Free-radical aqueous slurry polymerizations of acrylonitrile: 2. End-groups and other minor structures in polyacrylonitriles initiated by potassium persulfate/sodium bisulfite

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Polyacrylonitriles prepared by aqueous free-radical slurry polymerization using the potassium persulfate/sodium bisulfite redox initiation system have been examined by *FT* i.r. and high-field ^{13}C and ^{1}H n.m.r. spectroscopy. They have been shown to contain predominantly sulfonate and non-sulfur containing end-groups derived principally from initiation by bisulfite radicals and transfer to the bisulfite ion. Some sulfate end-groups are present also, although in much smaller amounts than the sulfonate end-groups, and are believed to arise from initiation by sulfate radical anions. In these respects, the polymers resemble closely those made by using ammonium persulfate/sodium metabisulfite as the initiator system.

(Keywords: polyacrylonitrile; persulfate/bisulfite; end-groups)

INTRODUCTION

Industrially, large quantities of polyacrylonitrile are made by aqueous slurry polymerizations, initiated by various free-radical redox systems. In a previous paper[1], we have described the characterization, especially with regard to end-groups and other minor structures, of polyacrylonitriles initiated with ammonium persulfate and sodium metabisulfite, an important commercial initiating system. In this paper, we describe the similar characterization of polyacrylonitriles prepared using a variant of the above mentioned initiating system, namely potassium persulfate and sodium bisulfite.

As with the use of ammonium persulfate/sodium metabisulfite, we expect, on the basis of previous reports on similar systems[2-7], the initiation of the polymerization of acrylonitrile by potassium persulfate/sodium bisulfite to involve mainly attack by the bisulfite radicals, sulfate radical anions and hydroxyl radicals produced in reactions (1)–(3):

$$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^{\bullet -} + HSO_3^{\bullet} \quad (1)$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} \quad (2)$$

$$R^{\bullet} + H_2O \rightarrow R{-}H + HO^{\bullet} \quad (3)$$

Tsuda[8] has suggested that the sulfate radical anions formed in reactions (1) and (2) may react further with bisulfite ions to produce more bisulfite radicals:

$$SO_4^{\bullet -} + HSO_3^- \rightarrow SO_4^{2-} + HSO_3^{\bullet} \quad (4)$$

Reactions (1) and (4) are expected to dominate under the conditions normally used in commercial systems, i.e. with bisulfite in excess over persulfate and with a polymerization temperature of ~40°C, thus producing polymers with mainly sulfonate end-groups. For reasons given by us previously[1], the thermal decomposition of persulfate (reaction (2)) is likely to become important only at temperatures above 60°C. Transfer to water (reaction (3)), giving rise to hydroxyl end-groups, may need to be considered also and, in view of our findings for the ammonium persulfate/sodium metabisulfite initiator system[1], so too may chain transfer to bisulfite ion (reaction (5)), which could introduce extra sulfonate and non-sulfur containing end-groups.

$$\sim CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH^{\bullet}}} + HSO_3^- + H^+ \rightarrow \sim CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH_2}} + HSO_3^{\bullet} \quad (5)$$

The most important initiation steps in the polymerization of acrylonitrile with potassium persulfate/sodium bisulfite are therefore likely to be similar to those

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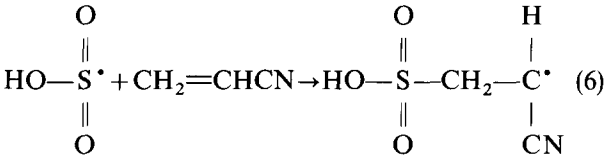
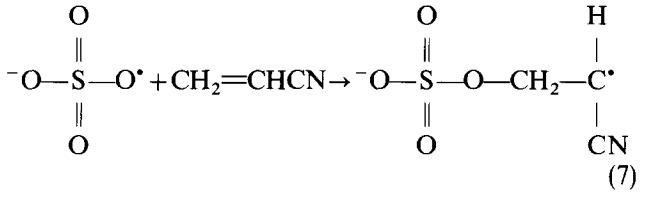
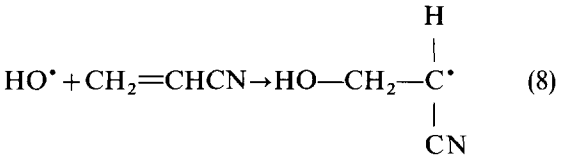
observed in the ammonium persulfate/sodium metabisulfite system, namely:



