Free-radical aqueous slurry polymerizations of acrylonitrile: 1. End-groups and other minor structures in polyacrylonitriles initiated by ammonium persulfate/sodium metabisulfite

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Polyacrylonitriles prepared by aqueous free-radical slurry polymerization at 40°C using ammonium persulfate and sodium metabisulfite as redox initiator have been examined by *FT*i.r. and by high-field ^{13}C and ^{1}H n.m.r. They have been shown to contain small quantities of acrylamide and acrylic acid units and to possess predominantly sulfonate and non-sulfur containing end-groups derived principally from transfer to bisulfite ion during the polymerization. Other end-groups present in low concentration are sulfate and hydroxyl; the former probably arises from initiation by sulfate radical anions and the latter either from transfer to water or by adventitious hydrolysis of some of the sulfate end-groups. Because they contain few groups capable of initiating intramolecular cyclization, the polyacrylonitriles are white with no sign of discoloration.

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

INTRODUCTION

Polyacrylonitrile is an important polymer used widely in the manufacture of synthetic fibres, particularly for applications in apparel. Commercially, polyacrylonitrile is produced by radical polymerization, much of it in aqueous slurry processes using various water-soluble free-radical initiators. For applications as fibres, polyacrylonitrile should initially be free of colour, a state which can be difficult to achieve given the well-known propensity for the pendent nitrile groups within the polymer to undergo intramolecular cyclization leading to conjugated imine sequences capable of absorbing visible light. Such cyclizations can be initiated by traces of base and other nucleophiles, some of which may be present in the polymer chain as end-groups, or which may have arisen within the polymer chains as a result of adventitious chemical reactions involving some of the repeat units[1].

As part of a programme to correlate the ease of colour formation in polyacrylonitriles with the conditions used in their manufacture, we have examined closely the microstructures of polyacrylonitriles prepared using various water-soluble thermal and redox initiators, concentrating particularly on minor structures. In this paper, we report the results of a study of such structures in polyacrylonitriles prepared by aqueous slurry polymerizations using ammonium persulfate/sodium metabisulfite as a free-radical redox initiator.

On the basis of various reports in the literature relating to similar systems[2–8], we expect the initiation of polymerization by ammonium persulfate/sodium metabisulfite in water to involve bisulfite radicals, sulfate radical anions and hydroxyl radicals, which are formed as shown in reactions (1)–(4):

$$S_2O_5^{2-} + H_2O \rightarrow 2HSO_3^- \qquad (1)$$

$$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^{\bullet\,-} + HSO_3^{\bullet} \qquad (2)$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet\,-} \qquad (3)$$

$$R^{\bullet} + H_2O \rightarrow R{-}H + HO^{\bullet} \qquad (4)$$

Reaction (2) is expected to be the dominant radical-producing reaction at ~40°C (the temperature at which the ammonium persulfate/sodium metabisulfite redox couple is normally used). The thermal decomposition of persulfate ion (see reaction (3)) is expected to only contribute significantly at higher temperatures; even at 60°C, published rate constants[9,10] indicate a half-life for potassium persulfate of 60 h or more. Reaction (4) (in which $R^{\bullet}$ could represent either of the radicals produced in reaction (2)) seems a likely contributor given the large quantity of water present in aqueous slurry systems, although the chain transfer constant for water has been reported to be very low, especially in radical polymerizations of acrylic monomers[11–13]. The dominant initiation reactions in the polymerization of acrylonitrile with ammonium persulfate/sodium metabisulfite are

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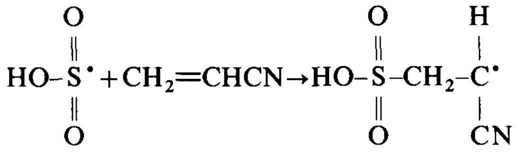
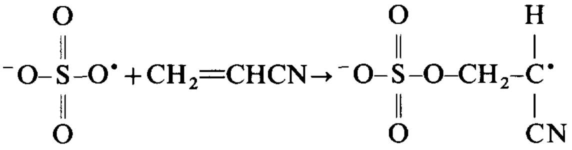
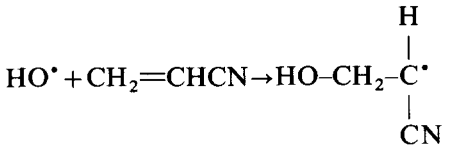
therefore likely to be:



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{}^{\bullet}+CH_2{=}CHCN\rightarrow HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}\underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}{}^{\bullet}} \qquad (5)$$



$$\mathrm{{}^{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O^{\bullet}+CH_2{=}CHCN\rightarrow {}^{-}O{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O{-}CH_2{-}\underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}{}^{\bullet}} \qquad (6)$$



$$\mathrm{HO^{\bullet}+CH_2{=}CHCN\rightarrow HO{-}CH_2{-}\underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}{}^{\bullet}} \qquad (7)$$

Reactions (5)–(7) would give rise to polyacrylonitrile chains with sulfonate, sulfate, and hydroxyl end-groups, respectively.

