Investigation of base induced cyclization and methine proton abstraction in polyacrylonitrile solutions

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When polyacrylonitrile (PAN) solutions are treated with bases, coloration occurs. It has been proposed in the past that this is due to a cyclization reaction which leads to conjugated structures. In this research, the effect of bases of differing strength was systematically examined and an attempt made to determine the extent of cyclization, if it took place at all. The literature has also suggested that cyclization would occur preferentially in isotactic sequences. Hence tacticity changes after base treatment were monitored by *in situ* ^{13}C nuclear magnetic resonance experiments to test this model. Strong bases caused coloration, chain scission, partial inversion of configuration and gelation induced by crosslinking. By using sodium deuteroxide, it was shown that the methine proton could be abstracted by strong bases. Weak bases caused only coloration at room temperature, while heating was needed to induce tacticity changes and gelation. Contrary to previous suggestions, we found no evidence for cyclization even in red–black solutions. We concluded that the (unidentified) chromophore was present in very low concentrations but was very intense.

(Keywords: base treatment; cyclization; proton abstraction; polyacrylonitrile; solutions)

INTRODUCTION

Carbon fibres from PAN precursors

Polyacrylonitrile (PAN) based precursors remain one of the best materials for making carbon fibres. The general process consists of wet spinning PAN copolymer fibres, orienting them by stretching, 'stabilizing' the fibres under tension between 200 and 300°C and then heating them to even higher temperatures to convert them to carbon (≈1000°C) or graphite (≈2000°C) fibres. The stabilization process is very slow, but it is essential to convert the PAN fibres into an infusible form before they can be heated to carbonization temperatures.

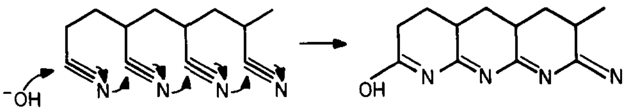
When PAN fibres are stabilized in air by heating between 200 and 300°C, they go from white to golden-yellow, then orange to dark brown and finally black. The stabilization process is very complex and involves many chemical reactions. In 1950, Houtz[1] proposed the formation of a fully condensed carbon–nitrogen cyclic aromatic structure as the primary result of stabilization. Since then, Burlant and Parsons[2], Grassie *et al.*[3] and LaCombe[4] have adapted this suggestion and proposed that the nitrile groups undergo a cyclization reaction to give a partially aromatic conjugated polyimine sequence $(\text{-C=N-})_x$.

Though the cyclization scheme now seems to be widely accepted, it has been contested in the past. For instance, Fester[5] and Berlin[6] have suggested the initial formation of a conjugated polyene $(\text{-C=C(CN)-})_x$ chromophore with pendant nitrile groups. Schurz *et al.*[7,8] have suggested instead that crosslinking via the azomethine linkage is the dominant reaction.

Solution pretreatments for PAN

Many reagents have been reported in the literature as pretreatments for moderating the stabilization exotherm. The polymer was either treated in solution before spinning or the spun fibres were treated before stabilization. In one case, stretched PAN fibres were treated in aqueous CuCl and precursor fibres with an improved modulus of 16 GPa were reported[9]. Similarly, PAN fibres have been dipped briefly in $KMnO_4$ and reduced stabilization times were found[10]. Grassie and McGuchan did an extensive thermal study on treatment of PAN by various reagents[11]. It is not always clear how these pretreatments improve mechanical properties or reduce the exotherm intensity.

It is well known that when bases are added to PAN solutions, coloration occurs similar to that observed during thermal stabilization of PAN fibres[12,13]. In 1953, McCartney postulated that the colour was due to cyclization of the nitrile groups and this theory has become popular[12]. The mechanism of cyclization by nucleophilic attack on the nitrile carbon is as follows:



A recent patent describes how the base treatment of PAN copolymers drastically reduced the intensity of the stabilization exotherm[14]. The mechanism by which this occurred was not explained. In this work, we used PAN homopolymer and re-examined the effect of bases using the more modern analytical techniques available today. In particular, we studied the effect of bases of different strengths and tried to establish if cyclization occurs as claimed in the literature.

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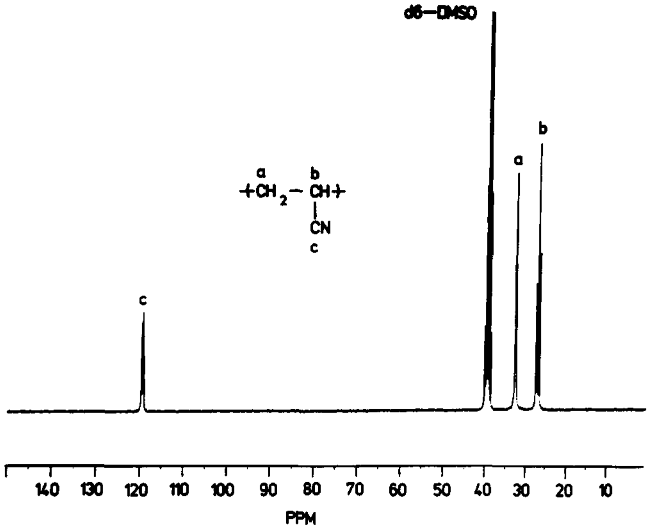


Figure 1 ^{13}C n.m.r. spectrum of free radical polymerized PAN, showing (a) methylene, (b) methine and (c) nitrile carbon resonances. d6-DMSO is the deuterated DMSO solvent signal

EXPERIMENTAL

PAN was prepared by free radical slurry polymerization. The potassium persulphate(KP)/sodium metabisulphite(SM) redox initiation system was used at 40°C. The KP:SM concentration was 1.3:0.7% w/w monomer. A chain transfer agent (propan-2-ol) was added to lower the molecular weight. All the monomer and initiators were added to the bulk (i.e. no feeding); consequently the reaction was very exothermic, reaching a temperature of 85°C. The reaction was complete within 2 h. The polymer was filtered, washed with methanol and dried at 40°C. The polymer had an inherent viscosity of 1.5 dl g^{-1} (measured in dimethylformamide at 25°C).