(6)



(7)



(8)

Reactions (6)–(8) would give rise to polyacrylonitrile chains with sulfonate, sulfate and hydroxyl end-groups, respectively. It is also possible for hydroxyl end-groups to arise from hydrolysis of the sulfate end-groups introduced through reaction (7), given the dilute aqueous conditions under which these polymerizations are performed.

EXPERIMENTAL

Materials

Acrylonitrile (Lancaster Synthesis) was freed from 4-methoxyphenol inhibitor by passing it down a column containing activated alumina, and was then distilled before use. Potassium persulfate and sodium bisulfite (Aldrich Chemical Co.) were used without further purification.

Polymerizations

Polyacrylonitrile samples were prepared by slurry polymerizations of acrylonitrile in water using potassium persulfate/sodium bisulfite as the redox initiator system. As in our previous work[1], it is necessary to consider here only the preparation of two such polymers: one with a relatively low molecular weight (polyacrylonitrile A) and one with a relatively high molecular weight (polyacrylonitrile B).

Polyacrylonitrile A was prepared as follows. To 195 ml of deionized water at 40°C, contained in a thermostated 1 l flange flask fitted with a reflux condenser, a nitrogen purge and a pH probe, were added 10 g of acrylonitrile. After a period of 15 min, 1.35 g of sodium bisulfite in 25 ml of water were added, followed, after a further 5 min, by 3.50 g of potassium persulfate in 100 ml of water. The mixture was then stirred under nitrogen at 40°C for 3 h. Polyacrylonitrile precipitated from the mixture as it was formed and was filtered off at the end of the reaction through a sintered glass disc. The recovered polymer was washed repeatedly with deionized water until the washings were neutral and was then dried *in vacuo* at room temperature for 4 days. The pH, measured at the completion of the polymerization, was 2. The yield of dried polymer was 84 wt%.

Polyacrylonitrile B was prepared in a similar way at 40°C over a period of 3 h, but this time by using 300 ml of water, 20 g of acrylonitrile, 0.56 g of sodium bisulfite, pre-dissolved in 10 ml of water, and 0.29 g of potassium persulfate, also pre-dissolved in 10 ml of water. The pH, measured at the completion of the polymerization, in this case was 5, and the yield of dried polymer was 71 wt%.

Molecular weights

Intrinsic viscosities of the polyacrylonitriles, $[\eta]$, were measured in DMF solutions at 30°C using an Ubbelhode viscometer. The $[\eta]$ values were converted to viscosity-average molecular weights, M_v, by using the Mark–Houwink–Sakurada equation and substituting K and a values of 0.0335 ml g^{-1} and 0.72, respectively[9].

Fourier transform infra-red (FTi.r.) spectroscopy

Infra-red (i.r.) spectra were recorded on finely ground dispersions of the polyacrylonitriles in spectroscopic grade KBr by using a Perkin-Elmer 1720-X *FT*i.r. spectrometer. The operating parameters were as follows: number of scans, 30; spectral resolution, 2 cm^{-1}; spectral range, 400–4000 cm^{-1}.

