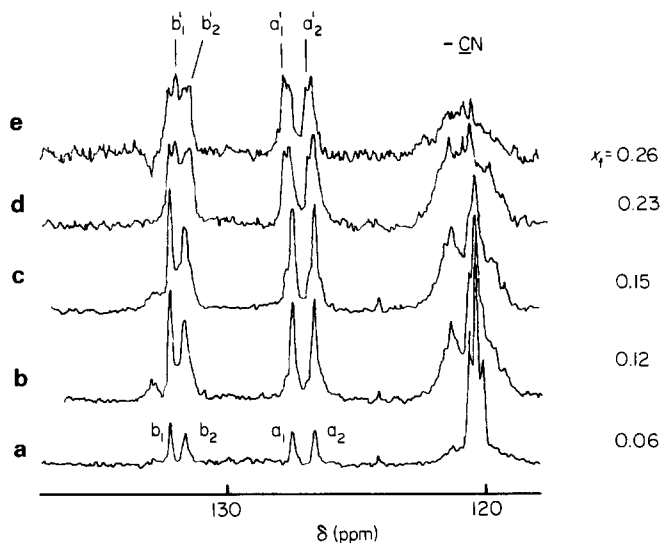
Figure 4 ^{13}C spectra at 75 MHz of a series of furan-acrylonitrile copolymers at low field. x_F, the mole fraction of structures derived from furan, was found from the proton spectra[5]. There is a small fold-over artefact to the left of the b peaks. Pulse width 7 or 11 μs, acquisition time 0.4 s, 1000 Hz window, about 16000 scans, time constant -0.1
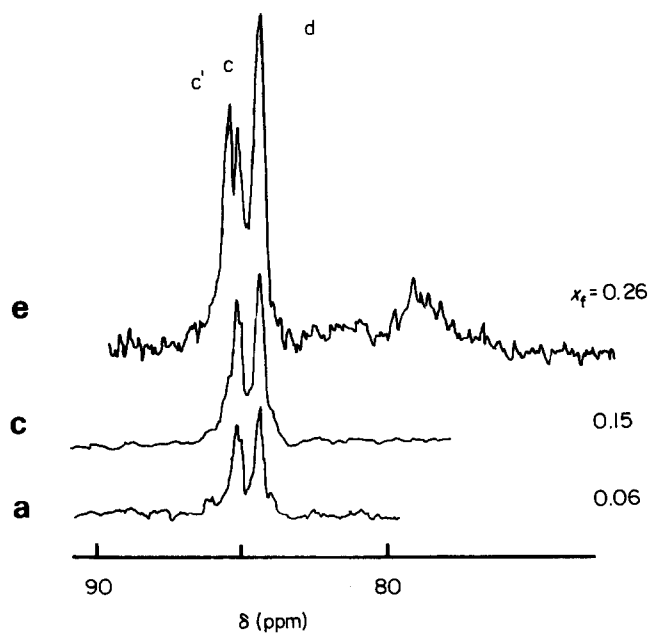

Figure 5 ^{13}C spectra of three furan–acrylonitrile copolymers near 85 ppm, showing the shifts of carbons linked to oxygen. The polymers were also used for *Figure 4*, to which the present labels correspond. Spectrometer settings as for *Figure 4*

lower spectrum and associated with an isolated I structure were joined by four more marked with primes in the upper spectrum, caused by the adjacent furan unit. While in the above scheme the perturbing unit, causing b' to differ from b is shown as a type I structure, type II or type III structures might well have the same effect: in each case a methine carbon would be at the position of the third atom along the chain. The oxygen bridgehead carbons of I showed a similar sequence effect near 85 ppm (*Figure 5*). The low-field peaks were assumed to be brought below the others by the β_{CN} effect.

High-field ^{13}C *spectra of the copolymers*

End groups and a possible side reaction. The furan copolymer whose ^{13}C spectrum is shown in *Figure 6a* had,

according to the ^{1}H spectrum, such a low degree of polymerization (~ 40) that the end groups and furan content ($x_F \sim 0.06$) were of similar proportions. The observation that the peak at $\delta = 31.2$ ppm was relatively higher in the absence of Nuclear Overhauser enhancement, and was thus quaternary, lead us to prepare a sample of PAN rich in end groups from AIBN. The spectrum of this had shifts at 26.1 and 25.3 ppm attributable to the terminal methyl and methine carbons, as well as the shift at 120 ppm of the terminal nitrile group. The shift of the terminal methylene carbon was predicted to be 43 ppm from the shift of the interior methylene of PAN by
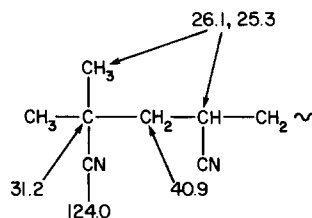
the addition of an iso β_{Me} factor ($+8$) and the subtraction of a γ_{CH} factor $(+2)^{14}$. The methylene shift observed at 40.9 ppm was assigned to this carbon. All the peaks thus associated with the end group were of lower intensity in *Figure 6b*, the spectrum of a copolymer of higher molecular weight ($\overline{DP}_n \sim 80$).

