STUDIES ON THE CYCLISATION OF POLYACRYLONITRILE

by

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ABSTRACT

The low temperature stabilisation reaction is an important stage in the production of carbon fibres from polyacrylonitrile. The resultant structure contains cyclised sequences, which enable the fibres to withstand carbonisation without disintegrating. In this thesis a technique has been developed to cyclise polyacrylonitrile using chemical additives. The reactions have been carried out under closely controlled experimental conditions at temperatures between 273 and 333 K.

The reaction of polyacrylonitrile solutions with n-butyllithium has been investigated for a series of experimental conditions. Isolation of the reaction products at various stages enabled a cyclisation mechanism to be proposed, from qualitative studies, using spectroscopic and thermal analysis techniques. Quantitative analyses established the relationship between the reduction in nitrile concentration and n-butyllithium concentration, as a function of reaction time. The extent of cyclisation was determined to be directly proportional to the residual enthalpy, recorded when the partially cyclised products were analysed using differential scanning calorimetry.

A reaction model was developed, invoking a simple two stage reaction to describe the cyclisation of polyacrylonitrile with n-butyllithium. Both stages were found to be first order with respect to nitrile concentration.

The chemical cyclisation reaction in polyacrylonitrile has also been proposed to be a possible substitute for the low temperature stabilisation reaction, as a precursor to carbon fibre production.
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The use of carbon fibres in a wide range of engineering applications, and their importance in modern technology, has been widely documented. The aims of carbon fibre research have been broadly threefold, and can be summarised as follows:

(i) To establish the nature of the chemical reaction which stabilises the precursor fibre prior to carbonisation.
(ii) To optimise the production conditions to attain the ultimate properties.
(iii) To modify the production process. Carbon fibres are produced by a three stage process, so a reduction in the time of any stage, or possibly the elimination of a step, could improve the economics of carbon fibre production.

The work presented in this thesis is primarily concerned with chemical reactions of the precursor polymer, and the possible use of chemical methods to modify the carbon fibre process. Although the emphasis of the following discussion will be the elucidation of chemical structures, it is of interest to summarise, briefly, the historical background to the methods of carbon fibre production.

Carbon fibres are attractive since they combine high modulus and strength over a wide temperature range. However, they are by no means a recent development. As early as 1880, carbon filaments were produced from cellulose\(^1,2\) and at the turn of the century, regenerated cellulose fibres were used as a carbon fibre precursor.\(^3\) Recently, interest in high strength fibres has revived interest in exploiting these early processes.

Carbon fibre production came to the fore in the 1950's, since when many materials have been considered as precursors. To qualify as
a suitable precursor a high carbon yield is essential, while to maintain the original fibre structure, fusion must not occur on heating.

Three materials have found commercial importance in carbon fibre production:

(i) Polyacrylonitrile (PAN) fibre; favoured in the U.K.
(ii) Regenerated cellulose fibres; favoured in the U.S.A.
(iii) Fibres spun from pitch.

Although processing the various precursors is not identical, three major stages are required for conversion to carbon fibres; low temperature stabilisation, carbonisation to remove non-carbonaceous elements, and a high temperature treatment to optimise the mechanical properties. The low temperature treatment is usually carried out in an oxidising atmosphere. Shindo\(^4,5\) published the first details for producing carbon fibres from oxidised PAN, the process was patented in 1962.\(^6\) Both Rolls-Royce Ltd.\(^7\) and R.A.E. Farnborough\(^8\) improved on Shindo's mechanical properties by restraining the fibres, to prevent shrinkage during the low temperature stabilisation reaction.\(^9-11\)

Tows of wet spun PAN fibres were oxidised under constraint in air, at 493 K. The black fibres were subsequently carbonised in an inert atmosphere, between 1273-1773 K. The high degree of molecular order in the precursor fibres was maintained, by using a sufficiently slow heating rate. The subsequent high temperature treatment was chosen to yield a high strength or high modulus fibre. Figure (1) shows a plot of tensile strength and modulus as a function of treatment temperature, indicating the dependence of the ultimate fibre properties on the temperature.

PAN is an attractive carbon fibre precursor, coupling good mechanical properties with high carbon yields. More than 50% by weight of the original fibre is retained as carbon\(^12\), compared with a
Figure (1) The variation of tensile strength and modulus with heat-treatment temperature for some PAN-based fibres of circular cross-section. (9)
typical yield of 15% from cellulose. Commercially, PAN is copolymerised to improve the production process. Courtelle is the major PAN based precursor in the U.K., and consists of approximately 93% PAN, 6% methylacrylate, plus 1% itaconic acid, added to aid dyeability. The copolymer can be stretched more readily than the homopolymer, which increases the degree of orientation prior to carbonisation. The acidic groups promote the stabilisation reaction by acting as initiators. Courtelle can be converted into carbon fibres with improved mechanical properties with rapid carbonisation, \(^{(13,14)}\) compared to the homopolymer.

When PAN is subjected to the low temperature treatment, it is converted from a linear polymer into a thermally stable structure. The chemistry of this process is well established when the reaction is carried out in an inert atmosphere. The precise nature of the reaction in the presence of oxygen is less well established. The structures and mechanisms proposed in the literature for thermally treated PAN, and the influence of a variety of additives on the reaction will be considered in subsequent sections.