Nuclear magnetic resonance (n.m.r.) spectroscopy

High-field ^{13}C (100 MHz) n.m.r. spectra were recorded on 5–10 wt% solutions of the polyacrylonitriles in DMSO-d_6 on a Bruker WH400 spectrometer. Typical operating parameters used for obtaining the ^{13}C n.m.r. spectra were as follows: probe temperature, 27°C; spectral width, 25 kHz; pulse width, 10 μs; acquisition time, 0.66 s; number of acquisitions, 40 000; repetition delay, 0.8 s. A ^1H 2-dimensional phase-sensitive COSY spectrum was recorded on a Jeol GSX400 spectrometer using a probe temperature of 90°C, a spectral width of 2 kHz and with, typically, 64 acquisitions per t_1 increment. Apodization using a 30% offset sinbell-squared window function and careful choice of contour levels were used to optimize the sensitivity of the COSY technique and to highlight weak resonances. Also, some low-field ^{13}C (25 MHz) and ^1H (100 MHz) n.m.r. spectra were recorded on some model compounds, in order to investigate certain minor structures expected to occur in these polyacrylonitriles, by using a Jeol FX100 spectrometer.

RESULTS AND DISCUSSION

Polyacrylonitriles A and B were found, by dilute solution viscometry, to have viscosity-average molecular weights of 11 400 and 98 600, respectively.

The i.r. spectra of the polyacrylonitriles are shown in *Figures 1a* and *1b*. Both spectra contain, in addition to the expected major peaks associated with the acrylonitrile repeat units, minor peaks at 1654 and 1735 cm^{-1}. Similar peaks are also seen in the i.r. spectra of the polyacrylonitriles prepared by using ammonium persulfate/sodium metabisulfite and are assigned to C=O stretching vibrations in the acrylamide and acrylic acid units, respectively. Such 'anomalous' units may arise from the adventitious hydrolysis of nitrile groups during polymerization or polymer work-up, or from reactions initiated by sulfate end-groups[10]. Subtraction of the i.r. spectrum of polyacrylonitrile B from that of polyacrylonitrile A produces the difference spectrum shown in *Figure 2*, in which the peaks arising from the end-groups are amplified

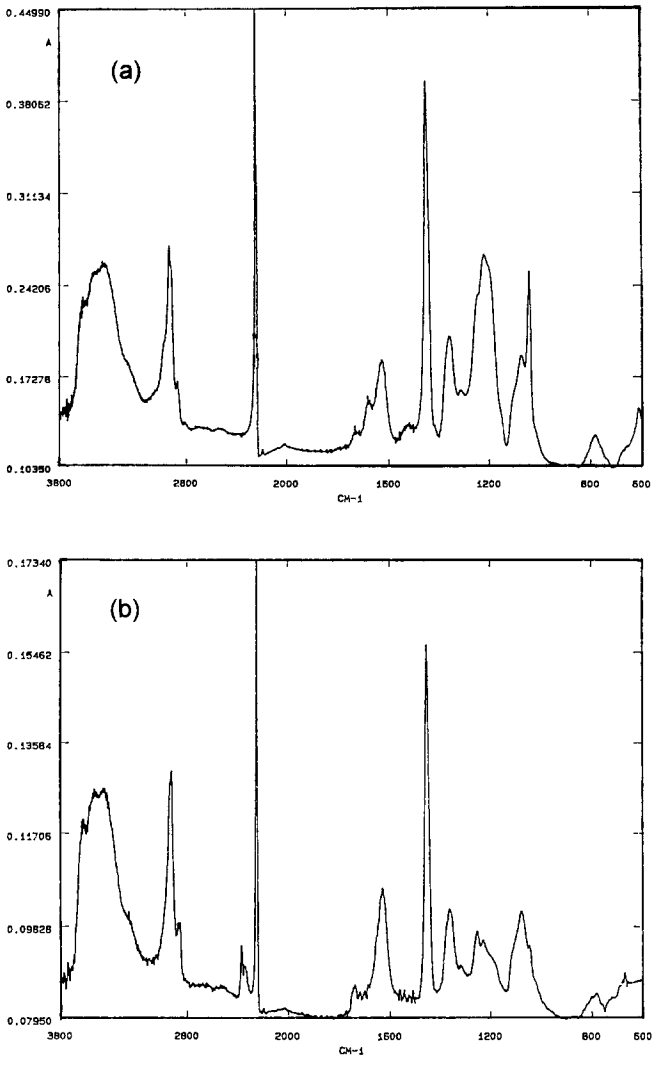
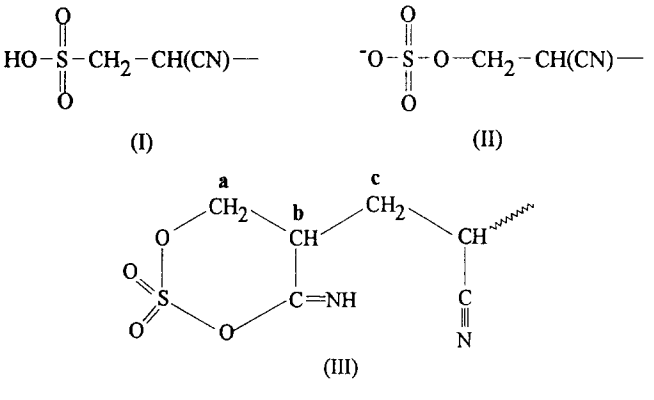