A methylene group peak was regularly seen in the spectra of copolymers and PAN itself at 14.3 ppm, its intensity being enhanced by the presence of a source of hydrogen atoms (such as a chain transfer agent). The structure shown to the right in *Figure 6* would be produced by H transfer to an acrylonitrile radical, and for the methylene group indicated, a shift of about 14 ppm can be predicted by modifying with a γ_{CH_2} the shift of the α-CH$_2$ group of glutaronitrile (16.3 ppm).

Furan copolymers at high field

Apart from the small number of shifts discussed in the previous section, this region contains the shifts of acrylonitrile units perturbed by adjacent structures derived from furan. In the unit below carbons are labelled α, β and γ
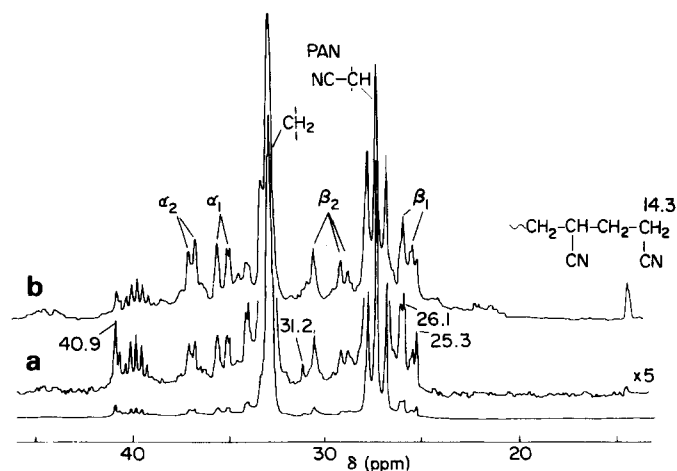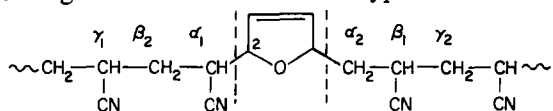

Figure 6 ^{13}C spectra of two furan–acrylonitrile copolymers at 75 MHz in the upfield region. The upper trace of part (a) had a vertical scale 5 × that of the lower trace: the polymer contained 6% of units derived from furan. The copolymer of part (b) had 15% of such units. Spectrometer settings as for *Figure 4*
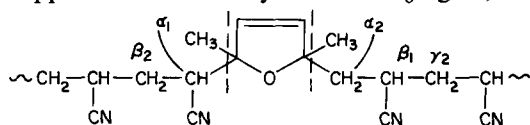
according to their distance from a type **I** structure,

$$\gamma_1 \quad \beta_2 \quad \alpha_1 \qquad \qquad \alpha_2 \quad \beta_1 \quad \gamma_2$$

~CH$_2$—CH—CH$_2$—CH$\overset{\text{O}}{\diagdown}$ CH$_2$—CH—CH$_2$—CH~
　　　|　　　　　|　　　　　　　　|　　　　|
　　　CN　　　　CN　　　　　　　CN　　　CN

and given subscripts according to the number of their hydrogen atoms. Taking the β_2 group as an example, from the right of the dashed line it suffers a β_{CH} effect from the C$_2$ of the furan unit, a γ_{CH} from C$_3$ and a γ_O from the oxygen, the sum of these shift effects being $+4$ ppm[14]. Had the chain continued instead with acrylonitrile units, β_2 would have experienced a β_{CH_2} and a γ_{CH} effect, the sum of which is $+8$ ppm. β_2 was thus predicted to occur at $33-8+4=29$ ppm. Similarly α_1, β_1 and α_2 were predicted to be at 37, 26 and 37 ppm respectively (γ effects from atoms across the ring were omitted because the bond in the ring did not have the *gauche* state.) Off-resonance experiments allowed the assignments indicated on *Figure 6* for α_1: 35.06, 35.20 and 35.72; α_2: 36.85 and 37.17; β_1: 25.50 and 25.90; and β_2 28.88, 29.25 and 30.66 ppm. Carbons γ with respect to the inserted unit would be less-influenced by its presence: the peak 0.4 ppm downfield of the shift of methylene carbons in normal PAN sequences may be γ_2. While these arguments have been conducted in terms of the isolated structure being of type **I**, the major form, for β carbons, at least, **II** and **III** structures would have similar effects. The minor peaks in the α region may have such an origin.

