Base-induced gelation of polymethacrylonitrile

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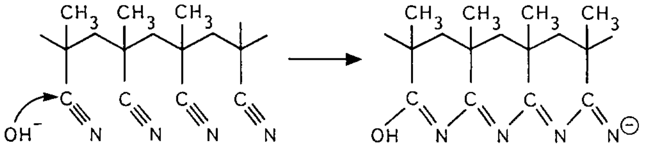
It is commonly stated that polyacrylonitrile (PAN) and polymethacrylonitrile (PMAN) undergo a cyclization reaction, which may be thermally induced or caused by addition of base to a polymer solution. However, in our previous work with PAN, no evidence for cyclization was found; instead, it was shown that base could abstract the methine proton leading to azomethine crosslinking and gelation. PMAN has no methine proton and hence this crosslinking mechanism should not operate. However, when strong base was added to a PMAN solution, gelation still occurred. It is proposed that base also induces intermolecular nitrile crosslinking reactions. No evidence for cyclization was found in base-treated or thermally treated PMAN. The results of dynamic mechanical testing of thermally discoloured PMAN films were also more consistent with a slight degree of crosslinking rather than extensive cyclization.

(Keywords: gelation; crosslinking; base; polymethacrylonitrile; polyacrylonitrile; cyclization)

INTRODUCTION: PREVIOUS WORK ON BASE TREATMENT OF POLYACRYLONITRILE

Recently, we investigated the base treatment of polyacrylonitrile (PAN)[1]. It was reported that, in PAN solutions, base caused colouration, chain scission, crosslinking and a partial inversion of configuration. Colouration by base has been attributed in the literature to cyclization[2], but we were unable to detect any direct evidence for this. Even if cyclization occurred to any significant extent, the acidity of the methine proton in PAN led to proton abstraction and crosslinking reactions[1]. This led to gelation, which hampered efforts to detect cyclization by solution-state n.m.r.

It is reported in the literature that polymethacrylonitrile (PMAN) also colours just like PAN, when heated, or when base is added to the polymer solution[3]. Again cyclization has been suggested[3,4] as shown below:



Now, if base-induced cyclization does occur to any significant extent, then PMAN would be a better candidate for assessing the degree of cyclization, as the absence of the methine proton in PMAN means that base would not induce gelation via the proton abstraction and azomethine crosslinking reaction we proposed for PAN[1].

Thus, this work aims to ascertain whether there is real basis to the claims made for cyclization. Two methods were chosen to try to achieve this. First, base was added to concentrated PMAN solutions to induce cyclization, and evidence for the presence of conjugated C═N species was sought. Secondly, a thermal process was used to induce colouration and (possible) cyclization of PMAN powder. This was followed by dissolving the coloured powder to form a concentrated solution, which was then examined for the presence of conjugated C═N.

EXPERIMENTAL: POLYMERIZATION AND CHARACTERIZATION

Free-radical polymerization of methacrylonitrile

PMAN, unlike PAN, is soluble in its monomer, thereby enabling emulsion polymerization to be carried out easily[5]. The polymerization was performed as a single batch reaction over a period of 18 h under an inert atmosphere of nitrogen. A thermally dissociative initiator, $K_2S_2O_8$, was used at a temperature of 60°C. The general recipe is shown below:

20% methacrylonitrile
80% demineralized water (deoxygenated)
0.5% surfactant (sodium dodecylsulphate)
0.25% $K_2S_2O_8$ initiator

Surfactant and initiator quantities were calculated as per cent w/w on monomer. The reaction exotherm was mild and a stable latex was produced with a solids content of 19%. The conversion of monomer to polymer was 95%. The polymer was isolated by a freeze-thawing technique and dried at 40°C.

Characterization of PMAN prepared by free-radical polymerization

Tacticity of PMAN by ^{13}C n.m.r. The tacticity of free-radically polymerized PMAN had to be characterized by carbon-13 n.m.r. spectroscopy before the experiments on base treatment could be conducted. PMAN can show differences in stereoregularity, depending on the method of polymerization.