On addition of a base to a PAN solution, the viscosity changes. Therefore, changes in relative viscosity with time were measured with an Ostwald viscometer, after addition of the base–solvent mixture to the PAN powder. All the initial polymer solutions had a concentration of ≈10% w/v. An hour was allowed to elapse before the first viscosity measurement was made, by which time the red solution was homogeneous. The various 10% polymer–base solutions were diluted by the same factor before using the Ostwald viscometer[15]. More viscosity measurements were made after suitable time intervals.

Carbon-13 nuclear magnetic resonance (n.m.r.) measurements were made using a Bruker AC300 n.m.r. spectrometer operating at 75 MHz. Samples were contained in 10 mm o.d. n.m.r. tubes as 20% w/v solutions in d6-dimethyl-sulphoxide (DMSO). Spectra were recorded at 353 K with a magnetization tip angle of 30° and a pulse repetition rate of 0.92 s, in the presence of complete broadband proton decoupling. A spectral width of 17 857 Hz was used, with a data size of 32 000 points, zero filled to 64 000 points before Fourier transformation (*FT*). This gave a final digital resolution of 0.545 Hz per datum point. No apodization function was used.

Infrared (i.r.) spectra of powdered specimens of PAN were recorded in a Nicolet 740 *FT*i.r. spectrometer by using the diffuse reflectance technique. Samples were dried *in situ* by a dry air purge in the spectrometer. Spectra were recorded at 4 cm^{-1} resolution and converted to Kubelka–Munk units for accurate intensity comparisons.

TACTICITY DETERMINATION OF FREE RADICAL POLYMERIZED PAN BY ^{13}C N.M.R.

Based on computer modelling studies, Coleman *et al.*[16] have suggested that tacticity determines the degree of intramolecular cyclization. In particular, they indicated that it is easier to cyclize isotactic sequences than syndiotactic configurations. Russian workers have shown that isotactic enriched PAN made by the urea canal complex method[17] undergoes much more rapid coloration and thermal stabilization than atactic PAN[18]. On the other hand, Chen *et al.* found evidence which suggested that thermal cyclization was not stereospecific[19]. However, in this work, we have assumed that (base induced) cyclization would occur preferentially in isotactic sequences.

Thus, if base does induce cyclization in PAN solutions, and cyclization proceeds via isotactic sequences, then we should see a drop in the proportion of isotactic material. However, before this could be tested, the tacticity of free radical polymerized PAN had to be determined. Tacticity was determined by ^{13}C n.m.r.

The proton decoupled ^{13}C n.m.r. spectrum of free radical polymerized PAN is shown in *Figure 1*; expansions are shown in *Figures 2* and *3*. The methine (–CH) carbon resonance gives rise to three well resolved resonances centred at ≈27 ppm, due to a triad chemical shift sensitivity. This set of peaks (*Figure 2*) may, therefore, be used for determining the triad tacticity.

Triad distribution from the methine carbon resonance

Assignments of the three methine resonances are shown in *Figure 2*. The areas under the peaks of the methine resonances in *Figure 2* give the abundance of the various configurations. *Table 1* shows that the percentage of isotactic triads (mm) was 28%, of syndiotactic (rr) 22% and heterotactic (mr = rm) 50%. The labels m and r stand for meso (same side) and racemic (opposite side) additions of the monomer to the growing chain end.

Pentad distribution from the nitrile carbon resonance

The methine carbon signals do not show chemical sensitivity to atoms further along the chain (i.e. pentad

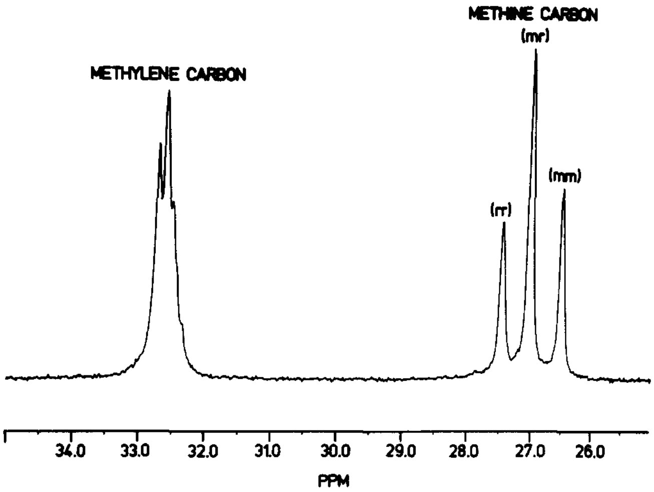


Figure 2 Expansion of the ^{13}C n.m.r. spectrum of PAN showing the methylene and methine carbon resonances. The triad (mr, rr, mm) abundance can be measured from the methine signal