2,5-Dimethylfuran copolymers at high field

We have used the following scheme to aid assignments of the peaks shown at higher fields by this copolymer. Using the method adopted for the furan copolymer we predicted the following shifts: α_1 at 45 ppm, α_2 at 45 ppm, β_1 at 24 ppm and β_2 at 27 ppm. Experimentally-observed methylene group shifts at 42.8 and 29.6 ppm were assigned to α_2 and β_2 respectively. The other shift (α_1) expected near 45 ppm was obscured by the dmso-d$_6$ signal, but in a

$$\alpha_1 \quad CH_3 \qquad \qquad CH_3 \quad \alpha_2$$
$$\beta_2 \qquad \qquad \qquad \beta_1 \quad \gamma_2$$

~CH$_2$—CH—CH$_2$—CH$\overset{\text{O}}{\diagdown}$ CH$_2$—CH—CH$_2$—CH~
　　　|　　　　|　　　　　　　|　　　　|
　　　CN　　　CN　　　　　　CN　　　CN

spectrum run in D$_2$O/ZnCl$_2$ solution peaks assigned to α_1 were seen 0.8 to 1.8 ppm upfield of the α_2 peak (see insert to *Figure 7*). Methyl shifts of **I** were identified at 26.2 ppm by an off-resonance experiment in the spectrum of another copolymer much richer in furan units. The remaining peaks near 25 ppm were therefore attributed to β_1. Besides the minor peak at 31.3 ppm from the end group quaternary carbon the more prominent peak at 34.2 ppm was attributed to γ_2. If a trace of structure **II** was present in the copolymer, the methyl group on the C$_5$ atom had a sharp peak at 13.0 ppm.

We may attribute the dyad splitting of the β_1 shifts to the influence of the next CHCN chiral centre along the chain, but the α_1 case is more interesting, for we found that in D$_2$O/ZnCl$_2$ the triad splitting of the methine carbon in PAN and in these copolymers was not seen. Perhaps the presence of the three peaks for α_1 is the consequence of two types of chiral centre at C$_2$ and an extra factor, two types of chiral centre at C$_5$, i.e. *cis* and *trans* type **I** structures.

2-methyl furan copolymers at high field

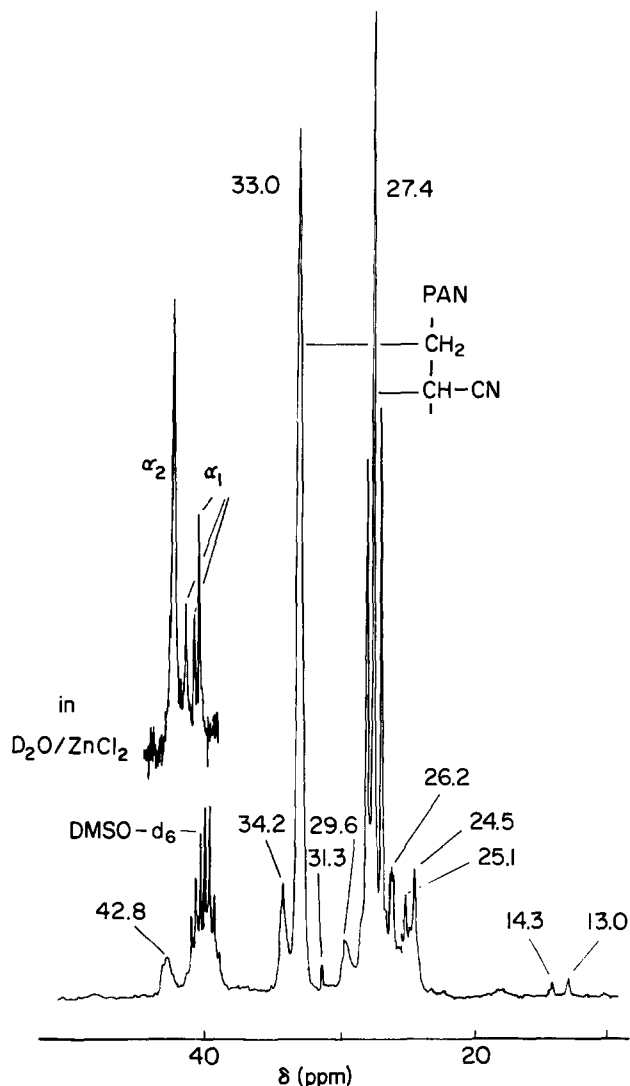The compositions of the three copolymers of 2-methyl-furan whose upfield spectra are shown in *Figure 8* are