However, another reaction expected to be of significance in this system and likely to influence the types and distribution of end-groups in the polymers is chain transfer to bisulfite ion (reaction (8)), leading to additional sulfonate end-groups (see reaction (5)) and also to non-sulfur containing end-groups[5,14–16].

$$\mathrm{{-}CH_2{-}\underset{\underset{CN}{|}}{CH^{\bullet}}+HSO_3^{-}+H^{+}\rightarrow{-}CH_2{-}\underset{\underset{CN}{|}}{CH_2}+HSO_3^{\bullet}} \qquad (8)$$

This reaction is expected to be particularly important in our work since we have used an excess of metabisulfite over persulfate in the preparation of the polymers. Molar ratios of bisulfite to persulfate of greater than one are routinely used in commercial aqueous slurry polymerizations of acrylonitrile, not only to remove possible oxidizing impurities and to prevent unwanted oxidation of the polymer, but also to control the molecular weight of the product.

EXPERIMENTAL

Materials

Acrylonitrile (Lancaster Synthesis) was freed from 4-methoxyphenol inhibitor by passing it down a glass column containing activated alumina, and was then distilled before use. Ammonium persulfate and sodium metabisulfite were both obtained from the Aldrich Chemical Company and were used without further purification.

Polymerizations

Polyacrylonitrile samples were prepared by slurry polymerizations of acrylonitrile in water at 40°C, using ammonium persulfate and sodium metabisulfite as the redox initiator system, with the latter (reducing) component always in excess. For present purposes, it is sufficient to consider only the preparation of two such polymers, namely A and B, both made with relatively high initiator concentrations and therefore having relatively low average molecular weights. Sample A was prepared as follows.

To 300 ml of deionized water at 40°C, contained in a thermostated 1 l resin kettle fitted with a reflux condenser, a nitrogen purge and a pH probe, were added 10 g of acrylonitrile. After a period of 10 min, 1.65 g of sodium metabisulfite in 25 ml of water were added, followed, after a further 5 min, by 0.34 g of ammonium persulfate in 25 ml of water. The mixture was then stirred under nitrogen at 40°C for 50 min. 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 yield of dry polymer was ~40 wt%.

Sample B was prepared at 40°C in a similar manner but this time by using 250 ml of water, 13.9 g of acrylonitrile, 1.44 g of sodium metabisulfite in 25 ml of water, 0.38 g of ammonium persulfate, also in 25 ml of water, and a reaction time of 80 min. The yield was also ~40 wt%. The pH throughout both reactions had a constant value of 5.

Molecular weights

Intrinsic viscosities of the polyacrylonitriles, $[\eta]$, were measured on DMF solutions at 30°C using an Ubbelhode viscometer. The $[\eta]$ values were converted to viscosity-average molecular weights, M_v, using the Mark–Houwink-Sakurada equation and substituting K and a values of 0.335 ml g^{-1} and 0.72, respectively[17].

Fourier transform infra-red (FT*i.r.*) *spectroscopy*

*FT*i.r. spectra were recorded on finely ground dispersions of the polyacrylonitriles in spectroscopic grade KBr by using a Perkin-Elmer 1720-X *FT* 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) and ^{1}H (400 MHz) n.m.r. spectra were recorded on 5–10 wt% solutions of the polyacrylonitriles in DMSO-d$_6$ using a Bruker WH400 spectrometer. The typical recording conditions that were used for obtaining the ^{13}C n.m.r. spectra were as follows: temperature, 27°C; spectral width, 25 kHz; pulse width, 10 μs; acquisition time, 0.66 s; number of acquisitions, 40 000 and; repetition delay, 0.8 s. The typical conditions that were used for obtaining the corresponding ^{1}H spectra were as follows: temperature, 21°C; spectral width, 3.5 kHz; pulse width, 4 μs; acquisition time, 4.7 s; number of acquisitions, 256 and; repetition delay, 1 s. A ^{1}H 2-dimensional phase-sensitive DQF-COSY spectrum was recorded on a Jeol GSX400 spectrometer under conditions similar to those used for the 1-dimensional spectra, except for an increased probe temperature (i.e. 90°C), a reduced 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 level values were used to optimize the sensitivity of the COSY technique and to highlight weak resonances. Also, some low-field ^{1}H (100 MHz) and ^{13}C (25 MHz) n.m.r. spectra were recorded, using a Jeol FX100 spectrometer, on some model compounds in order to investigate certain minor structures that were expected to occur in these polyacrylonitriles.