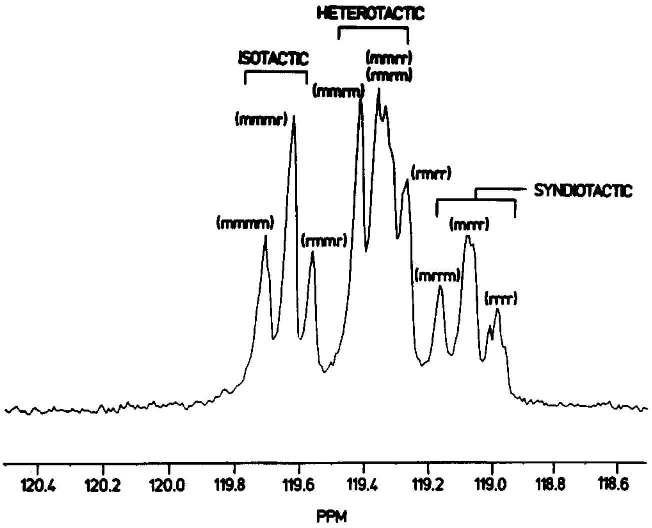


Figure 3 Expansion of the ^{13}C n.m.r. spectrum showing the nitrile carbon resonance. The pentad and triad abundances can be measured from this signal

Table 1 Triad abundances from ^{13}C n.m.r.

Triad	Abundance from spectrum	Calculated abundance^a	Comments
(mm)	0.28	0.28	Isotactic
(mr)	0.50	0.50	Heterotactic
(rr)	0.22	0.22	Syndiotactic

^{a}Calculated from Bernoullian statistical model; see text

sensitivity). The nitrile carbon band, on the other hand, shows a much greater chemical shift sensitivity, with pentad sequences clearly resolved (*Figure 3*). In some cases, even heptads are partially resolved in *Figure 3*. The measured and calculated pentad abundances are shown in *Table 2*.

Assignments within the nitrile band follow directly from the triad assignments originally made by Schaefer in 1971[20] and agree with those made subsequently by Turska *et al.*[21]. Though Turska has noted pentad resonances, they are not as well resolved as in our n.m.r. spectrum in *Figure 3*. The triad abundances can of course be measured from the nitrile band as well.

Calculated abundances from Bernoullian statistical model

Even though heptad splittings are not well resolved in *Figure 3*, heptad abundances may be calculated if the statistics of the polymerization stereochemistry are known. We were particularly interested in determining the concentration of long isotactic sequences to assess the potential lengths of cyclized units.

The simplest statistical model describing polymer stereochemistry is the Bernoullian type[22], in which the probability of addition of a monomer unit to give a particular chain end stereochemistry is independent of the preceding chain end stereochemistry. In the first-order Markov model[22], the probability of monomer addition to give a particular streochemistry does depend upon the stereochemistry of the preceding chain unit. Higher order models can also be developed.

Here, we adopted the procedure developed by Bovey[22] to check conformity to a statistical model. We started by assuming that the first-order Markovian model applied. Two independent probabilities, $P_{m/r}$ and $P_{r/m}$, are necessary, where $P_{m/r}$ is the probability that the monomer adds in r fashion to an m chain end and $P_{r/m}$ is the probability of m addition to an r chain end[22]. Only two probabilities are required since $P_{m/m}+P_{m/r}=1$ and $P_{r/r}+P_{r/m}=1$. The empirical probabilities $P_{m/r}$ and $P_{r/m}$ are readily calculated from the observed triad abundances using the relationships

$$P_{m/r}=\frac{(\mathrm{mr})}{2(\mathrm{mm})+(\mathrm{mr})}, \qquad P_{r/m}=\frac{(\mathrm{mr})}{2(\mathrm{rr})+(\mathrm{mr})}$$

where (mr), (mm) and (rr) are experimental abundances of mr, mm and rr sequences. If $P_{m/r}+P_{r/m}=1$, then the polymer conforms to Bernoullian statistics and $P_{r/m}$ and $P_{m/r}$ reduce to P_m and P_r, respectively (where P_m is the probability of m addition and $P_r=1-P_m$, the probability of r addition).

For this PAN, we obtained from the n.m.r. abundances the empirical probabilities $P_{m/r}=0.47$, $P_{r/m}=0.53$ and $P_{m/r}+P_{r/m}=1$. Thus, within experimental error, the polymer fitted the Bernoullian model. Abundances of triads and pentads can now be calculated simply by using the usual Bernoullian relationship. For example, the abundance of a perfect isotactic pentad would be $\mathrm{mmmm}=P_m^4=(0.53)^4=0.08$ (i.e. 8%). *Tables 1* and *2* show that the measured and calculated abundances are in good agreement for triads and pentads. Note, for an ideally random polymer, $P_r=P_m=0.5$; PAN in fact showed a slight bias towards isotacticity because $P_m=0.53$. The tacticity of free radical polymerized PAN appeared to be independent of molecular weight as we measured the same abundances for polymers of different molecular weight.