Figure 7 ^{13}C spectrum at 63 MHz of a copolymer of 2,5-dimethylfuran with acrylonitrile ($x_F \simeq 0.09$, preparation in ref. 5). The insert to the left is on the same scale as the main spectrum, which was obtained at 70°C. This is part of the same spectrum as in *Figure 3a*

entered in *Table 5*. Since **I**, **II** and **III** types of structure were in similar proportions, and sequence effects were expected, such that an acrylonitrile unit between two furans would have different shifts from those of an acrylonitrile unit next to one furan structure, a complete assignment of the spectrum was not made. We first deal with shifts that we have associated with structures derived from the furan molecule.

In *Figure 8c*, the polymer of which was rich in **II** and lacked **III**, the methine doublet at 45 ppm was assigned to C$_3$ in **II**(1). Taking 2,3-dihydrofuran as a model, in which C$_4$ had a shift of 29.6 ppm, and allowing for the extra substitution encountered in the polymeric structure, C$_3$ in that should have a shift about 20 ppm further downfield. The methine shift at 47 ppm, in contrast, was less intense in *Figure 8c* relative to the other peaks nearby, and may be from a C$_3$ or C$_4$ in a structure **III**. In the spectrum of the copolymer of 2,3-dihydrofuran, C$_3$ in that ring had a shift of 46.4 ppm in support of this assignment. The methyl peaks of **I** and **II** were seen at 27.6 and 13.2 ppm respectively, the former being coincident with the methine carbons of long acrylonitrile sequences in parts (a) and (b) of *Figure 8*, but being clearly identified in the off resonance spectrum of the polymer of part (c).
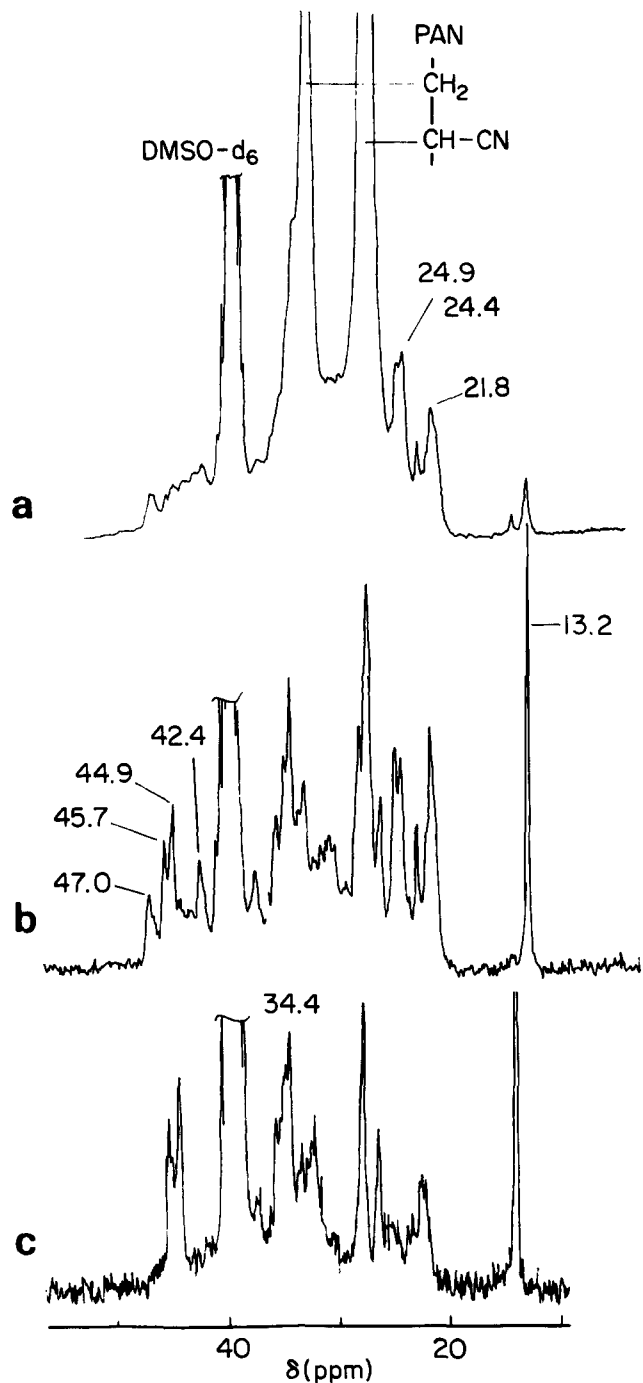
Figure 8 ^{13}C spectrum at 63 MHz of copolymers of 2-methylfuran with acrylonitrile at 70°C in dmso-d$_6$. Pulse width 12 µs, acquisition time 0.67 s, line broadening 1 Hz, number of scans 84 826, 82 400 and 4627 respectively. *Table 5* contains the compositions of these copolymers