The preceding summary has indicated that the three stage production scheme for carbon fibres is energetically expensive. Emphasis has therefore been placed on modifying the process to reduce its energy requirements. The use of additives to modify the first stage by chemically inducing thermal stability prior to carbonisation could obviate the need for an oxidation stage. Should oxidation prove essential, prior stabilisation with additives may reduce the oxidation time, or enable the temperature to be altered to accelerate the thermal reaction.

Some workers have investigated the effect of additives on the thermal stability of PAN, but few attempts have been made to qualify and subsequently quantify such reactions, and to relate the resulting
structure to the production of carbon fibres.

The work presented in this thesis has concentrated on the reaction of PAN with additives to induce thermal stability in the polymer to enable it to withstand direct carbonisation.
2.1 Introduction

The mechanical properties of PAN fibres deteriorate when they are heated in inert or oxidising atmospheres. Thermal stability can be induced by heating the polymer under specific conditions. This is the major step in the production of good carbon fibres.

Thermal stabilisation is a result of chemical changes in the polymer which are manifest by a progressive change of a single spectral colour. The original white homopolymer changes from light to deeper shades of brown on heating, rather than progressing through the spectrum from yellow to red as for polymethacrylonitrile.\(^{(15)}\) The extent of the colour change is greater in oxidising atmospheres, while occurring at higher temperatures, than in inert atmospheres. The colour change is accompanied by a vigorous exotherm, simultaneous reduction in nitrile concentration and a small weight loss.\(^{(16,17)}\) Many workers have postulated molecular rearrangement rather than chain scission reactions to account for these observations. The resultant structure consists of sequences with a ladder structure produced by the polymerisation of the pendant nitrile groups, and separated by unreacted nitrile groups.

In an inert atmosphere the mechanism is believed to be relatively simple whereas in an oxidising atmosphere the thermal structure is subsequently oxidised.

The theories of cyclisation will be discussed together with a summary of the various structures and mechanisms which have been proposed in the literature. Furthermore, the effect of various additives on the cyclisation reaction will be discussed. The use of chemical methods as an alternative to the thermal stabilisation process will also be considered.
2.2 Formation of a ladder polymer

Thermal stability can be induced by cyclising the linear polymer to produce a ladder polymer, with enhanced stability; since more than one bond needs to be broken to cause chain scission in a ladder sequence. Consequently the reduction in mechanical properties on heating would be minimised.\(^{(18)}\)

Thermal stability in PAN is thought to be a result of ladder formation on heating. The ladder polymer is produced by the secondary addition polymerisation of the pendant nitrile groups. The extent of cyclisation is governed by a number of factors; the physical nature of the polymer particularly the presence of abnormalities and impurities, the atmosphere, the presence of additives or comonomers, and the rate of heating.

Random self-initiation of the cyclisation reaction is thought to occur. Grassie\(^{(19)}\) for example, has proposed a cyclic transition state, shown in Figure (2), with the formation of some isolated nitrile groups. The initiating species could then react in any direction along the polymer chain, producing interruptions to the ladder sequences. Therefore reaction of all the nitrile groups would appear to be impossible, since the initiation reaction gives rise to isolated nitrile groups. Similarly, reaction in opposite directions would lead to isolated groups. Experimentally 20% of nitrile groups are reported to remain unreacted. Noh and Yu\(^{(20)}\) attributed this value to the random thermal initiation which produced an unreactable nitrile in a ring. Therefore cyclised PAN was concluded to consist of an imperfect structure of ladder sequences with a variable number of condensed rings, separated by isolated nitrile groups.

2.3 The exothermic reaction in PAN

It has been generally concluded that the exotherm observed when PAN is heated, is a consequence of the secondary polymerisation of the
Figure (2) The self initiation mechanism proposed for the thermal cyclisation reaction in PAN. (19)

\[
\begin{align*}
I & \\
\text{CH}_2\text{C}_n\text{NH} & \rightarrow \text{C}_n\text{N} + \text{NH}_3 \\
II &
\end{align*}
\]

Figure (3) Mechanisms proposed for the evolution of ammonia during the thermal cyclisation reaction in PAN. (25)
In contrast, Hay, while fundamentally agreeing with the proposed cyclisation reaction, postulated three competing thermal degradation reactions:

(i) coloration by nitrile polymerisation.

(ii) evolution of ammonia from terminal cyclic structures either unimolecularity or bimolecularity.

(iii) chain scission and decomposition.