Abundances of perfect isotactic heptads, nonads and higher sequences not resolved in the spectrum can be calculated. These are even rarer: for instance, the abundance of perfect isotactic heptads is only $P_m^6=0.022$. The abundances of other sequences may be calculated by using the two probabilities P_m and P_r, e.g. $\mathrm{rmmr}=P_m^2P_r^2$.

Base treatment of PAN in solution

Viscosity changes occur when bases are added to PAN solutions. It is shown that the viscosity changes depend on base strength. Evidence for cyclization in the coloured, base treated polymer was sought by n.m.r. and i.r. spectroscopy. N.m.r. spectroscopy was used to monitor

Table 2 Measured and calculated pentad abundances from ^{13}C n.m.r.

Pentad	Observed abundance	Calculated abundance
(mmmm)	0.08	0.08
(mmmr)	0.13	0.14
(rmmr)	0.07	0.06
(mmrm)	0.15	0.15
(mmrr)^a (rmrm)^a	0.23	0.25
(rmrr)	0.12	0.11
(mrrm)	0.06	0.06
(mrrr)	0.10	0.11
(rrrr)	0.06	0.05

^{a}mmrr and rmrm are not fully resolved

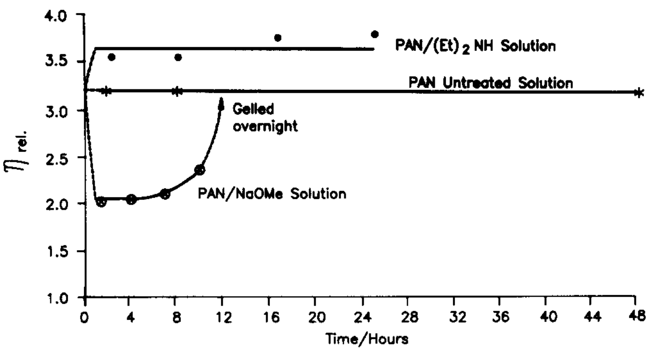


Figure 4 Relative viscosity *versus* time for PAN/DMSO solutions. No measurements were made in the first hour to allow the polymer to dissolve. For NaOMe, no measurements were possible after ≈10 h due to gel particles appearing in the solution

tacticity changes and the degree of conversion (i.e. cyclization of isotactic sequences) achieved with various bases.

Strong bases

Viscosity changes and gelation. For our initial experiment, a strong base such as sodium methoxide was used. 0.025 g of sodium methoxide (NaOMe) was added to 10 ml of dimethyl sulphoxide (DMSO), which was then added to 1 g of PAN homopolymer and stirred. NaOMe is very sparingly soluble in DMSO at room temperature; 0.025 g in 10 ml DMSO exceeds the solubility limit.

As soon as the DMSO–base mixture was added to the PAN, the polymer dissolved, but coloration occurred simultaneously. The solution rapidly turned red–black but it can be seen from *Figure 4* that within the first hour, there was a great drop in viscosity compared with an untreated solution. The drop in viscosity indicates that chain scission occurs[12]. However, *Figure 4* shows that after a period of a few hours the viscosity appeared to increase and after 12 h a dark red–black gel was formed, with the stirring magnet embedded in it. We think that gelation here is due to chemical crosslinking as the gel could not be redissolved in excess DMSO, under any conditions. Though insolubility can also arise due to a rigid chain backbone caused by cyclization we think this would cause polymer precipitation rather than formation of a solvent swollen network. (Note that PAN can exhibit 'physical' gelation behaviour[23]. For example, PAN–DMSO solutions will gel if water is added, or if water is absorbed from the atmosphere, but this takes a period of days. Such gels are translucent and are reversible if excess solvent is added. The red–black gels formed here were due to chemical reactions that were irreversible.) McCartney has indicated that the rapid viscosity drop is due to random chain scission rather than unzipping of monomer units from the chain ends[12] but he did not report any subsequent increase in viscosity. Battie and Guthrie[24] reported an increase in viscosity with sodium hydroxide (after the initial drop) but they did not mention that their solution gelled. The probable reason is that they conducted their viscosity studies in dilute polymer solutions. However, we chose a concentrated polymer solution and diluted it for viscometry. Crosslinking effects are more apparent in a concentrated polymer solution, which is why we were able to observe gelation.

Identical behaviour was observed with other strong bases such as n-butyl lithium/hexane (which is fully soluble in DMSO) and sodium ethoxide (NaOEt). It is important to note that NaOMe and NaOEt are air and moisture sensitive and liable to be less reactive if they have discoloured and become yellow during storage.

Cyclization and tacticity changes. If cyclization occurred preferentially in isotactic sequences, we would have expected a drop in the isotactic triad level from 28%. Additionally, we thought we might have been able to pick up direct evidence for cyclization by detecting $-(C{=}N)_x$ sequences, both in the n.m.r. and the i.r. spectra. However, after prolonged treatment with strong base, the gelled product could only be examined by solid state n.m.r., but the bands were broad and uninformative.