Figure 1 *FT*i.r. spectra of (a) polyacrylonitrile A ($M_v = 11\,400$) and (b) polyacrylonitrile B ($M_v = 98\,600$)

in comparison with the peaks from the repeat units. This difference spectrum is similar to that recorded for polymers prepared with ammonium persulfate/sodium metabisulfite and highlights the peaks at 1217 cm^{-1} (S=O asymm. str.), 1043 cm^{-1} (S=O symm. str.), 612 cm^{-1} (C—S str.), 560 cm^{-1} (S=O symm. def.) and 520 cm^{-1} (S=O asymm. def.), associated with the sulfonate end-groups. It is to be noted that, despite the use of equal molar concentrations of persulfate and bisulfite in the preparation of polymer A, no peaks characteristic of sulfate end-groups are to be seen, i.e. it would appear that the dominant sulfur-containing end-groups in the polyacrylonitriles are sulfonate end-groups, indicating the predominance of reaction (6) among the possible initiation steps. However, as we have seen before, the absence of peaks characteristic of sulfate end-groups in the i.r. spectra does not necessarily mean that such end-groups are absent, merely that they are relatively few in number[1]. The negative peaks in the difference spectrum at ~3500 and 2300 cm^{-1}, and the positive peak at 1650 cm^{-1}, arise from water, atmospheric CO_2 and the carbonyl groups of acrylamide units, respectively. The first two are evident because of the different moisture contents of the two samples and because of different efficiencies of purging of the sample compartment in the two infra-red experiments. The last is evident because sample A contains more adventitiously hydrolysed repeat units than sample B, presumably because the lower pH during the preparation of A encouraged greater acid hydrolysis.

The COSY n.m.r. spectrum of polymer A (*Figure 3*) shows, in addition to the expected dominant methylene and methine proton resonances centred at ~2.1 and 3.1 ppm, respectively, a cross-peak (A) connecting minor resonances at 3.2 and 2.8 ppm. The former of these is assigned to the methylene protons of the sulfonate end-group (I) and the latter to the adjacent methine proton of the same end-group. The COSY spectrum also shows cross-peaks (B) connecting small peaks on the diagonal at 3.7 and 3.0 ppm, which we assign to the methylene and methine protons, respectively, of the sulfate end-groups (II). These peaks all lie, within experimental error, at the same chemical shifts as similar small peaks in the COSY n.m.r. spectrum of a polyacrylonitrile made with ammonium persulfate/sodium metabisulfite, and the assignments are supported by the chemical shifts in the ^1H n.m.r. spectra recorded on the model compounds sodium sulfopropionitrile, sodium 1-hexadecane sulfonate and sodium n-hexadecyl sulfate[1]. There are further cross-peaks (C and D) connecting weak resonances at 4.0, 3.15 and 2.1 ppm. Assignment of these is more tentative, but we suggest that they arise from the methylene (a), methine (b) and methylene (c) protons, respectively, in the cyclic sulfate ester (III) formed by the nucleophilic addition of a sulfate end-group on an adjacent nitrile group during or after polymerization.