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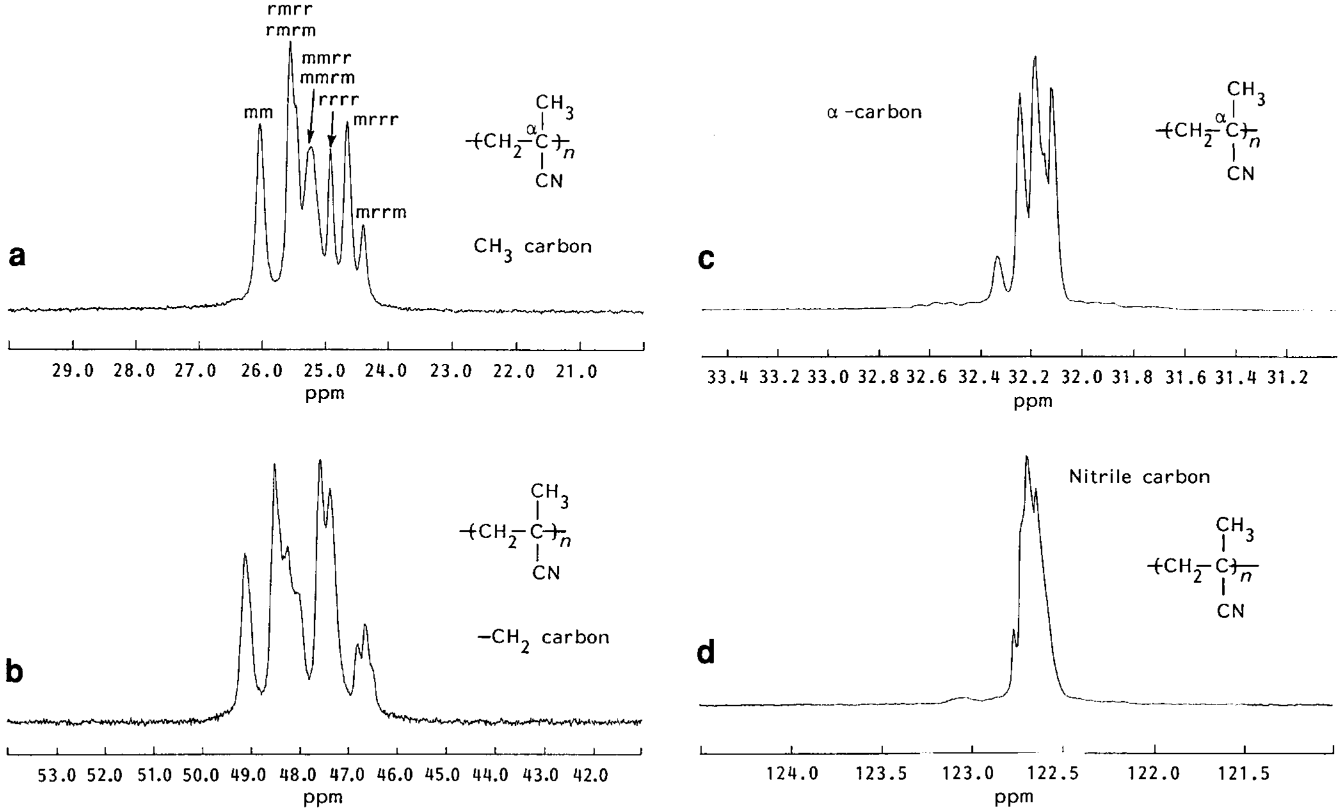

Figure 1 The solution-state ^{13}C n.m.r. spectra of polymethacrylonitrile: (a) methyl carbon resonance; (b) methylene carbon resonance; (c) α carbon resonance; (d) nitrile carbon resonance. The spectra do not change after addition of strong base. In polyacrylonitrile, a change in tacticity is observed in the spectra as soon as strong base is added

Table 1

Pentad	Abundance		Notes
	Measured	Calculated	
mmmm *mmmr* *rmmr*	0.19	0.19	Isotactic; pentads not fully resolved
rmrr *rmrm*	0.28	0.28	Heterotactic; pentads not resolved
mmrr *mmrm*	0.21	0.21	
mrrm	0.06	0.06	Syndiotactic; pentads fully resolved
mrrr	0.15	0.15	
rrrr	0.11	0.10	