RESULTS AND DISCUSSION

Molecular weights

The measurements of intrinsic viscosity indicated a value of 11 300 for the viscosity-average molecular weight, M_v, of polyacrylonitrile A and a corresponding value of 23 500 for the polymer B.

I.r. spectra

The i.r. spectra of polyacrylonitriles A and B are shown in *Figures 1a* and *1b*, respectively. Both spectra contain, in addition to the expected major peaks associated with the acrylonitrile repeat units, minor peaks at 1654 and 1735 cm^{-1} which are assigned to C=O stretching vibrations in acrylamide and acrylic acid units, respectively. Both types of unit arise from adventitious hydrolysis of acrylonitrile units during the polymerization process.

Subtraction of the i.r. spectrum of polyacrylonitrile B ($M_v = 23500$) from that of A ($M_v = 11300$) produced the difference spectrum shown in *Figure 2*. This spectrum highlights several minor peaks that were not clearly visible in the parent spectra, particularly bands at 1209 cm^{-1} (S=O asymm. str.), 1046 cm^{-1} (S=O symm. str.), 614 cm^{-1} (C–S str.) and 523 cm^{-1} (S=O asymm. str.), which are characteristic of sulfonate end-groups. It is to be noted that there are apparently no peaks in the spectrum characteristic of sulfate end-groups, which, by analogy with peaks from the sulfate group in the model compound, sodium n-butyl sulfate, would be expected to appear at, or near, 1252 cm^{-1} (S=O asymm. str.), 1081 cm^{-1} (S=O symm. str.), 971 cm^{-1} (C–O str.), 836 cm^{-1} (S–O str.), 624 cm^{-1} (S=O symm. def.) and 595 cm^{-1} (S=O asymm. def.). That such peaks would be evident if sulfate end-groups were present in significant quantities can be seen by reference to the i.r. spectrum shown in *Figure 3*, which is the difference between the spectra of two polyacrylonitriles with M_vs of 28 400 and 36 500, respectively, prepared in water at 60°C using only ammonium persulfate as the initiator (pH 1.5). This spectrum shows clear evidence for the presence of sulfate end-groups in these latter polymers, namely the bands at 1267 cm^{-1} (S=O asymm. str.), 1010 cm^{-1} (C–O str.), 780 cm^{-1} (S–O str.) and 577 cm^{-1} (S=O asymm. def.).

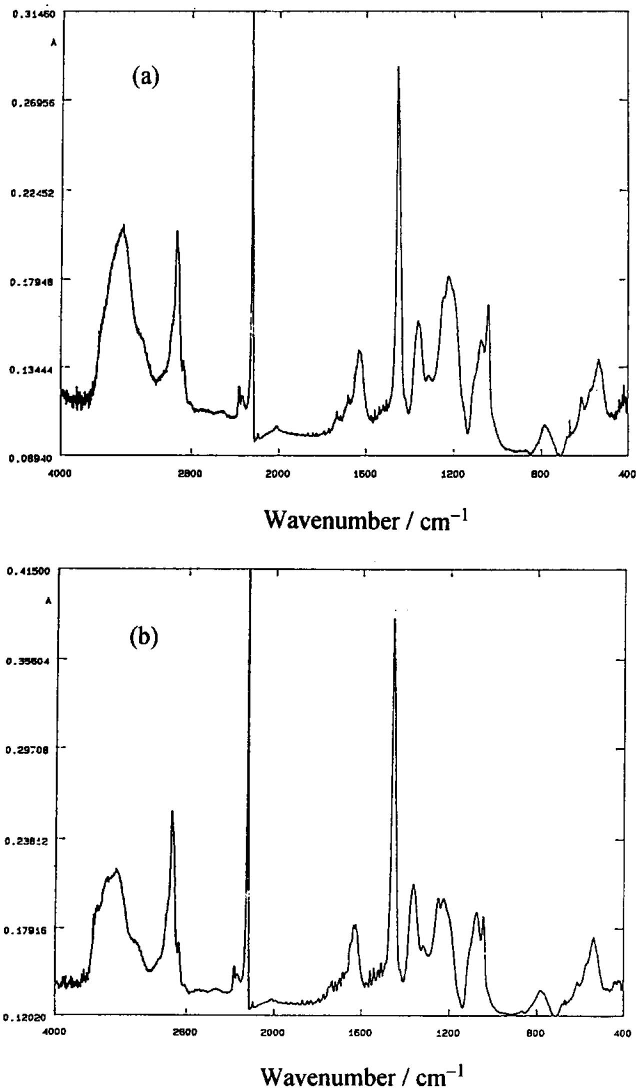


Figure 1 *FT*i.r. spectra of: (a) polyacrylonitrile A ($M_v = 11300$) and; (b) polyacrylonitrile B ($M_v = 23500$)