The relative intensities of the cross-peaks and the peaks on the diagonal that they connect confirm the predominance of the sulfonate end-group (I) over the sulfate end-groups (II and III) and account for the absence of any signals from the sulfate end-groups in the i.r. spectra. A similar situation was observed with the polyacrylonitriles made with the ammonium persulfate/sodium bisulfite redox initiator system[1]. Further evidence for the sulfonate end-groups is seen in the ^{13}C n.m.r. spectrum of polymer A (*Figure 4*) which contains a weak signal at 51.2 ppm, which we assign to the methylene carbon adjacent to the sulfonate group[1]. Resonances from the corresponding methylene group of the sulfate end-group (II), if present, are unfortunately probably hidden by a small solvent impurity signal at 65 ppm.

The sulfonate end-groups arise as a consequence of attack on the monomer (reaction (6)) by the bisulfite radicals formed in reactions (1), (4) and (5). The transfer reaction (reaction (5)), if significant, should also lead to the production of non-sulfur containing end-groups.

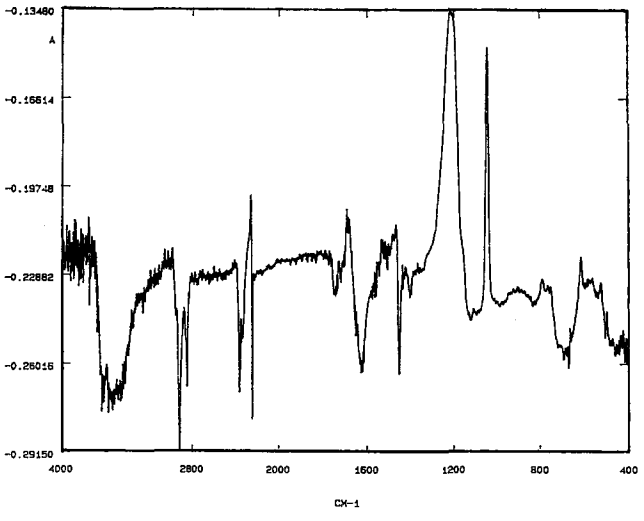


Figure 2 *FT*i.r. difference spectrum, obtained after subtraction of the spectrum of polyacrylonitrile B from that of polyacrylonitrile A

Evidence for such end-groups is seen in the small cross-peaks (E) connecting the resonances at 2.65 and 2.0 ppm in the COSY spectrum shown in *Figure 3*. These are assigned to the methylene protons d and e, respectively, in structure (IV). The presence of this end-group is supported also by the appearance of a peak at 14.3 ppm in the ^{13}C n.m.r. spectrum of the polymer (see *Figure 4*) which we have assigned to the methylene carbon d. The calculated chemical shift for this particular carbon, based upon published additivity parameters[11], is 12.7 ppm. The adjacent methylene carbon, e, has a calculated chemical shift, using the same additivity parameters, of 25.1 ppm, which puts it too close to the main-chain methylene resonances between 26.5 and 29.5 ppm to be clearly distinguished. Neither ^{13}C nor COSY n.m.r. spectroscopy provides evidence for the presence of hydroxyl end-groups, in contrast to the polyacrylonitriles made with ammonium persulfate/sodium metabisulfite, in which low concentrations of such end-groups were evident. It is not clear why there should