The PMAN spectra are shown in *Figure 1*. In PAN, the triad tacticity can be measured from the methine carbon while the pentad tacticity can be determined from the nitrile carbon resonance[1]. In PMAN, the methyl carbon resonance instead of the nitrile carbon resonance proved to be the most useful for pentad tacticity determination[7]. The methyl carbon gives rise to six resonances centred at ~25 ppm (*Figure 1a*). Of these, the three signals to low frequency are due to the three syndiotactic *rr*-centred pentads (i.e. *mrrm*, *mrrr* and *rrrr*). The two central resonances are due to the heterotactic *mr*-centred pentads (i.e. *mmrm*, *rmrm*, *mmrr* and *rmrr*, where the peaks arising from the first two overlap, as do the peaks from the last two). The remaining resonance at high frequency is due to isotactic *mm* triads, for which pentad chemical shift sensitivity is not resolved.

From the areas under these signals it has been established that the polymer propagation mechanism follows Bernouilli statistics[1,8], where the probability of *m* (meso) addition to a polymer chain end is $P_m = 0.435$ and the probability of *r* (racemic) addition to a chain end is $P_r = 0.565$. Thus, our PMAN showed a slight tendency towards syndiotacticity, unlike free-radical PAN, which showed a slight bias towards isotacticity[1]. For an ideally random polymer, $P_m = P_r = 0.5$. Observed and calculated pentad abundances[1] are given in *Table 1*.

From the remainder of the spectra (*Figures 1b–d*), we note that the methylene carbon also shows a marked chemical shift dependence on tacticity, giving rise to partially resolved tetrad resonances (*Figure 1b*). Similarly, the α carbon of PMAN shows resonances assignable to triad/pentad sequences (*Figure 1c*). Surprisingly, the nitrile carbon resonance of PMAN in *Figure 1d* shows little splitting, which is in marked contrast to PAN, where the pentad tacticity was well resolved in the nitrile carbon resonance[1]. Further work to explain this difference is in progress.

Crystallinity of PMAN. It has been reported[6] that PMAN can show not only differences in tacticity but varying degrees of crystallinity depending on the method of polymerization. Hence, the crystallinity was checked by wide-angle X-ray diffraction. The sample used was an acetone cast film, which was dried overnight in an oven at 70°C. Nickel-filtered Cu Kα radiation was used. The X-ray diffraction picture (not shown) indicated that the polymer was amorphous.

Thermal analysis

Differential scanning calorimeter (d.s.c.) studies were conducted on PMAN using a Du Pont 910 DSC/9900 computer thermal analyser. The polymer powder was heated in open pans at $10^\circ C\,min^{-1}$ from ambient temperature to 450°C in air.

Dynamical mechanical properties of moulded sheets of PMAN, before and after thermal discolouration, were measured using a DuPont 983 DMA/9900 computer thermal analyser. The instrument was fitted with a liquid-nitrogen cooling accessory (model LNCA II) to allow subambient operation to −170°C. Samples were made into 10 mm wide strips, 15 mm long. Measurements were made from −100 to 150°C at a heating rate of $4^\circ C\,min^{-1}$ with a fixed oscillation frequency of 1 Hz.

RESULTS

Base treatment of PMAN

In situ *n.m.r. study of the effect of base on PMAN tacticity.* An *in situ* n.m.r. experiment was conducted in order to see if any of the cyclized species alleged to be responsible for colour could be detected, and to check whether any tacticity changes occur (similar to that which occurs in PAN) on addition of strong base[1].

A solution of PMAN (200 mg in 3 ml DMSO-d_6) was treated with approximately 2 mg sodium methoxide (NaOMe), which caused the solution to become orange-red in colour. The sample was transferred to an n.m.r. tube and its ^{13}C n.m.r. spectrum was recorded at 353 K. Comparison of the spectrum with that of untreated PMAN indicated that no detectable changes in tacticity had occurred, unlike PAN, where an immediate partial inversion of configuration was detected[1]. Moreover, no new species indicating cyclization were detected. The sample was maintained at 353 K and its spectrum was re-recorded after 2 h. Again, no change was seen and the spectra were identical to the originals in *Figure 1*, which are from untreated PMAN.