The exotherm was directly associated with the evolution of ammonia, for which two mechanisms were proposed, both of which succeed the cyclisation reaction. Figure (3) illustrates the mechanisms, structure (I) showing ammonia evolved during the subsequent aromatisation of the cyclised molecules, while structure (II) invokes the termination of two oppositely propagating imine sequences to produce ammonia. The latter mechanism was thought to be rather unlikely for two reasons. Firstly there would be a large number of residual nitrile groups to be accommodated into the structure, while it has been shown that 80% of nitrile groups react on heating. Secondly the stereochemistry is such that the probability of two terminal groups at the end of long cyclised sequences reacting must be limited. Further evidence against Hay's proposal is the small reduction in weight when PAN is heated through the exotherm. Cyclised lengths must be large, which results in small quantities of ammonia being evolved. Therefore stereochemistry does not favour Hay's proposal. It will be proposed in section (6.6) that the residual nitrile groups are produced because they are sandwiched between cyclised sequences. Where nitrile groups have been totally isolated, further reaction could only occur via an intermolecular crosslinking reaction, for which no evidence has been reported, at this low temperature.
The reduction in weight observed when PAN was heated through the exotherm has been attributed to the formation of small fractions of low molecular weight compounds such as hydrogen cyanide and ammonia. Chain fragmentation has also been reported.\textsuperscript{(26-29)}

The exotherm is characteristically sharp when observed in both inert and oxidising atmospheres. The peak maximum temperature is reported to be approximately 548 K in an inert atmosphere, and about 598 K in an oxidising atmosphere.

2.4 Cyclisation of PAN in an inert atmosphere

The thermal behaviour of PAN heated in an inert atmosphere has been well established. Therefore, the structure and reaction mechanisms proposed in this case will be used as a model for subsequent reactions. Additives used to modify the reaction, including oxygen, comonomers and chemical species will be discussed in terms of their effect on the model structure. Generally, reaction mechanisms have been proposed by the identification of the structures formed on heating. Therefore the various structures proposed in the literature will be summarised, and an attempt will be made to identify the initiation and propagation mechanisms.

Houtz\textsuperscript{(30)} attributed the colour formation observed when PAN is heated to a cyclisation reaction, and proposed a condensed pyridine structure, shown in Figure (4.1), to account for his observations. The structure resulted from cyclisation and dehydrogenation. However his experimental conditions were obscure and in the absence of oxygen containing groups it was unclear how oxidation could produce an aromatised structure.

Since these early studies much work has been carried out to explain the behaviour of PAN on heating. It has been generally accepted that when PAN is heated in an inert atmosphere a condensed naphthyridine
Figure (4) A series of structures proposed for PAN, thermally cyclised in inert atmospheres.
ring structure is formed. Figure (4.2) shows the polymerisation of adjacent nitrile groups to produce a conjugated \(-\text{C}^\equiv\text{N}\)-structure. In contrast to this secondary polymerisation, reaction in the polymer backbone has been preferred by some workers. Figure (4.3) shows the double bond in the backbone conjugated with a nitrile group as suggested by Conley and Bieron. This idea was extended by Fester, Berlin and Litovchenko et al. who proposed a conjugated polyene structure with pendant nitrile groups as shown in Figure (4.4). These structures are based on spectroscopic analysis, but since \((\text{C}^\equiv\text{C})\) and \((\text{C}^\equiv\text{N})\) groups are known to absorb at similar wavelengths in both the infrared and the ultraviolet, and have a broad absorption band, it is difficult to differentiate between them. Conley observed that the nitrile stretching absorption in the infrared had not decreased when coloration occurred, and that a peak at 2215 cm\(^{-1}\) was formed. Therefore, since the nitrile groups had apparently not reacted and an absorption typical of a conjugated nitrile was formed, he proposed the structure shown in Figure (4.3).

However, this structure does not explain the ultraviolet absorption spectrum of thermally treated PAN because the model compound 2-cyano-2-butenenitrile \((\text{CH}_3\text{C}=\text{CHCH}_3)\) does not absorb in the near UV. The conjugated polyene structure (Figure (4.4)) was inferred from the constant nitrile absorbance at 2240 cm\(^{-1}\). This was not reported elsewhere. Since spectroscopy does not allow the possible conjugated systems to be identified, Peebles et al. developed a chemical method to distinguish between \(-\text{C}^\equiv\text{C}\)_\(_x^n\) and \(-\text{C}^\equiv\text{N}\)_\(_x^n\) species. They observed that products from degradation by heat and bases always behaved like a \(-\text{C}^\equiv\text{N}\)_\(_x^n\) system, which eliminated the conjugated polyene structure.

In contrast to these intramolecular mechanisms, Skoda and Schurz have proposed an intermolecular crosslinking reaction to account for their observed spectroscopic changes. Figure (4.5) shows
the condensation of a pendant nitrile group with a tertiary hydrogen to produce a crosslinked structure. Evidence against this proposal was cited by Grassie et al.\(^{45}\), Takata et al.\(^{46}\) and Friedlander et al.\(^{47}\) as a result of analysing model compounds. The latter workers prepared 2-imino-3-cyanobutane as a model for the azomethine link. These compounds exist predominantly as enamines;

\[
\begin{align*}
\text{CH}_2\text{C-CHCH}_3 & \leftrightarrow \text{CH}_2\text{C-CCH}_3 \\
\text{NH-CN} & \leftrightarrow \text{NH}_2\text{CN}
\end{align*}
\]

and they possess a strong ultraviolet absorption at 255 nm.\(^{48}\)

Enamines produced during the polymerisation of acrylonitrile have a characteristic ultraviolet absorption at 265 nm. The model compound was white and readily hydrolysed to a ketonitrile species on addition of an acid\(^{49}\) while the chromophore in PAN is not hydrolysed even under more rigorous conditions.\(^{42,50}\) Thermal oxidation of the model compounds did not produce the hydrolyseable azomethine structure, which constituted direct evidence against Schurz's proposal. Grassie\(^{45}\) and Takata\(^{46}\) came to the same conclusion based on indirect evidence.