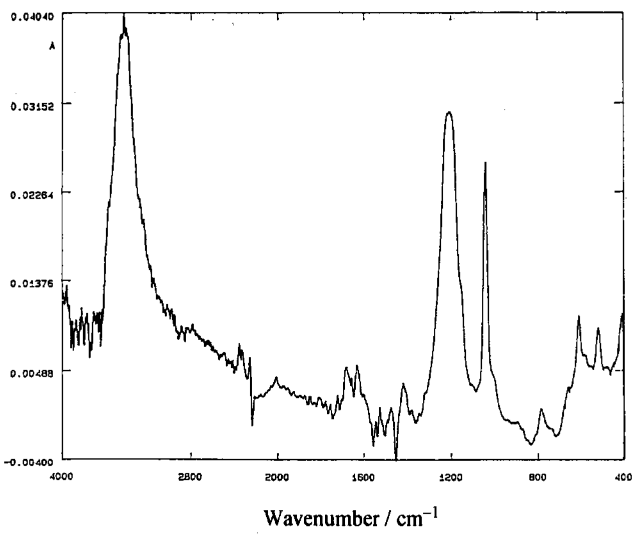


Figure 2 *FT*i.r. difference spectrum obtained after subtraction of the spectrum of polyacrylonitrile B ($M_v = 23500$) from that of polyacrylonitrile A ($M_v = 11300$)

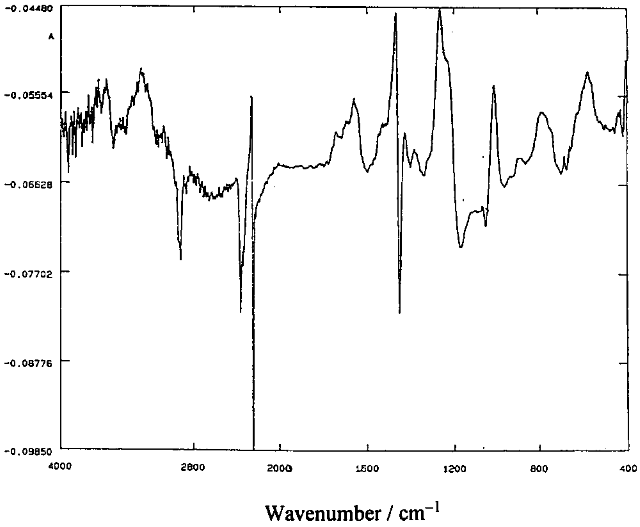
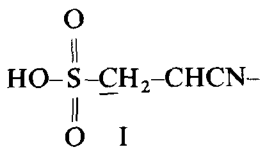


Figure 3 *FT*i.r. difference spectrum obtained after subtraction of the spectrum of a polyacrylonitrile with $M_v = 36500$ from that of a polyacrylonitrile with $M_v = 28400$: both polymers were initiated with ammonium persulfate at 60°C and pH 1.5

^{13}C n.m.r. spectra

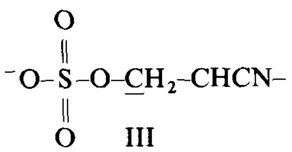
The ^{13}C n.m.r. spectra of the polymers show, in addition to the expected dominant methine, methylene and nitrile carbon resonances of the acrylonitrile repeat units centred at ~27, 33 and 120 ppm, respectively, several small peaks arising from end-groups and other minor structures. Of particular interest are the small methylene carbon signals found at 51–52, 61–62 and 64–65 ppm (shown in *Figure 4* for polymer A). These small signals are assigned in order of decreasing field (i.e. increasing chemical shift) to the methylene carbons that are adjacent to sulfonate, hydroxyl and sulfate end-groups, respectively (shown as underlined carbons in structures I–III).


$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\underline{C}H_2-CHCN-$

I

$HO-\underline{C}H_2-CHCN-$

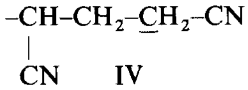
II


$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\underline{C}H_2-CHCN-$

III

These assignments are supported by our observations that the methylene carbons adjacent to the terminal functional groups in long-chain n-alkyl sulfates, alcohols and sulfonates give rise to ^{13}C n.m.r. peaks at 66, 57 and 51 ppm, respectively. The assignment of the peak at 61–62 ppm to methylene carbons adjacent to hydroxyl end-groups is also supported by the fact that in the ^{13}C n.m.r. spectra of polyacrylonitriles prepared using hydrogen peroxide as the initiator, in which only hydroxyl end-groups would be expected, similar small methylene signals are observed at ~61 ppm.