Acrylonitrile units next to isolated type I structures in this copolymer were expected to have shifts close to certain of those seen in the two previous copolymers, as may be appreciated from the following scheme. Thus the
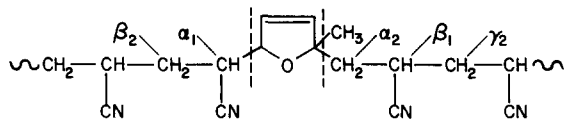
pair of peaks near 24.7 ppm were assigned to β_1, consistent with the assignment for the 2,5-dimethylfuran copolymer, where the β_1 carbon had a similar environment. The fall of the prominence of these shifts in *Figure 8c* was attributed to the lack of –F–AN–AN– sequences in

that copolymer. The peak at $\delta = 42.4$ ppm behaved similarly, and was associated with α_2. The probable presence of shifts from carbons in type **III** structures has made it difficult to recognize near 35 and 30 ppm the shifts of α_1 and β_2, which would be expected there, by analogy with the furan copolymer. In none of the spectra of *Figure 8* was found the broad peak at $\delta = 49$ ppm that was observed in the ^{13}C spectrum of the copolymer prepared with the methylfuran Diels–Alder adduct: probably none of the peaks could be attributed to iv.

The infra-red spectra of the copolymers

The i.r. spectra of copolymers of acrylonitrile with the three different furans are shown in *Figure 9*. An olefinic C–H stretch band was found at 3080 cm^{-1}, being particularly strong in the furan copolymers that contained a high proportion of type **II** structures, and a C–H stretch band was found at 2970 cm^{-1} in the copolymers known to contain methyl groups. Between 1600 and 1700 cm^{-1} occurred bands we assigned to C=C stretch: at 1670 cm^{-1} (**I**) and 1620 cm^{-1} (**II**) in the furan copolymers, and at 1680 cm^{-1} in the methylfuran copolymers (**I** and **II**). (Water sometimes intruded at 1630 cm^{-1}.) Below 1500 cm^{-1} we have marked with an asterisk a number of bands not seen in the spectrum of polyacrylonitrile, those between 1000 and 1100 cm^{-1} probably arising from C–O–C stretches.
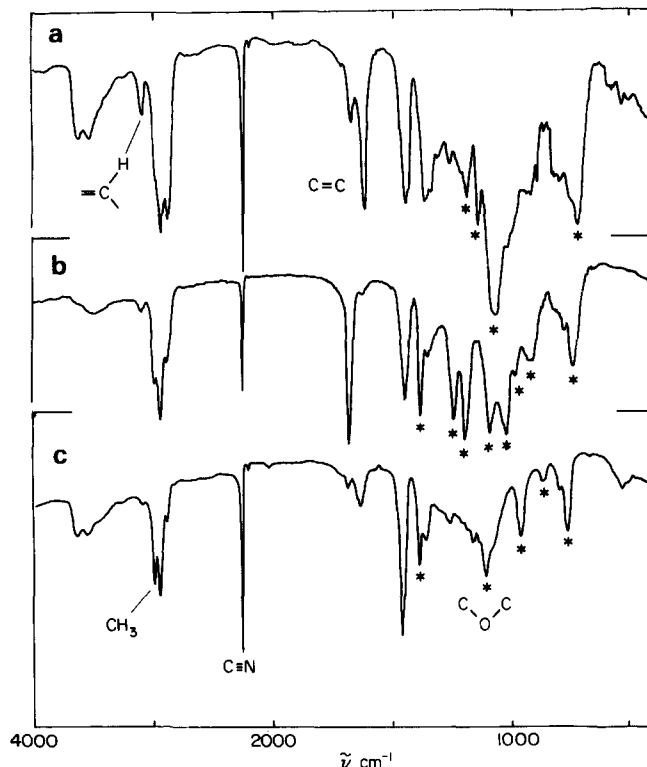
ACKNOWLEDGEMENTS

Figure 9 Infra-red spectra of copolymers of acrylonitrile with (a) furan, (b) 2-methylfuran and (c) 2,5-dimethylfuran. The copolymers had been prepared from feeds in the molar ratios, furan to acrylonitrile, of 10:1, 10:1 and 1:1 respectively

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