In conclusion, the bulk of the evidence in the literature favours the proposed naphthyridine structure for the inert thermal reactions in PAN. This conclusion was further substantiated by recent work carried out by Coleman and Petcavich,\(^{51}\) who carried out an intensive study of the thermal degradation of PAN films under reduced pressure, using the sensitive Fourier Transform infrared spectroscopic technique. They proposed a simple mechanism to fit their experimental data, which is shown in Figure (5). (I) shows nucleophilic attack on the nitrile group by the anion \(X^-\), which could be generated by cyano-, carboxylic- or amide-type functional groups, followed by (II)- the cyclisation of sequences along the polymer chain. Subsequently structures (III) and (IV) tautomerise, giving an enamine-imine equilibrium, since imines
Figure (5) A scheme proposed for the reaction of PAN at 473 K under reduced pressure. (51)
{C=C=N} are thought to readily tautomerise to enamines\(^{\text{C}=-\text{N}}\).

For mesomerism to be present between structures (III) and (IV) a planar rearrangement of the 3 enamine atoms and the five adjacent atoms is required. Fulfillment of these requirements is thought to lead to full interaction of the \(\pi\) orbitals of the double bond and the lone pair of electrons on the nitrogen atoms.\(^{52}\) In their scheme structure (IV) fulfills these requirements. Further evidence is presented from consideration of the analogous tetrahydropyridine series, where the enol-like structure is more stable.\(^{53}\)

\[
\text{N} \quad \rightleftharpoons \quad \text{NH}
\]

The enamine intermediate then reacted with the trace amounts of oxygen which were present in the reduced atmosphere to produce the pyridone-type structure (V). Heterocyclic enamines are known to be sensitive to oxidation.\(^{54,55}\) The infrared assignments upon which this mechanism has been proposed will be given in section 6.3.2 and are very similar to those observed for the reaction of PAN with \(n\)-BuLi. However the oxygen sensitivity reported was not apparent in the chemical reaction, therefore the imine-enamine tautomeration was thought to be less likely. This mechanism will be discussed in greater depth in Chapter 6, in conjunction with the results reported in Chapter 5, for the chemical reaction. The FTIR technique used by the above authors has produced better resolved spectra for thermally degraded PAN than previously reported in the literature.

The cyclised structure results from a chain reaction which can be considered to have three stages: initiation, propagation and termination. Initiation can occur in a number of ways:

(i) by intramolecular reaction of a tertiary hydrogen with an adjacent nitrile group,\(^{56,57}\) to produce an imine group, which is the true initiator. This is the so-called "self initiation" reaction,
which has been used to explain the presence of isolated nitrile groups remaining after heat treatment.

(ii) by the production of free radicals on heating. These may result from a number of reactions which may or may not involve chain scission. Three possible mechanisms are shown in Figure (6)\(^{(57)}\) with structure (II) illustrating the importance of the tertiary hydrogen in the thermal reactions of PAN. The resonance stabilised radical is produced without any chain scission. However initiation by the linear \(-\text{C}=\text{C}=\text{N}\) radical would be less likely.

(iii) by reactions in the polymer to produce \(\beta\)-ketonitrile groups, which could initiate the cyclisation reaction. This reaction is favoured by Peebles' group\(^{(41)}\), whose proposed initiation mechanisms are schematically represented in Figure (7). The possible production routes for ketonitrile groups has been summarised in Figure (8)\(^{(58)}\) demonstrating that they may be produced by the oxidation of PAN by oxygen (B+C), or by water (D), or by interaction between structural defects and humidity present in the polymer. The result of side reactions during the polymerisation of acrylonitrile could produce enamine groups which readily hydrolyse to ketonitriles.\(^{(59)}\) Subsequent initiation of the cyclisation is brought about by nucleophilic attack of the nitrile groups, which Grassie et al\(^{(29)}\) concluded was responsible for all initiation reactions. Enamines could be produced by polymerisation through the pendant nitrile group by the growing chain, or by oxidation of the methylene carbon atoms.

(iv) by the addition of species which may initiate the cyclisation reaction. Comonomers effectively introduce both abnormalities and initiating species into the polymer. Such additions may act preferentially as initiation sites for the cyclisation reaction. For example, PAN is commercially comonomerised with itaconic acid and methacrylate.
Figure (6) Mechanisms for the production of free radicals in PAN. (57)
Figure (7) Schematic representation of possible initiation mechanisms for the cyclisation of PAN. (41)
Figure (8) Production routes for ketonitrile groups as a precursor to the cyclisation reaction in PAN. (58)
The acid groups are ionic species which can initiate the cyclisation reaction by nucleophilic attack. Since ionic initiation is more rapid than free radical initiation, ionic mechanisms predominate in the presence of such species.