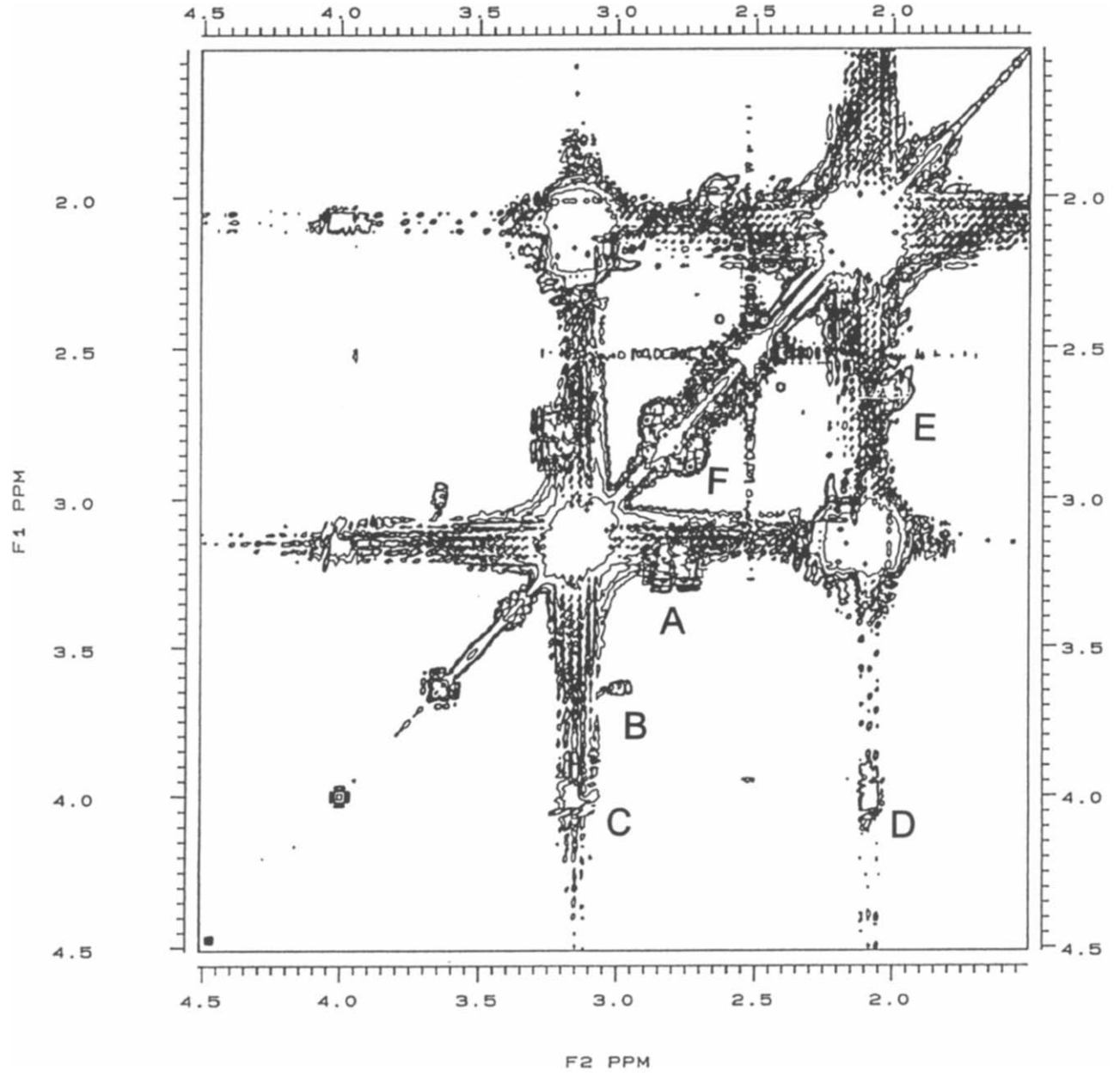


Figure 3 COSY ^{1}H n.m.r. spectrum of polyacrylonitrile A (see text for significance of the cross-peaks labelled A–F)