Also present in the ^{13}C n.m.r. spectra of the polymers prepared with ammonium persulfate/sodium metabisulfite is a sharp signal at 14.4 ppm. Similar signals at an almost identical chemical shift have been reported previously for polyacrylonitriles of relatively low molecular weight and for acrylonitrile–furan copolymers[18,19]; they have been assigned to methylene carbons in end-groups produced by chain transfer (shown as the underlined carbon in structure IV)[19].


$-\underset{\underset{CN}{|}}{C}H-CH_2-\underline{C}H_2-CN$

IV

Although our ^{13}C n.m.r. spectra have not been obtained under conditions that are ideal for making quantitative measurements, it is instructive to compare the areas of the methylene signals at 14.4, 51–52, 61–62 and 64–65 ppm with that of the main-chain methylene signals at 32–33 ppm. The areas are in the ratio 1.59%:1.61%:0.03%:0.16%:96.61%. From this ratio, and

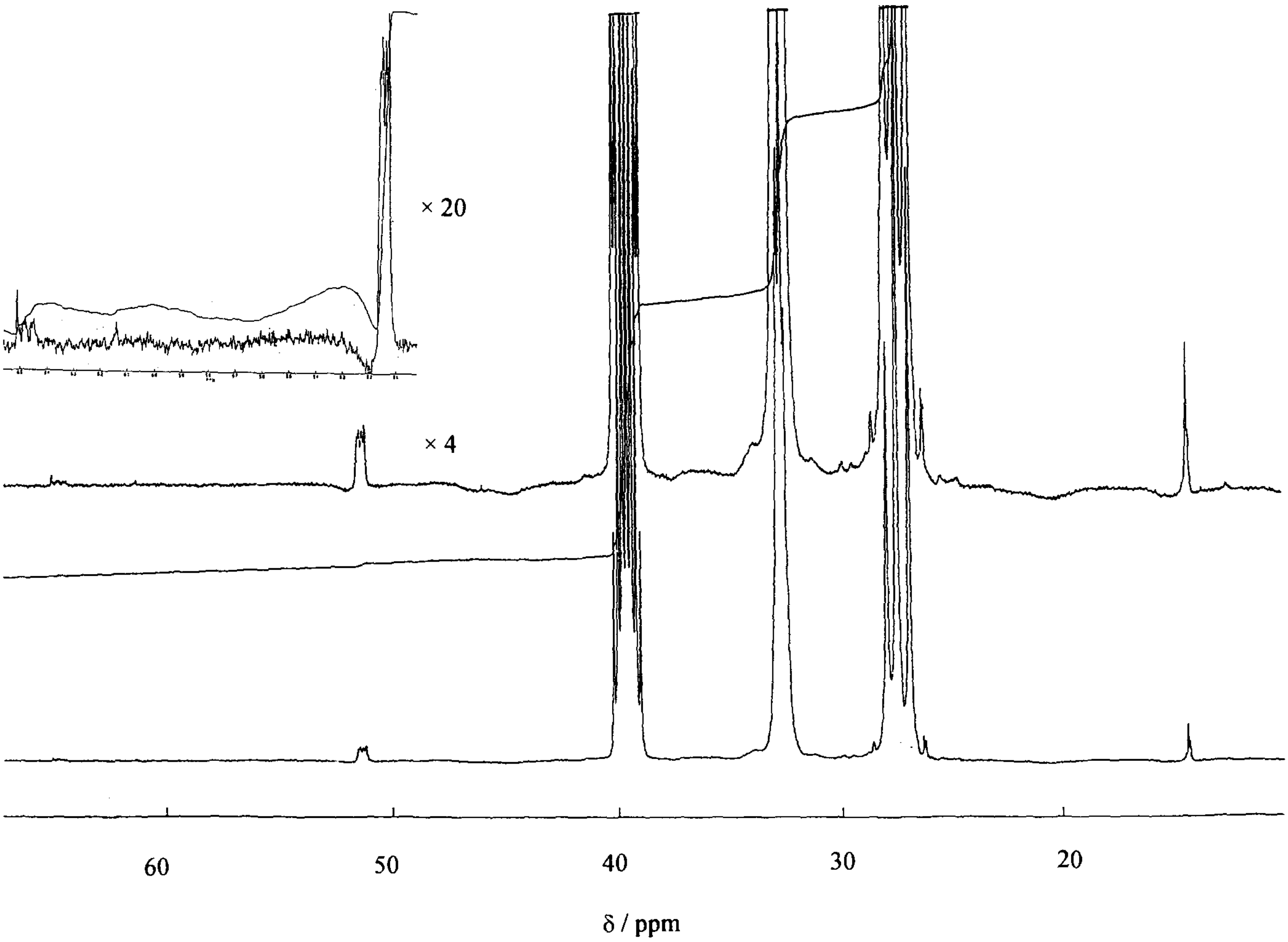


Figure 4 ^{13}C n.m.r. spectrum of polyacrylonitrile A ($M_v = 11\,300$): expansion of end-group signals between 50 and 66 ppm are shown in the inset