One possibility is that base treatment leads to abstraction of α methyl protons, thereby providing a mechanism for crosslinking. If these protons are labile in the presence of base, then treatment of PMAN with sodium deuteroxide/D_2O should lead to incorporation of deuterium at the α methyl sites. However, the carbon-13 n.m.r. spectrum of a solution of PMAN (200 mg in 3 ml DMSO-d_6), which had been treated with 0.1 ml of a solution of NaOD in D_2O ($10\ mg\ ml^{-1}$), was identical to that of untreated PMAN. Thus, the α methyl protons of PMAN are not labile under the chosen conditions.

Viscosity changes and gelation in PMAN solutions on addition of base. Unlike PAN, no initial drop in viscosity was detected on addition of strong base to PMAN. In fact, an increase in viscosity was found on addition of base to PMAN. On addition of 25 mg of NaOMe to a 10% w/v solution of PMAN in DMSO, it turned red in colour but formed a red gel when left overnight. A control solution of PMAN with no base was transparent and did not gel. In our previous work, we explained the base-induced gelation of PAN in terms of methine proton abstraction leading to crosslinking via an azomethine linkage[1]. In the case of PMAN, there is no methine proton, so this gelation needs to be explained and will be discussed later.

Attempted cyclization by thermal treatment of PMAN

As PMAN solutions unexpectedly gelled when base was added, an alternative route to examine colouration and cyclization was attempted. Accordingly, white PMAN (nascent powder) was heated at 200°C for 1 h till a maroon coloured powder was obtained. The literature attributes this to cyclization. A small amount of dimethylsulphoxide (DMSO) was added to the maroon powder to form a concentrated solution. The heat-treated polymer swelled and formed a red, rubbery material, which had the flow properties of a gel. The red polymer was not sufficiently soluble for solution-state n.m.r.

D.s.c. and d.m.a. studies of thermally treated PMAN films. These experiments also shed some light on colouration and cyclization in PAN and PMAN. The d.s.c. traces of PMAN and PAN are shown in *Figure 2*.

Dynamic mechanical analysis (d.m.a.) is not a technique that has been used to study cyclization of PAN or PMAN. However, in the case of PMAN, d.m.a. can

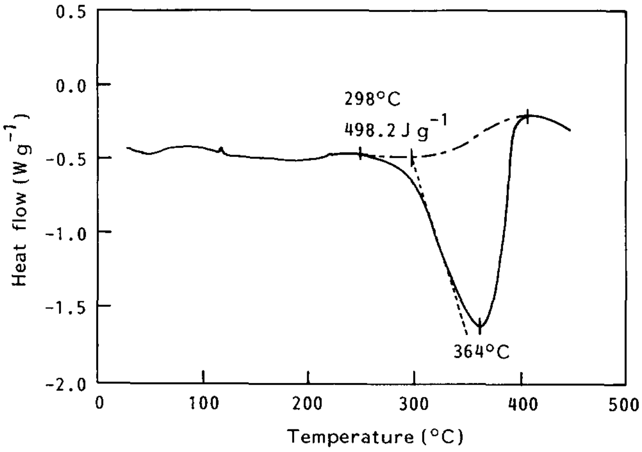

Figure 2 Differential scanning calorimeter trace showing the thermal behaviour of amorphous PMAN on heating. PMAN turns red-black at about 200°C when heated in air, yet there is no reaction exotherm at any temperature. There is in fact a depolymerization endotherm. In contrast, when PAN is heated, there is colouration, accompanied by a violent exotherm at 320°C, which is often attributed to a cyclization reaction

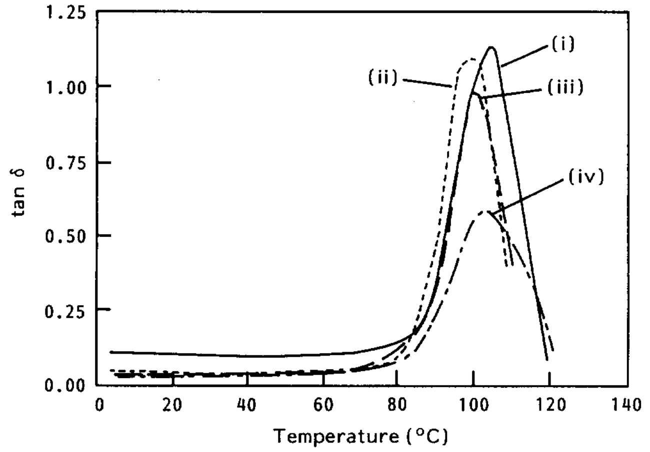

Figure 3 Dynamic mechanical data obtained from PMAN films before and after heat treatment, showing tan δ plots: (i) transparent film moulded at 180°C from nascent powder; (ii) after heating film at 200°C for 30 min; (iii) after 200°C for 1 h; and (iv) 200°C for 2 h. The heat-treated films (ii)–(iv) were red-black