Many investigators who have studied the thermal stabilization of PAN in air attribute the broad bands that appear in the i.r. spectrum at ≈1600 cm^{-1} to conjugated C=N vibration[25]. Föchler *et al.*[26] quote the broad bands at ≈1590–1610 cm^{-1} to mixed C=N, C=C stretching. Rafalko[27] investigated stabilization in air of ^{15}N labelled PAN and attributed a band at 1582 cm^{-1} to conjugated C=N stretching. *Figure 5a* shows the i.r. spectrum of PAN, with the prominent nitrile band at 2243 cm^{-1}. *Figure 5b* is the spectrum obtained after treating PAN with NaOMe; the specimen

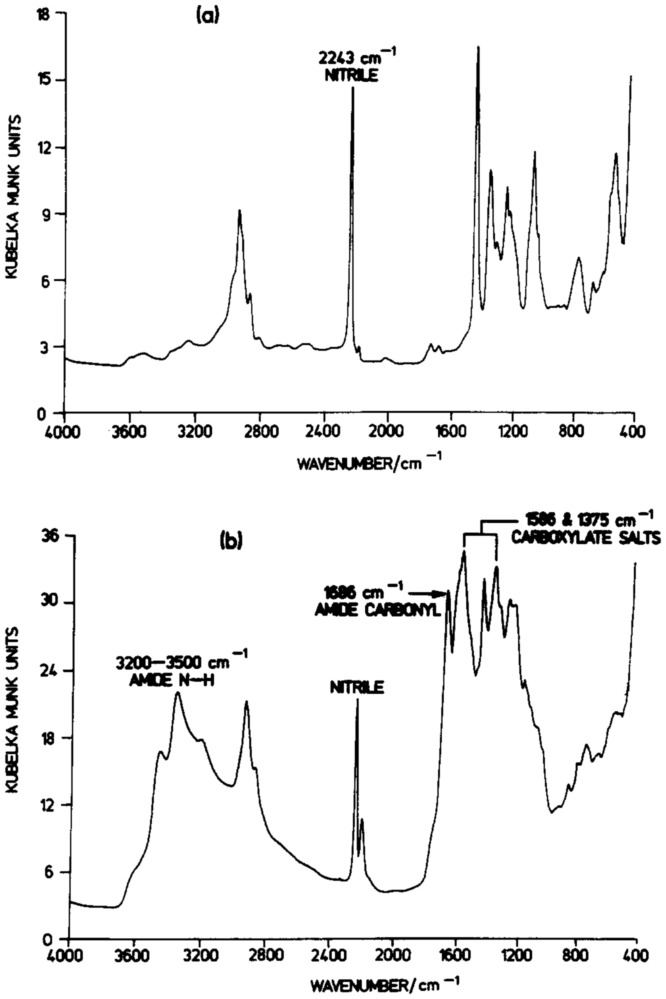


Figure 5 Diffuse reflectance i.r. spectra of (a) nascent PAN powder and (b) PAN after treating with NaOMe. The sample used in (b) was obtained by coagulating the red–black gel in water to remove the DMSO, drying and grinding to give a brown powder

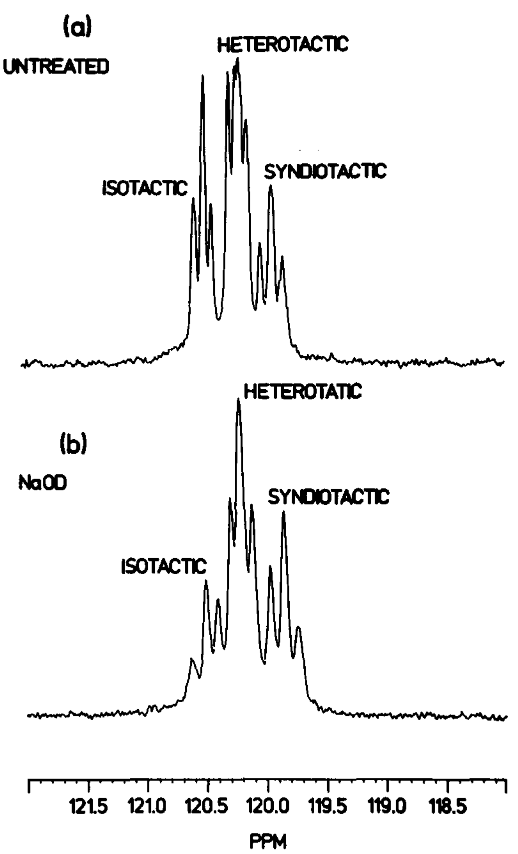


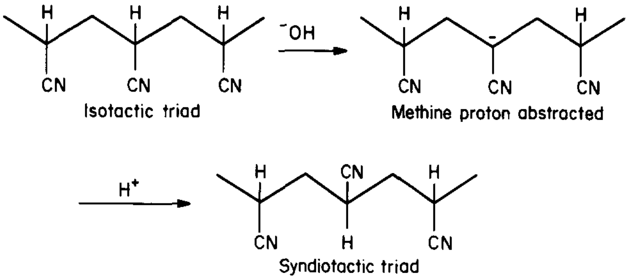
Figure 6 The nitrile band in the ^{13}C n.m.r. spectrum of PAN showing the change in tacticity after addition of base: (a) untreated PAN; (b) after addition of $NaOD/D_2O$, showing a 9% drop in isotactic content and a 9% increase in syndiotactic content. This suggests inversion of configuration instead of preferential cyclization of isotactic sequences

used was the red-black gel from which the solvent had been extracted. The peaks at 1686 cm^{-1} in *Figure 5b* may be assigned to amide carbonyl when taken in conjunction with the appearance of N-H stretching bands in the 3200–3500 cm^{-1} region. The bands at 1586 and 1375 cm^{-1} could be attributed to carboxylate salts[28] resulting from the hydrolysis of nitriles. Bands from $(\text{-C=N-})_x$ stretching would also occur in the region 1590–1610 cm^{-1} but, even if they were present, they would be masked by the amide and carboxylate bands. Thus cyclization might be present, but in our opinion this cannot be deduced from the i.r. spectrum.