assuming that the minor peaks do indeed arise from end-groups, it can be calculated that there are approximately 28.5 repeat units per end-group which, assuming that all the end-groups have been detected and that there are two end-groups per chain, gives a number-average degree of polymerization of 57, i.e. a number-average molecular weight, M_n, of 3021. This M_n value does not seem unreasonable, given that M_v for this polymer is 11 300. The roughly ten-fold preponderance of sulfonate over sulfate end-groups may be an indication that the reactivity of acrylonitrile towards the bisulfite radical is an order of magnitude greater than the reactivity towards the sulfate radical anion. However, we think it is significant that the methylene peaks from end-groups I and IV are very similar in area, and we believe that this is because the majority of these end-groups are formed by the transfer reaction involving a growing polyacrylonitrile radical and a bisulfite ion (see reaction (8) above).

Alternative reactions that could lead to the end-group IV would be transfer of growing polyacrylonitrile radicals to water and also termination of growing radicals by disproportionation. However, transfer to water would produce hydroxyl radicals which would reinitiate polymerization and as a consequence there would be roughly equal amounts of end-groups II and IV in the polymer, and not a considerable excess of end-group IV over end-group II as is the case here. The possibility that end-group IV arises from termination by disproportionation can also be ruled out. There are no olefinic carbon signals visible in the ^{13}C n.m.r. spectrum of the polymer; such signals would be expected if termination by disproportionation were significant, since one of the end-groups formed by disproportionation is unsaturated. In any case, it has been demonstrated previously that combination, rather than disproportionation, is the predominant mode of termination in radical polymerizations of acrylonitrile in the absence of chain transfer agents[20,21].

Whether the hydroxyl end-groups arise from initiation by hydroxyl radicals or from hydrolysis of sulfate end-groups is not clear. Certainly we have found (from changes in the i.r. spectra) that sulfate end-groups can be removed from polyacrylonitriles initiated by ammonium persulfate alone if the polymers are refluxed with 1 M HCl for up to 3 h. However, the polymers prepared in this study have not been subjected to temperatures higher than 40°C, nor a pH lower than 5.

^1H and COSY n.m.r. spectra

High-field ^1H n.m.r. spectra of the polymers provide some evidence to corroborate the conclusions drawn about structures from the i.r. and ^{13}C n.m.r. spectra. The ^1H n.m.r. spectrum of polymer A (*Figure 5*) contains a small broad band between 7.0 and 7.1 ppm which is assigned to NH_2 groups in isolated acrylamide units. The area of this NH_2 signal, relative to that of the main-chain methylene signals at 2.0–2.2 ppm, indicates that approximately 0.6% of the acrylonitrile units have been hydrolysed to acrylamide units during the preparation and recovery of the polymer. There are also very weak methylene signals in the spectrum at ~4.2 and 3.8 ppm; the former of these is assigned to methylene protons in the end-group structure II, and the latter to methylene protons in the end-group structure III. These assignments are supported by our observation that the proton signals of the methylene groups adjacent to the sulfate group and the hydroxyl group in the model compounds, sodium n-hexadecyl sulfate and 3-hydroxypropionitrile, respectively, are at 3.7 and 4.0 ppm. Sodium sulfopropionitrile, a model compound for the sulfonate end-group, gives rise to a methylene proton signal at 3.2 ppm, thus indicating that proton signals from methylenes that are adjacent to sulfonate end-groups will not be visible in the ^1H n.m.r. spectra of the polymers, since they will be obscured by the methine proton signals from the acrylonitrile repeat units that occur between 3.0 and 3.3 ppm.

The presence of the sulfonate end-group is, however, revealed in a COSY spectrum of a polymer A (*Figure 6*)