Propagation of the reaction is brought about by the secondary polymerisation of the nitrile groups. Figure (9) demonstrates this stage in the presence of both free radicals and ions. The rate of propagation is controlled by a number of factors. Rotation about the polymer backbone must occur to bring the adjacent nitrile group into the reaction volume. A similarly important factor is the tacticity of the polymer. In the fibre form orientation introduced by stretching results in neighbouring isotactic nitrile groups of the fully extended conformation being in close proximity, thus requiring less energy for the subsequent cyclisation reaction. Propagation through isotactic sequences produces less strained cyclised sequences than through syndiotactic sequences, which in oriented polymers can only react if the chain relaxes to a more random conformation. In this case the ladder polymer formed will not be planar but curved. Grassie(29) and Madorsky(55) have proposed a backbiting mechanism, shown in Figure (10), to provide a transfer mechanism, although its feasibility in a highly oriented system crosslinked by the strong dipole forces of the nitrile groups is questioned by Clarke.(57) Therefore propagation occurs along the polymer chain, its rate and degree being dependent on factors such as steric hinderance, or oppositely growing chain ends which prevent further reaction.

Termination may be brought about in a number of ways. Free radicals may combine, while ionic termination is probably a function of steric factors, or the reaction environment becoming insufficiently polarising to maintain separation of the charge.
Free radical propagation

Anionic propagation

**Figure (9)** Mechanisms for the free radical and ionic propagation of the cyclisation reaction in PAN.
Figure (10) A proposed "backbiting" transfer mechanism in the cyclisation of PAN. (29)
2.5 Cyclisation of PAN in the presence of additives

2.5.1 Introduction

Cyclisation will be affected by the presence of additives, whether in the environment (e.g. oxygen), as comonomers (e.g. itaconic acid and methacrylate added to produce Courtelle), as impurities or specifically added initiators.

Commercially, PAN is thermally stabilised by heating in an oxidising atmosphere, resulting in both cyclisation and oxidation of the fibres. However unless the exotherm is controlled, fusion can occur, leading to the loss of individual fibres. Economically, it would be advantageous to produce a precursor fibre which could either be carbonised directly, or oxidised for the minimum time. Therefore interest has been generated in determining the effect of additives on the thermal behaviour of PAN.

Grassie\(^{29}\) has reported that the exothermic behaviour of PAN is different in the presence of additives. The exotherms were generally extended over a broader temperature range, so that the heat generated at any temperature was reduced. Consequently fusion and chain fragmentation which would result from a vigorous exotherm is reduced.

The effect of additives on the coloration, cyclisation and exothermic reactions in PAN have been reported in the literature. The following sections review the possible methods of incorporating additives into the polymer.

2.5.2 Additives introduced during the polymerisation of acrylonitrile

This is the least exploited method of incorporating additives into PAN. However aluminium residues have been incorporated into PAN by initiating the polymerisation with the reaction product of trialkylaluminium and a carboxylic acid salt.\(^{60}\) It has been reported that the resulting polymer could be spun and directly carbonised, producing a carbon fibre with good mechanical properties. It has also been reported
that the coloured PAN can be produced by polymerising acrylonitrile with organometallic compounds.\cite{61,62}

Comonomers can also be considered as additives, introduced during the polymerisation of acrylonitrile. The major carbon fibre precursor in the UK. is Courtelle, which is a copolymer of PAN containing 6\% methacrylate plus 1\% itaconic acid (added to aid dyeability). Internally plasticised polymers can be stretched to a higher degree, while it is believed that the carboxylic acid group acts as an initiator for the cyclisation reaction.

2.5.3 Additions to the low temperature and carbonising atmospheres

Gaseous additives are reported to improve the ultimate strength of carbon fibres, and to promote the expulsion of non-carbonaceous atoms, increasing the carbon yield.

The major example is the use of oxygen in the low temperature stabilisation reaction. The mechanism of oxidative initiation is less certain than the proposed inert reaction, and disagreement as to the precise method of oxygen incorporation still exists in the literature. Generally the oxidation of polymers involves the formation and decomposition of hydroperoxides, followed by subsequent radical chain reactions. It has been observed that nitrile polymerisation is slower in oxygen than in inert atmospheres. It is likely that oxygen inhibition occurs, i.e. free radicals are immediately stabilised by hydroperoxide formation. Furthermore large scale structural changes prior to cyclisation are unlikely since Watt\cite{63} has shown convincingly that most oxidation is subsequent to the nitrile reaction.

The initiation reaction is thought to be the same in oxygen as in inert atmospheres. Subsequent oxidation produces peroxo radicals which propagate the reaction. Stabilisation in an oxidising atmosphere has been attributed to a variety of structures. Although Houtz\cite{30} concluded
that oxygen must be present in heat treated PAN, no mechanism for its inclusion was proposed. Burlant and Parsons\(^{(32)}\) analysed oxidised PAN. Although incomplete analysis with respect to carbon, nitrogen and hydrogen was recorded, no explanation was given. Similar discrepancies recorded by Vosburgh\(^{(64)}\) were attributed to the formation of hydroxyl groups in the polymer backbone, in conjunction with dehydrogenation. However no reference to a cyclisation reaction was given. Opinions on the precise role of oxygen vary, depending whether its role as a catalyst for the aromatisation of the naphthyridine rings, or incorporation into the polymer backbone is favoured. The latter is preferred but the nature of the oxygen containing groups has caused some disagreement.