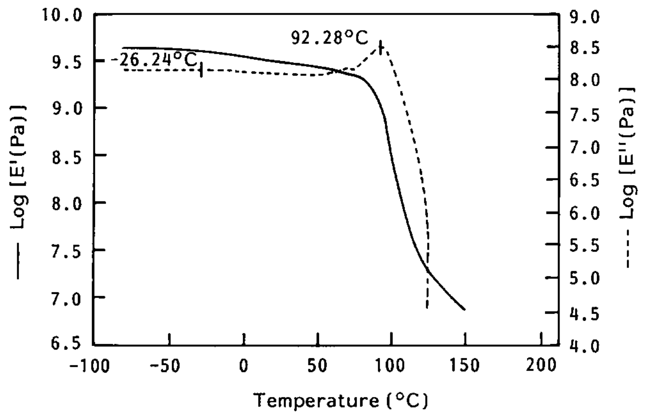

Figure 4 Storage and loss moduli, E' and E'', of red-black films heated at 200°C for 2 h. The storage modulus drops by three decades, suggesting the polymer is not stiff backboned with cyclized units. Despite the colour change, there is no evidence for cyclization and the drastic drop in E' is more reminiscent of a flexible backboned polymer

be used to obtain indirect information on molecular structure. Transparent PMAN films were moulded at 160°C as PMAN is thermoplastic. Some of these films or sheets were thermally 'stabilized' at 200°C for various times (30, 60 and 120 min), which caused them to go red-black. The dynamic mechanical properties of PMAN sheets before and after heat treatment at 200°C are shown in *Figures 3* and *4*.

DISCUSSION

Base treatment of PMAN

Tacticity changes in PMAN and PAN. Our previous work with PAN showed that strong bases abstracted the methine proton and this allowed a partial inversion of configuration, leading to a 10% decrease in isotactic triads and a complementary increase in syndiotactic triads[1]. The absence of any tacticity change in PMAN on addition of base should be expected as the PMAN cannot undergo inversion via a proton abstraction mechanism. This result complements the results obtained with PAN previously. Further, as with PAN, there was no evidence for C=N sequences or cyclization in the n.m.r. spectrum of coloured PMAN solutions.

Gelation of base-treated PAN and PMAN solutions: intermolecular nitrile reactions. In PMAN, we did not observe a drop in viscosity because there is no methine proton to abstract and cause chain scission[1] as in PAN. Grassie and Hay have suggested 'propagation crosslinks' whereby cyclization skips from one chain to another during solid-state stabilization of PAN[9]. But they say[9] 'When the reaction [i.e. cyclization] is initiated by alkali in solution, crosslinking is inhibited by the separation of molecules and deeply coloured, homogeneous solutions are obtained.' This would give cyclization as in *Figure 5a.*

However, it is clear that, in a 10% solution, there are crosslinking reactions which cause gelation. As gelation in PMAN cannot occur (as in PAN) via the azomethine crosslink, the only available mechanism is through intermolecular nitrile reaction as shown in *Figure 5b.* This does not mean that intra- and intermolecular reactions are exclusive to each other, as in reality both can occur, and this is shown in *Figure 5c.* This indicates