The most fruitful approach was to study the effect of strong base by *in situ* solution state n.m.r., before gelation occurred. As soon as the base was added to the polymer solution in the n.m.r. tube, there was a remarkable drop in isotactic triad levels from 28% to ≈19% and this was reproducible with a variety of strong bases.

At first, this drop in isotactic triad content coupled with the dark coloration that was obtained on addition of NaOMe was taken as evidence for preferential cyclization of such sequences. However, there was no indication of where these isotactic triads had disappeared, as there was no evidence for any $(\text{-C=N-})_x$ in the i.r. or n.m.r. spectra of the samples. ^{13}C n.m.r. resonances would be expected in the region 150–170 ppm if C=N groups were present. A closer examination revealed that along with the ≈9% drop in isotactic triads, there was a simultaneous ≈8–9% increase in syndiotactic triads. This suggested that an inversion of configuration was taking place, whereby a certain proportion of isotactic sequences was being converted to syndiotactic sequences.

For inversion, the methine proton needs to be abstracted. Strong bases are evidently capable of this. The resulting anion would be resonance stabilized by delocalization of the negative charge onto the nitrile group. After the abstraction of the proton from an isotactic triad, the nitrile can rearrange to a syndiotactic configuration on the return of the proton, thus giving an inversion of configuration at the methine carbon. The mechanism is shown below.



Inversion due to proton abstraction by strong base. If inversion occurs as indicated above, then mm triads convert to rr triads, and mr/rm triads convert to rm/mr triads (i.e. the hetero mr/rm triads effectively remain unchanged). To prove that proton abstraction occurred, base treatment of PAN was performed using NaOD (instead of NaOMe) in the presence of deuterium oxide (D_2O). Any proton abstraction and replacement should lead to incorporation of deuterium at the PAN methine carbon sites.

A solution of 200 mg of PAN in 3 ml of d6-DMSO was treated with 0.1 ml of NaOD in D_2O (10 mg ml^{-1}). The PAN solution immediately became yellow–orange. Solution state ^{13}C n.m.r. spectra were recorded at ambient temperature immediately after addition of $NaOD/D_2O$.

Comparison of the nitrile band of the base treated PAN in *Figure 6b* with the untreated PAN in *Figure 6a* shows that NaOD caused a marked change in tacticity. The triad content, after base treatment is mm 19%, mr 51% and rr 30%, compared with mm 28%, mr 50% and rr 22% in the original PAN. In addition, the resonance pattern observed from the methine carbon sites in *Figure 7b* is more complex than that observed from untreated PAN in *Figure 7a* (a simple three-line pattern reflecting mm, mr and rr triads) and it suggests that some deuterium incorporation had occurred. To confirm this, 'spectral editing' experiments were also performed on the sample.

Figure 8a shows the unedited methine carbon signal after base addition. *Figure 8b* shows the methine carbon signals obtained using a ^{13}C DEPT (distortionless enhancement by polarization transfer) experiment[29], which detects only protonated carbon atoms. This sub-spectrum comprises the three triad resonances normally observed for (protio) PAN and therefore corresponds to protonated methine carbon sites in the polymer.

Figure 8c shows the methine carbon signal obtained from a GASPE (gated spin echo) experiment set up to detect only non-protonated carbons[30]. Again this sub-spectrum comprises three resonances, but this time shifted to low frequency compared with the protonated

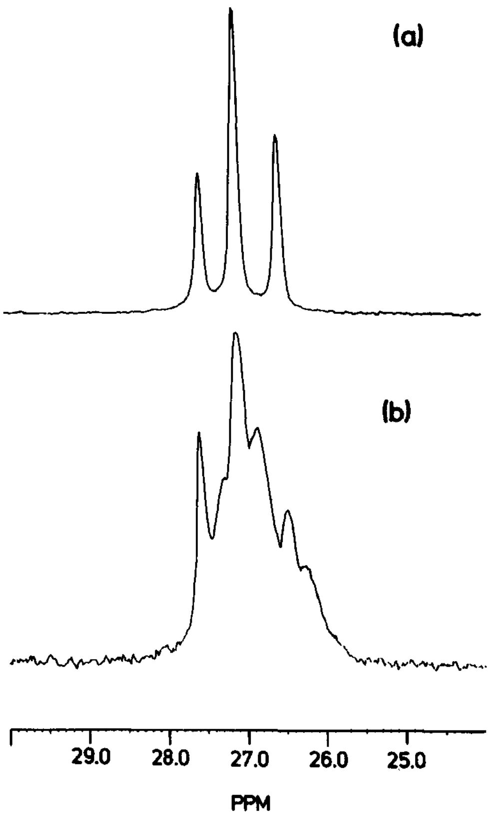


Figure 7 ^{13}C n.m.r. spectrum of PAN showing the methine carbon resonance: (a) untreated and (b) after addition of NaOD/D$_2$O, leading to deuterium incorporation

methine carbon resonances. We assign these to deuterated methine carbon atoms. The low frequency shift of these resonances reflects a deuterium isotope shift effect invariably observed between protio and deuterio analogues[31]. The resonances observed for the deuterated sites are broader than those observed for their protonated counterparts. This presumably results from poorly resolved carbon–deuterium coupling. We also note that the addition of the sub-spectra shown in *Figures 8b* and *c* yields a spectrum which closely matches the unedited ^{13}C methine signal of the sample in *Figure 8a*. Finally, examination of the methylene carbon resonances revealed that the methylene protons were not abstracted by base.