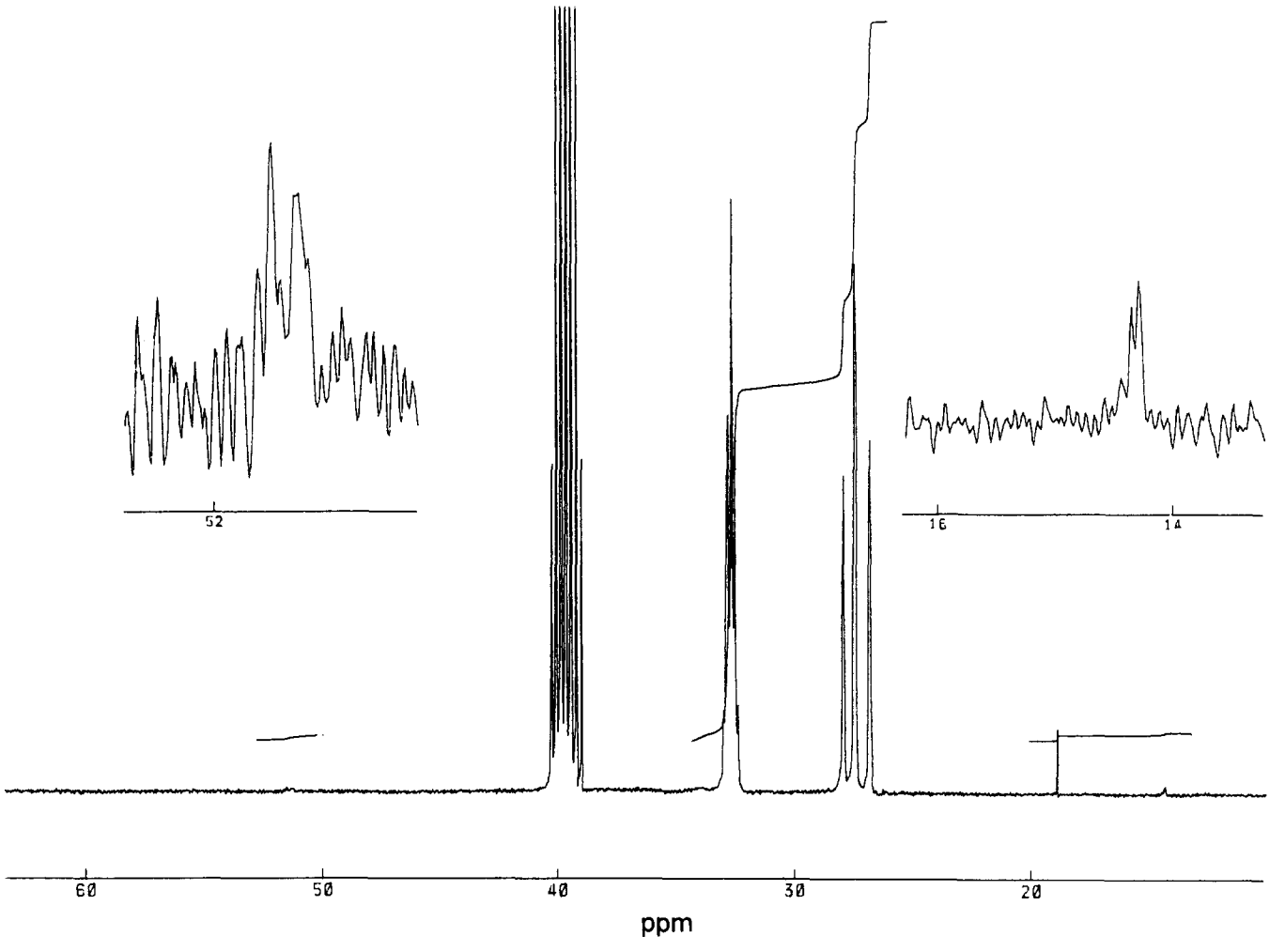
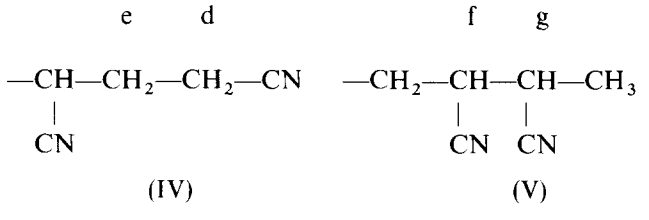


Figure 4 ^{13}C n.m.r. spectrum of polyacrylonitrile A, where the insets show expansions of the minor signals at 51.2 and 14.3 ppm

be this difference between these two, otherwise very similar, systems.