Oxidation can occur either at the α- or β-hydrogen atoms, and mechanisms involving both positions have been proposed. Danner\(^{(65)}\) suggested that initiation of the cyclisation reaction is brought about by imino groups produced by peroxidation at the α-hydrogen. Since the nitrile group is electron attractive, the α-carbon is rendered proton releasing, enabling the reaction to occur. This reaction results in simultaneous nitrile polymerisation and free radical attack at the α-carbon. The hydroperoxide group produced in the latter case reacts to produce hydroxyl groups which in turn condense with the β-hydrogen, introducing backbone unsaturation. Figure (11) demonstrates this mechanism. Evidence for the reaction producing aromatic naphthyridine rings was based on results from infrared spectroscopy, and ESR studies of solutions of PAN in DMSO, heat treated in the presence of oxygen. The band which developed at 1600\(\text{cm}^{-1}\) was assigned to a conjugated -(C=CH)– double because poly α-chloroacrylonitrile treated with an HCL acceptor resulted in a structure whose degree of conjugation was a function of the pyridine concentration. Little modification to the
Formation of hydroperoxo groups

Figure (11) The production of hydroperoxide groups and subsequent cyclisation reaction proposed for the oxidation of PAN (65).
1600 cm$^{-1}$ region was observed. A peak at 2210 cm$^{-1}$ was recorded, which was not apparent when PAN was heated in air, from which it was inferred that cyclised PAN does not contain ($\text{C}=$CH)$_2$-sequences in great quantities. Complete dehydrochlorination of PaClAN to polycyanoacetylene greatly reduced the nitrile absorption, while producing a new single band at 1600 cm$^{-1}$, from which it had been concluded that aromatic naphthyridine cycles had been produced. The peak at 2210 cm$^{-1}$ has been reported when PAN has been treated under a variety of conditions. Its assignment was fundamental to the study of the reaction of PAN with n-BuLi and will be fully discussed in Chapter 6. There is however more evidence for the peak resulting from a change in the nitrile environment, than for the proposed conjugated nitrile of Danner$^{(65)}$. Muller et al.$^{(58)}$ and Miyamichi$^{(66)}$ agreed with this mechanism. They observed that the presence of humidity in the polymer during thermal treatment was not dependent on the effect of air, rather the environment accelerated the cyclisation reaction as shown by the enhanced rate of coloration.$^{(32)}$ Conley and Bieron$^{(36)}$ similarly proposed α-carbon susceptibility for the oxidation reaction, although their initiating species were different.

In contrast, other workers have favoured the β-position as the most susceptible to oxidative attack.$^{(49,67-71)}$ Peebles et al.$^{(49)}$ drew their conclusion from the observation that three times the amount of oxidation occurred at the methylene bridge. A similar conclusion was drawn by Scott$^{(72)}$ by considering the electrophilic nature of the alkyl peroxy radical, which could react more readily at this position.

A variety of structures have been proposed even though the point of attack had been agreed upon. Standage et al.$^{(73,74)}$ have suggested two structures, shown in Figure (12), based on results from elemental
Figure (12) Two structures proposed for oxidised PAN. (73,74)
analysis, infrared spectroscopy and nuclear magnetic resonance studies of oxidised PAN fibres. Structure (II) was preferred, although it was less favourable from steric considerations. No other evidence for epoxide groups has been reported in the literature.

The final structure of Potter and Scott\(^{(75)}\) for oxidised Courtelle seems to present the most likely representation of the structure formed during oxidation, shown in Figure (13). The structure is a mixture of cyclised sequences, aromatised cyclics and oxygen containing groups, indicating that oxygen possibly catalyses aromatisation via reactions with the polymer backbone. Watt's ultimate structure was very similar.\(^{(63)}\) The cyclisation reaction was initiated, propagated and subsequently oxidised. Oxidation occurred in the $\beta$-position producing hydroperoxide groups, loss of water led to keto-formation, with tautomeration to a hydroxypyridine structure, which subsequently tautomerised to produce the final pyridine structure. Thus oxygen would be present in the polymer backbone as both carbonyl and hydroxyl groups. A similar conclusion was drawn by Clarke\(^{(57)}\) who thoroughly investigated the oxidation of acrylic fibres, and surprisingly discovered that oxidation at 493 K for only 15 min produced carbon fibres with good mechanical properties. Commercially much longer oxidation times are used. Clarke's proposed structure is shown in Figure (14). In contrast, Peebles\(^{(49)}\) suggested that nitrene groups were produced by the addition of oxygen to the polyimine cycles during the propagation and oxidation of the cyclised sequences. This conclusion was used to explain the deeper colours produced on oxidation of PAN and the fact that oxygen was absorbed without reducing the hydrogen concentration. However no direct evidence for this structure was
Figure (13) The final structure proposed for oxidised Courtelle. (75)

Figure (14) The structure proposed for oxidised PAN. (57)
presented. In fact Rose\textsuperscript{(76)} and Uchida\textsuperscript{(77)} concluded from infrared studies that nitrone groups were not produced.