As the decrease in the isotactic triad level is complemented by an equal increase of syndiotactic triad units, we think that inversion rather than preferential cyclization of isotactic sequences is the correct explanation of the observed changes in the n.m.r. spectrum. Though monomer addition to a growing PAN chain (during polymerization) showed a slight bias towards isotacticity, when the methine proton is abstracted from the middle of a chain, it seemed to prefer adopting a syndiotactic configuration on the return of the proton, probably due to interactions from both portions of the chain, on either side of the methine carbon. The second possibility is that there is preferential chain cleavage in isotactic sequences, but there is no reason to believe this as all methine protons should be equally accessible to base due to conformational transitions in solution.

Previous demonstrations in the literature[32] of the labile nature of the methine proton have involved deuterium exchange in PAN dissolved in NaSCN/D$_2$O. Hunter[32] showed by proton n.m.r. that at 170°C there was H–D exchange, but the reaction was very slow at room temperature. Inversion could not be detected directly from proton n.m.r. of PAN but it was postulated as a possibility; however, it was implied that the overall tacticity would not change: atactic PAN would give atactic partially deuterated PAN[32]. Rhodes *et al.*[33] also showed by proton n.m.r. the isotopic exchange of the methine hydrogen during hydrolysis by acid or base, but they could not monitor tacticity changes directly in the way we have done here. We note here that inversion at the methine carbon has also been reported to occur during acid hydrolysis of PAN[34] although the mechanism for this is not clear. However, there is no indication of what we observed, namely the fact that there is a decrease of isotactic triads which is complemented by an increase of syndiotactic triads, thus resulting in a net change of tacticity.

Mechanism for chain scission and crosslinking based on methine proton abstraction. The susceptibility of the methine proton to abstraction by strong base can also explain two of the other observations, chain scission and crosslinking. The mechanism postulated by Zahn and Schaefer[35] in 1959 for chain scission is supported by the experimental observation of methine proton abstraction reported here.

The mechanism for chain scission[35] due to methine

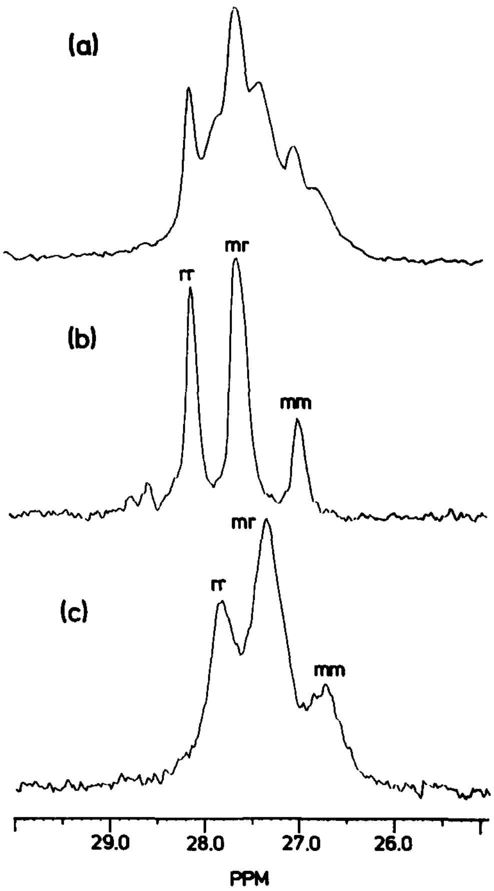
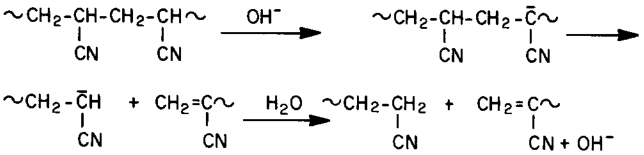
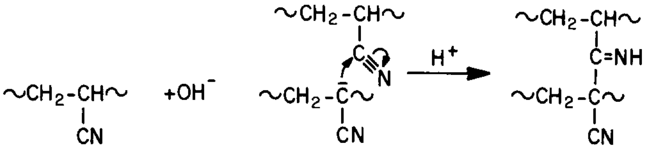


Figure 8 ^{13}C n.m.r. spectrum of PAN treated with NaOD/D$_2$O, showing the methine carbon signal: (a) unedited; (b) DEPT experiment showing only protonated carbons; (c) GASPE experiment showing deuterated carbons. Adding spectra (b) and (c) gives (a)

proton abstraction is



and that for azomethine crosslinking due to methine proton abstraction is



Azomethine crosslinking was postulated by Schurz[7,8] for thermal stabilization of PAN, whereby the nitrile nitrogen from one chain abstracted the methine proton from another chain, but there was no way of verifying this. However, the mechanism suggested above for azomethine crosslink formation due to base in solution is plausible as it is consistent with the experimentally observed methine proton abstraction and gelation reported here.