Finally, in the COSY n.m.r. spectrum (*Figure 3*) a small cross-peak (F) can be seen connecting the resonances at 2.85 and 2.75 ppm. These particular signals, we suggest, might arise from the methine protons (f and g) of an end-group (V) formed by head-to-head addition followed by an immediate transfer step. There is no evidence for significant regio-irregularity (head-to-head and tail-to-tail links) in polyacrylonitriles made by radical polymerization and it seems reasonable to suppose that the highly reactive methylene radical formed by head-to-head addition would be likely to react with the nearest hydrogen atom donor (solvent or monomer) before it has a chance to propagate in the normal way.



Note, however, that these latter assignments are, at this stage, very tentative since the end-group, V, would be expected also to give rise to methine carbon signals at ~21.2 and 18.8 ppm (f and g, respectively) and to a methyl carbon signal at ~11.7 ppm[11], and no signals from the polymer are visible at, or near, these chemical shifts in the ^{13}C n.m.r. spectrum (*Figure 4*).

CONCLUSIONS

The combined application of *FT*i.r. and high-field ^{13}C and COSY ^{1}H n.m.r. spectroscopy has highlighted the presence, in polyacrylonitriles made by aqueous slurry polymerizations initiated by potassium persulfate/sodium bisulfite, of mainly sulfonate and non-sulfur containing end-groups arising from the initiation of polymerization by the bisulfite radical, and termination by transfer, probably mainly to the bisulfite ion. In addition, however, there are small numbers of sulfate end-groups and possibly also cyclic sulfate ester and methyl end-groups, with the former arising from the attack of a sulfate end-group upon an adjacent pendent nitrile group and the latter arising from the head-to-head addition of the monomer to a growing radical, followed by immediate transfer. The polymers also contain small quantities of acrylamide and acrylic acid units formed by adventitious hydrolysis of nitrile groups during formation and/or work-up of the polymer. In all important respects, polyacrylonitriles made by using the potassium persulfate/sodium bisulfite redox initiation system resemble, in respect of their end-groups and other minor structural irregularities, the polyacrylonitriles initiated with the ammonium persulfate/sodium metabisulfite system.

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REFERENCES

1 Ebdon, J. R., Hunter, T. C. and Huckerby, T. N. *Polymer* 1994, **35**, 250
2 Kolthoff, I. M. and Miller, I. K. *J. Am. Chem. Soc.* 1951, **73**, 3055
3 Sworski, T. J. *J. Am. Chem. Soc.* 1956, **78**, 1768
4 Peebles Jr, L. H., Thompson, Jr, R. B., Kirby, J. R. and Gibson, M. E. *J. Appl. Polym. Sci.* 1972, **16**, 3341
5 Peebles Jr, L. H. *J. Appl. Polym. Sci.* 1972, **17**, 113
6 Wilmarth, W. K., Schwartz, N. and Giuliano, C. R. *Coord. Chem. Rev.* 1983, **51**, 243
7 Sarkar, S., Adhikari, M. S., Banerjee, M. and Konar, R. S. *J. Appl. Polym. Sci.* 1988, **36**, 1865
8 Tsuda, Y. *J. Polym. Sci.* 1961, **5**, 104
9 Shibukawa, T., Sone, M., Uchida, A. and Iwahari K. *J. Polym. Sci. A-1* 1968, **6**, 147
10 Ebdon, J. R. and Hunter, T. C. unpublished results
11 Brown, D. W., Floyd, A. J. and Sainsbury, M. 'Organic Spectroscopy', Wiley, Chichester, 1988, Ch. 4, pp. 98–100