The role of oxygen in the thermal stabilisation of PAN has been the subject of major research programmes. It has not been the intention to review all the information reported for the reaction. The various mechanisms reported in the literature have been summarised to highlight the complexity of the reaction. Therefore in the context of this study the role of oxygen has been considered in terms of being an addition to the low temperature stabilisation atmosphere. Comparing the proposed structures with the model structure produced in an inert atmosphere, oxygen appears to catalyse aromatisation of the cyclised sequences and react with the polymer chain. Therefore the final structure is a mixture of cyclised and aromatised sequences with various oxygen containing groups attached to the polymer backbone, which promote the subsequent crosslinking reaction to produce a dense final structure after carbonisation.

Preoxidising the precursor fibres in a variety of oxidising atmospheres has also been reported to improve the ultimate carbon fibre properties. Examples of such reactions include using atmospheres of nitric oxide\textsuperscript{(78)} mixtures of hydrogen chloride and oxygen,\textsuperscript{(79)} hydrogen sulphide or sulphur dioxide,\textsuperscript{(80)} prior to carbonisation in an inert atmosphere.

Finally, additives can be introduced into the carbonising atmosphere. Shindo\textsuperscript{(81)} observed a marked increase in the tensile strength of carbon fibres carbonised in the presence of hydrogen chloride vapour.

2.5.4 Additives in bulk or fibrous PAN

Grassie et al\textsuperscript{(29)} have suggested that a variety of compounds can accelerate the cyclisation reaction. Their conclusion was drawn
from observing the coloration and exothermic behaviour of PAN in the presence of additives. The coloration of nitrile containing polymers is known to be accelerated by carboxylic acids, phenols and inorganic bases.\textsuperscript{(82)} Amides, amines, ketones and alcohols were found to be slightly less effective. Grassie\textsuperscript{(15)} lists a series of such additives which successfully coloured PAN, and broadened the characteristic exotherm, which was initiated at a lower temperature. The carbon yields of the products were substantially increased, from 28\% for the homopolymer to 40-50\% in the presence of additives.

As discussed in section 2.5.2 itaconic acid is a comonomer in the production of commercial carbon fibre precursor. The acid groups have been shown to initiate the cyclisation reaction. Figure (15.1) shows the initiation mechanism proposed by Grassie,\textsuperscript{(34,35)} where the polar hydroxyl groups were thought to polarise the adjacent nitrile group forming an imine anion, which subsequently initiated the cyclisation polymerisation. Therefore the initiation mechanism for both carboxylic acids and phenols is the conventional reaction between acids and nitriles.\textsuperscript{(83)}

The reaction characteristics of strong inorganic bases has also been the subject of much research. There appears to be some dispute in the literature as to their precise effect: both cyclisation and chain scission have been reported. Grassie's mechanism, shown in Figure (15.11), favours the former. Similarly, Danner\textsuperscript{(65)} concluded that cyclisation occurred when solutions of PAN were treated with small quantities of potassium hydroxide (KOH). He observed a slight coloration, through yellow to orange. Infrared studies showed that the nitrile peak virtually disappeared, while peaks developed at 3400 cm\textsuperscript{-1} and 1640 cm\textsuperscript{-1}. It was concluded that cyclised sequences were of minimum length to produce a coloured product. The kinetic
**Figure (15)** Mechanisms proposed for I acid, II alkali initiation of the cyclisation reaction in PAN. (34,35)

**Figure (16)** A mechanism proposed for the reaction of PAN with a base, resulting in chain scission. (84)
chain length of the reaction was limited by the number of groups in a sequence. Aurich\(^{(84)}\) however concluded that competition between cyclisation and chain scission occurred. Their mechanism suggests that if the reaction was carried out in air, autoxidation of the α-carbon results (Figure (16)). Zahn and Schafer\(^{(85)}\) and Schurz et al\(^{(86,87)}\) also favour the chain scission mechanism, which is also demonstrated in Figure (16). However direct evidence for cyclisation initiated by strong inorganic bases has been presented by Takata and Hiroi\(^{(46)}\), who examined the UV spectra of model compounds. Therefore there is strong evidence for cyclisation initiated by strong inorganic bases, however, it is feasible that under rigorous conditions chain fragmentation could also result.

Many other compounds have also been reported to initiate cyclisation of PAN. Lewis acids were shown to both initiate and accelerate cyclisation. Examples include boron fluoride, stannous chloride, ferric chloride, aluminium chloride, sulphur trioxide, indium dichloride\(^{(88)}\), stannic chloride,\(^{(88-91)}\) titanium tetrachloride, plumbic chloride, stannic bromide,\(^{(88,92)}\) and the complex between ethylene diamine and copper nitrate.\(^{(93)}\) Most experiments have been carried out using doped solids. In contrast, Gump and Stuetz\(^{(88)}\) immersed fibres in solutions of Lewis acids and their complexes, at temperatures between 433-573 K. Sufficient cyclisation occurred to enable thermally stabilised fibers to withstand direct carbonisation.