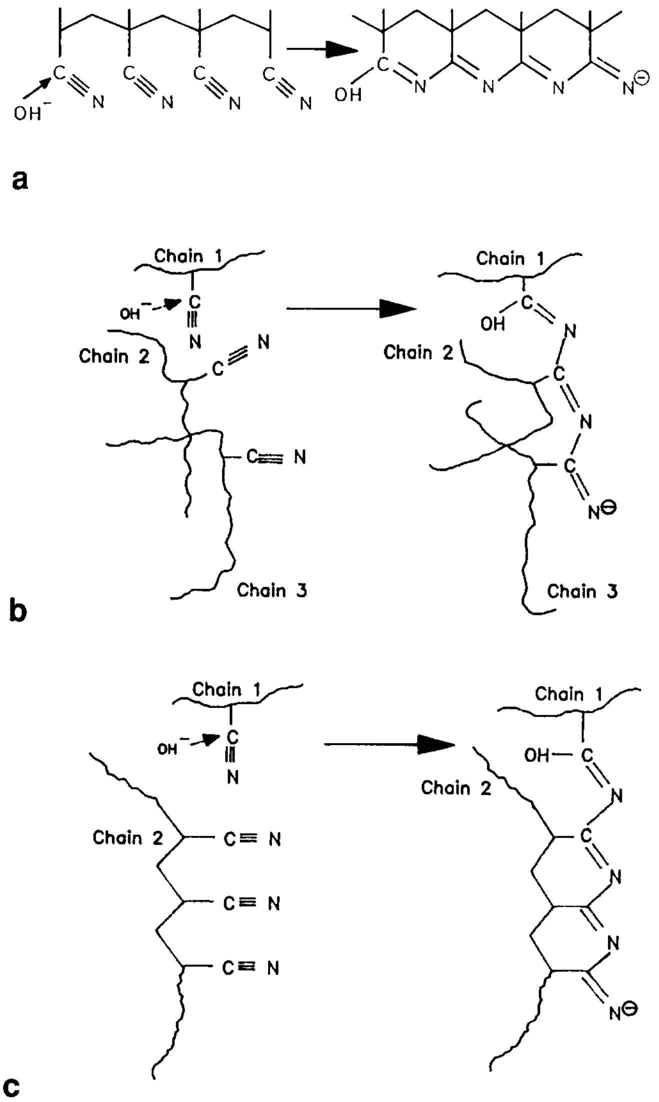

Figure 5 Intra- and intermolecular reactions of nitriles. (a) Conventional base-induced cyclization scheme giving fused six-membered rings with conjugated (C=N) sequences. (b) Base-induced intermolecular reaction of nitriles can give crosslinking of two or more chains and also conjugated (C=N) sequences. Note chain backbones are just drawn as lines without showing bonds. (c) Combined intra- and intermolecular reaction, giving crosslinking and cyclization (a combination of (a) and (b))

that in a 10% PMAN solution, there is the possibility for the crossover of cyclization and we think *Figure 5c* is the most realistic representation of what happens. This would account for the fact that the homogeneous red solutions turn into red gels.

If we look back on the previous work on PAN[1], it must be accepted that the intermolecular nitrile reaction proposed here for PMAN can also occur in PAN, in addition to the azomethine-type crosslink. However, this is masked by the initial drop in viscosity that occurs due to chain scission in PAN. Subsequent gelation in PAN can be regarded as a result of the azomethine-type linkage proposed previously, as well as the intermolecular nitrile reaction suggested here. Thus, in PAN two mechanisms can operate, while in PMAN there is only one mechanism for crosslinking.

Thermally coloured PMAN

Swelling of thermally coloured PMAN. Swelling of the thermally treated red powder in DMSO gave a solvent-swollen red material, which deformed like a piece of rubber, regaining much of its original size when the deforming stress was removed. This suggested that the red polymer was slightly crosslinked, rather than extensively cyclized; it was no longer as soluble as the nascent, white powder but it swelled in the usual solvents for the polymer. This behaviour is commonly observed with lightly crosslinked polymers such as vulcanized rubber swollen with a hydrocarbon solvent. Again, this result is consistent withs light crosslinking rather than extensive cyclization.

D.s.c. and d.m.a. of thermally coloured PMAN. PMAN is known to degrade above 250°C by depolymerization to monomer[10]. Unlike PAN, there is no stabilization exotherm which can be attributed to cyclization. After the exotherm, PAN is virtually black in colour and this has also been attributed to cyclization. However, in PMAN we observe that the polymer goes red-black very quickly at 200°C, though the d.s.c. in *Figure 2* shows no exotherm at this temperature and instead shows a depolymerization endotherm at a higher temperature. Since it is argued that intramolecular cyclization is associated with both the colouration and the exotherm in PAN, then this argument is not consistent with the observation that, in PMAN, intense colour is obtained without any exotherm.