Thus we have been able to explain three of the experimental observations, drop in viscosity, inversion, and gelation, on the basis of methine proton abstraction by strong base. Coloration is a fourth effect that occurs on base addition, and though the received opinion is that this is due to cyclization, we were unable to prove (or disprove) this, as we could not detect any unambiguous evidence for conjugated (C=N).

Weak bases

Room temperature treatment with diethylamine. $(Et)_2NH$ was fully soluble in DMSO and a solution of the following composition was used: 1 g PAN dissolved in 9 ml DMSO + 1 ml $(Et)_2NH$. The DMSO–base mixture was added to the PAN powder with stirring. There was immediate coloration to orange, but the solution did not go as dark as when NaOMe or NaOEt were added, and the viscosity did not drop. *Figure 4* shows a plot of relative viscosity η_{rel} against time, where

$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}} \approx \frac{t_{solution}}{t_{solvent}}$$

which is the ratio of flow times; here the solvent was taken to mean 9 ml DMSO + 1 ml Et_2NH. As can be seen in *Figure 4*, there was in fact a slight increase in viscosity compared with a PAN solution consisting of 1 g PAN in 10 ml DMSO ($t_{solvent}$ was measured with pure DMSO). Moreover, the viscosity of the diethylamine–PAN solution did not change with time. The fact that the viscosity did not drop indicates that there was little or no chain scission. We are unable to explain the slight increase in viscosity in *Figure 4*.

^{13}C n.m.r., however, detected no changes in isotactic sequences after treatment with $(Et)_2NH$ at room temperature and the spectrum was virtually identical to untreated PAN. A number of changes were made, such as increasing the concentration of $(Et)_2NH$ and increasing the treatment time to 5 days, but there was no detectable change in the n.m.r. and i.r. spectra after room temperature treatment. Clearly, the methine proton abstraction and the subsequent reactions that ensue depend on base strength rather than the amount of base. Further, though the amine treated solution was orange in colour, the precipitated polymer had i.r. and n.m.r. spectra (not shown) identical with those of the untreated polymer. This suggested that the chromophore was present in undetectably low concentrations but was very intense.

Thus weak bases behave in the same way as strong ones, but these reactions all occur at a very slow rate under ambient conditions. Reactivity with respect to coloration, chain scission and gelation clearly followed the order of base strength: $(Et)_2NH < NaOH < NaOEt < NaOMe < BuLi$.

PAN solutions treated with $(Et)_2NH$ and heat. To see if the reaction rate could be increased, the above composition (1 g PAN in 9 ml DMSO + 1 ml $(Et)_2NH$) was heated to 70°C for 24 h. Such heating caused further darkening compared with solutions treated at room temperature but the solutions did not darken as much as methoxide treated PAN. The viscosity increased, probably due to a limited amount of crosslinking, but there was no gelation. N.m.r. examination of the above $(Et)_2NH$/heat treated PAN solutions showed no detectable changes in tacticity.

In a second experiment, a PAN solution of the same composition was heated for 72 h at 70°C followed by 3 h at 150°C. Now ^{13}C n.m.r. detected a 7% drop in isotactic triad content and a corresponding increase in syndiotactic triad content. As with strong bases, there was no indication of where these triads had disappeared to; there was no evidence of conjugated C=N in the n.m.r. Thus the results obtained with strong bases can be reproduced with weaker bases but with the addition of heating.

CONCLUSIONS

The starting premises of this work were that cyclization of PAN could be achieved in solution by base treatment and that isotactic sequences cyclize preferentially. This was based on previous reports in the literature. However, our investigation does not support this.

Strong bases like NaOMe and BuLi appear to have five main effects:

(1) coloration;
(2) initial viscosity drop;
(3) gelation after a certain period;
(4) hydrolysis of nitriles; and
(5) enrichment of syndiotactic triads at the expense of the isotactic triads.

Effects 1, 2 and 4 have been noted in the literature, but 3 and 5 have not been reported. Using $NaOD/D_2O$ led to deuterium incorporation on the chain. This showed that the strong bases abstracted the methine proton, which could explain the viscosity drop (chain scission) and gelation (crosslinking). Enrichment of syndiotactic triads could be due to inversion of configuration after methine proton abstraction and/or due to selective cleavage of isotactic triads.

An intensely coloured chromophore(s), present in extremely low concentrations, is responsible for the coloration; it may be that the cyclized units are indeed the chromophores, but the concentration even in red–black solutions is so low that it cannot be detected in the n.m.r. or i.r. spectra. Thus cyclization remains an unproved postulate; colour cannot be used as direct evidence for cyclization.

Weak organic bases such as $(Et)_2NH$ did not cause rapid chain scission or gelation at room temperature. No change in tacticity was detected. All this is consistent with the fact that weak bases do not abstract the methine proton at room temperature. Coloration still occurred but was milder than that induced by strong bases. On prolonged heating at 150°C with diethylamine, further darkening took place, and a drop in isotactic triads was then detected. Prolonged heating also caused gelation. This is consistent with methine proton abstraction by weak base at elevated temperatures.

As a sequel to this work we shall be reporting analogous experiments on base treatment of polymethacrylonitrile. The results of that investigation are complementary and support the conclusions drawn here.

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