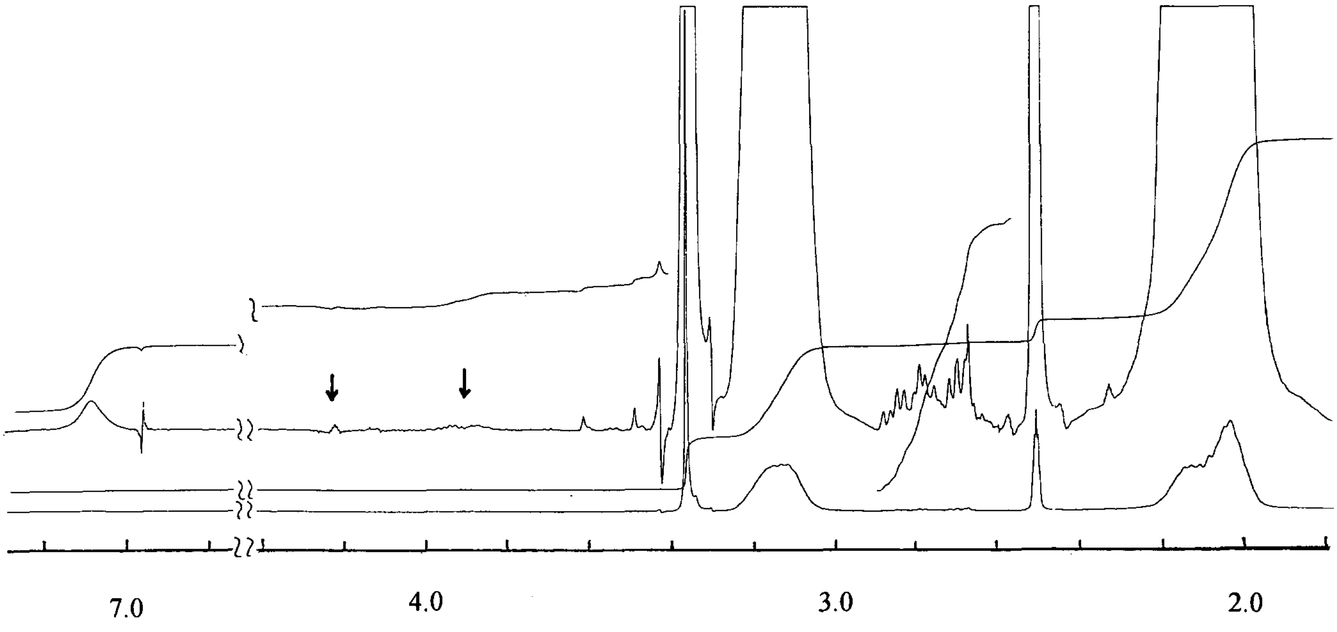


Figure 5 ^1H n.m.r. spectrum of polyacrylonitrile A (M_v = 11 300): weak end-group (methylene) signals are shown by ↓

which contains a small cross-peak connecting the resonances at 3.3 and 2.8 ppm. The former of these is assigned to the methylene protons of the sulfonate end-group (structure I) and the latter to the adjacent methine proton. The COSY spectrum also contains a small cross-peak connecting the resonances at 3.7 ppm and 3.1 ppm, which we assign to the methylene and methine protons of the sulfate end-group (structure III), and a small cross-peak connecting the resonances at 2.7 and 2.1 ppm, which is assigned to the terminal and penultimate methylene groups of structure IV. As with the ^{13}C n.m.r. spectrum, there is no evidence for any unsaturation in the polymer as would be expected if termination by disproportionation were significant.

CONCLUSIONS

Polyacrylonitriles prepared using ammonium persulfate and sodium metabisulfite at pH 5 have been shown to possess sulfonate, sulfate and hydroxyl end-groups, with the first type of end-group present in considerable excess. Of the sulfonate end-groups, the majority almost certainly arise from transfer to bisulfite ion, a reaction which also gives rise to non-sulfur containing end-groups. The polymers also possess small quantities of acrylamide and acrylic acid units which presumably arise by adventitious hydrolysis of the polymers during preparation or recovery.

The polymers prepared in this study were all white in colour with no obvious signs of discoloration (yellowing). We attribute this to the conditions under which the polymers have been prepared, i.e. under only mildly acidic conditions with an excess of reducing agent in the redox system, conditions which have led to the introduction of relatively few acrylic acid and acrylamide units into the chains and which have given rise to relatively few sulfate end-groups.