Our free-radical PMAN was an amorphous polymer and, in the molten state, heat was more likely to induce intermolecular nitrile reaction than cyclization. For the 'planar' cyclization scheme commonly quoted in the literature, the adjacent nitrile groups on a chain have to be in the right configuration and conformation (i.e. isotactic sequences in an all-*trans* conformation). In an amorphous polymer, such sequences would be rare and chain mobility even above T_g is not great enough to allow many nitriles to get into a position for such a planar cyclization. It is more probable that, in an entangled, unordered system such as would be found in amorphous PMAN, nitriles of different chains are likely to meet each other. Intermolecular reactions would be even more probable than intramolecular cyclization in the undiluted molten state. As in solution, a combination of the two types of reaction could lead to a small concentration of conjugated structures that could account for the colour.

Figure 3 shows the tan δ peaks for the heat-treated and untreated PMANs on the same plot. The treated samples were red-black, the untreated one was transparent. It can be seen that there is little difference in mechanical properties between the untreated sample (*Figure 3*(i)) and the one heated for 1 h at 200°C (*Figure 3*(iii)) despite the marked change in colour. In the untreated sample in *Figure 3*(i), the damping peak at the glass transition is at 105°C; a prominent glass transition is still observed in the heated sample in *Figure 3*(iii) with a large tan δ peak at 101°C. There is however a reduction in the damping after heat treatment as shown in *Figure 3*(i) and (iii). Despite the colour difference between the samples in *Figure 3*(i) and the heated samples of (ii), (iii) and (iv), this is more consistent with a flexible chain polymer that has become slightly crosslinked rather than an extensively cyclized polymer. Even after a 2 h treatment (*Figure 3*(iv)), T_g remains around 104°C, though tan δ maximum has now decreased to 0.6. The decrease in tan δ without a shift in T_g after 2 h heat treatment is also consistent with crosslinking rather than cyclization. A highly cyclized polymer would have a stiff backbone and the result should be that T_g should increase.

Figure 4 shows that for the PMAN heated at 200°C for 2 h, the storage modulus E' drops by three decades after the glass transition, as is observed with other polymers with flexible backbones. With stiffer backboned polymers like poly(ether ether ketone) and liquid-crystal polymers, we found that the storage modulus E' did not drop so drastically near the glass transition.

It seems that strong colouration after thermal treatment in the molten state appears without much change in molecular structure. As in solution, this change is not exclusively due to cyclization, but is due to a small amount of both intra- and intermolecular nitrile reactions, which lead to very intense chromophores.

CONCLUSIONS

The aim of the investigations on PAN[1] and PMAN was to see if base induces cyclization. The literature suggested that solution cyclization would give chains with rigid cyclized species, 3–5 units long, separated by flexible spacers of acrylonitrile or methacrylonitrile units[9,10].

However, the current investigations show that even 10% homogeneous PAN or PMAN solutions turn to red gels when strong bases are added. This is due to various intermolecular nitrile reactions. Intramolecular cyclization, if it occurs in solution, does not take place to a high degree of conversion, and is below the detection limit of the instrumental technique available to us; this is contrary to suggestions in the literature[3,4]. In the literature, it is often accepted that the colour arising on addition of base is due to cyclization, but we think that it is due to an unidentified chromophore which is very intense. In a 10% solution, the chains are close enough for crosslinking reactions. Thus, a mixture of intra- and intermolecular reactions occur in solution and there is no indication that pure cyclization can be obtained with rigid chain units separated by flexible spacers.

In thermally coloured PMAN also, there was no indication of cyclization. The dynamic mechanical tests on discoloured PMAN again pointed to a small degree of crosslinking rather than to extensive cyclization as the glass transition temperature remained unchanged despite the change in colour. The chromophore was again very intense but could not be identified as it was present in very low concentrations after the thermal treatment used.

Finally, the results obtained on base treatment of PMAN are in accord with our previous results on PAN. We had found that addition of strong bases to PAN lead to chain scission and inversion of configuration. We attributed this to the base abstracting the methine proton in PAN[1]. In PMAN, there is no methine proton and consequently no chain scission or inversion of configuration was observed.

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