The sulfonate and hydroxyl end-groups, being polar

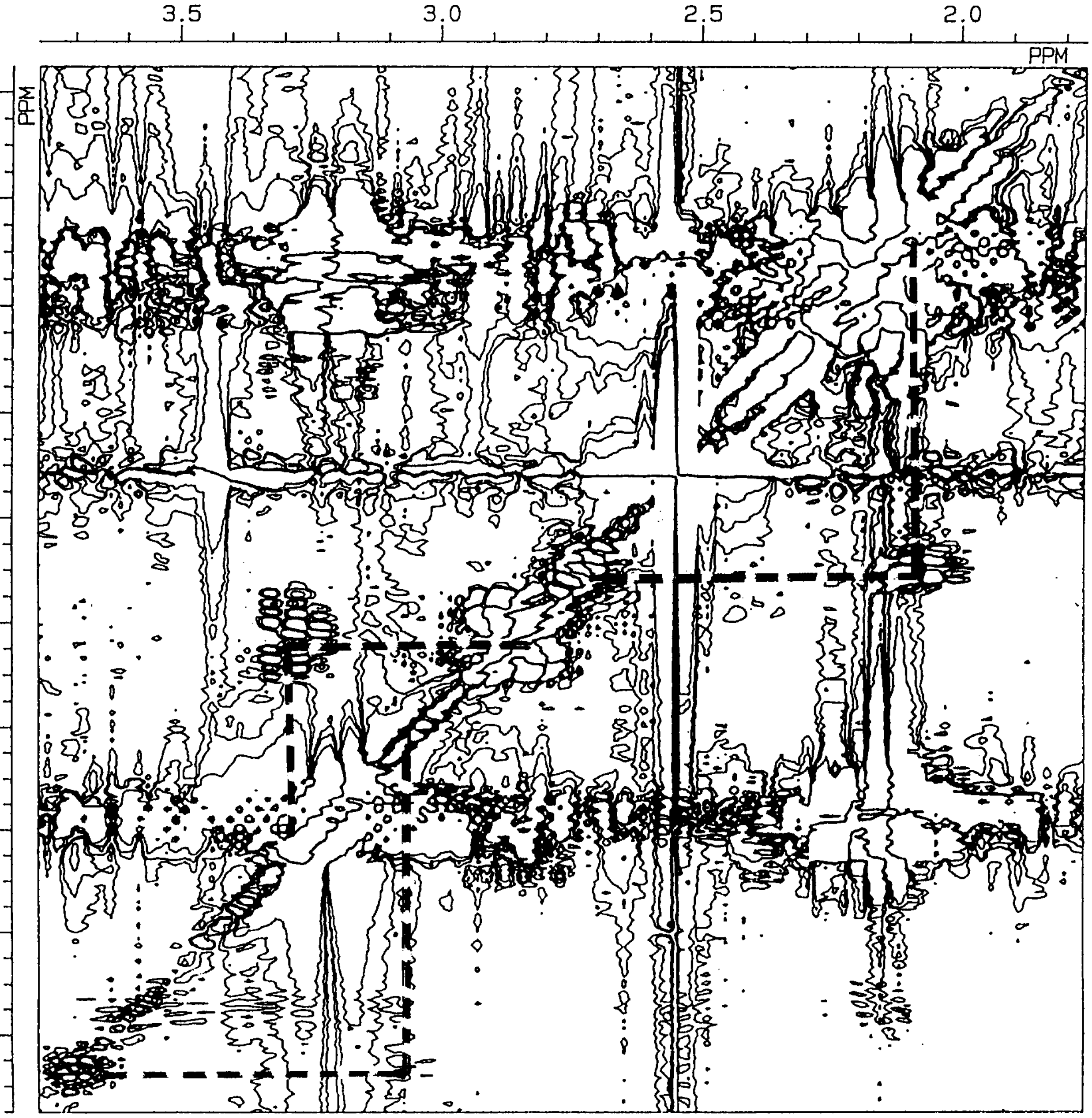
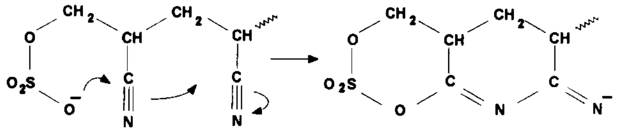
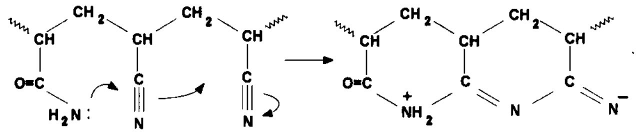


Figure 6 ^1H n.m.r. phase-sensitive DQF-COSY spectrum of polyacrylonitrile A ($M_v = 11\,300$): see text for explanation of connectivities

in character, may act as dye sites in fibres made from the polymers but are unlikely to contribute significantly to the initiation of intramolecular cyclization, and therefore to colouring. However, sulfate end-groups, acrylamide units and acrylic acid units may all be implicated in colouring, since all may initiate cyclization (see reactions (9)–(11)).



(9)



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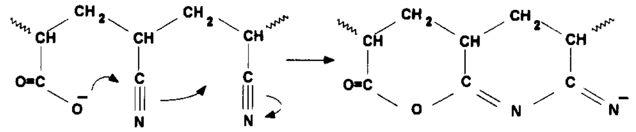

(11)

The combined use of i.r. and n.m.r. techniques to identify (and potentially also to quantify) end-groups in polyacrylonitriles we believe represents a significant advance over techniques previously used to identify such groups, i.e. the dye acceptance method[22], the use of ^{35}S-labelled initiators[5] and various titrimetric methods.

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