Organotin compounds reportedly initiate cyclisation in a similar manner to Lewis acids.\(^{(94,95)}\) Figure (17) shows the proposed initiation mechanism which is similar to the trimerisation of isocyanates.\(^{(96)}\) Bloodworth et al\(^{(96,97)}\) has shown that organotin compounds add to nitrile groups with adjacent electron with drawing substituents.
Figure (17) A mechanism proposed for the cyclisation of PAN by organotin compounds (94,95).
Inorganic cyanides have also been studied as initiators for the cyclisation reaction. Lockheed(98), Potter and Scott(72) and Grassie(29) used sodium cyanide to initiate the secondary polymerisation of nitriles. Figure (18) shows the proposed mechanism, indicating its nucleophilic nature. Potter and Scott's propagation reaction includes partial aromatisation, although their experimental conditions were more severe than those of this study (420 K for 12 hrs), and it is not entirely clear whether their investigation was carried out using bulk PAN, or in solution. They discovered that polymers produced in this way were extremely oxygen sensitive. By investigating model compounds they concluded that the α-hydrogen abstraction is an important step. The oxygen sensitivity was observed both when oxygen was present in the reaction medium, or if the product was exposed to the atmosphere after isolation. The final structure was a fully aromatic, or 4-pyridone species, but that ultimately the structure is a mixture of 1,4-dihydropyridines and 4-pyridones. Figure (19) shows their complete proposed reaction.

Much of the work so far discussed has been carried out using bulk PAN. Improved carbon fibres have also been produced from acrylic fibres swollen in aqueous solutions containing iron, nickel, zinc, aluminium and/or magnesium ions. Oxidised fibres have been treated with potassium permanganate, potassium dichromate and/or inorganic acids such as sulphuric acid, prior to carbonisation. Similarly recent work has suggested that thermal oxidation can be drastically shortened or replaced altogether by heterogeneously catalytically polymerising the nitrile groups of partially swollen PAN using an organometallic catalyst. The reaction was reportedly fast, and propagation was reflected by colour development as the length of the conjugated imine structure increased. The major
Figure (18) A mechanism proposed for the initiation of cyclisation of PAN by cyanide ions. (29)

Figure (19) A complete scheme proposed for the cyclisation of PAN with cyanide ions. (72)
advantages of this technique are

(a) commercial acrylic fibre can be used rather than a rapid oxidiser, especially developed for carbon fibre formation,

(b) shorter process at lower temperature can be used, thus saving energy,

(c) minor accompanying weight losses observed,

(d) tensioning of the fibres is less important as lower T (close to \( T_g \)) is used, although this latter point seems unlikely.

In summary, additive initiated cyclisation has the advantage that the time consuming preoxidation time and the exotherm can be reduced. There is also the possibility of producing more uniform carbon fibres, without the generally observed core structure. Additive concentrations need to be controlled to allow the correct extent of cyclisation. It has been shown that preoxidation times as short as 15 mins. can produce suitably stabilised precursor, although the length of cyclised sequences is relatively short. This study will show that cyclised sequences can also be introduced by catalysed cyclisation. Grassie concluded that pyrolysis of additive treated PAN would be no substitute for preoxidation, since the latter seems to be essential to prevent fragmentation. He did however observe that improved carbon yields were apparent on carbonisation, when additives had been employed. This area requires further work, since good carbon fibres have apparently been produced without the pre-oxidation stage. \(^{(88,101)}\)
CHAPTER 3 DEVELOPMENT OF THIS STUDY

The preceding literature survey has shown that pyrolysis of PAN in an inert atmosphere presents a simple, well established cyclisation model. However the introduction of chemical species into the reaction environment complicates this simple reaction. It has also been shown that the additives can induce cyclisation at much lower temperatures, than in the thermal reaction.

The major interest in this thesis was to investigate the reaction of PAN with additives under closely controlled experimental conditions. The literature had indicated that previous work in this area had been carried out under a variety of experimental conditions, which made comparisons difficult.

The first aim of this study was to qualitatively confirm the effect of various additives on the coloration of PAN solutions. Having established the coloration reaction, a specific additive was chosen for an extensive study in order to determine the precise nature of a chemically initiated cyclisation reaction. The structures produced by the reaction were qualitatively analyzed using a variety of spectroscopic techniques. A combination of spectral evidence was required since it was decided that evidence based on one technique alone could be ambiguous. This was the case particularly in the case of infrared spectroscopy. The literature indicated that many workers have used this technique to study the thermal cyclisation reaction. However the evidence has shown that unsaturated, conjugated species develop as the reaction proceeds, and it is difficult to distinguish between groups such as (C=C), (C=N) and (C=O), which may be produced by the thermal reaction, depending upon the experimental conditions. For this reason a combination of infrared and ultraviolet absorption spectroscopy, H'-nuclear magnetic resonance, and gel permeation
chromatography were used to provide conclusive structural evidence.

A reaction technique was developed, so that the reaction could be followed using a sampling method under carefully controlled experimental conditions. Low molecular weight PAN was produced to minimise structural abnormalities which could influence the cyclisation reaction. All reactions were carried out under vacuum or where an atmosphere was necessary in an inert atmosphere of argon. A well characterised anionic initiator was used to study the influence of a catalyst on the cyclisation reaction. Specimens were therefore produced under a variety of experimental conditions, to determine the effect of initiator concentration, polymer concentration, reaction temperature and reaction environment on the cyclisation reaction.

Having established the qualitative effect of additives, the reaction was quantified by determining the number of nitrile groups which had reacted as a function of experimental condition. A calculation of the average length of cyclised sequences could then be made. A relationship between the extent of reaction of the nitrile groups and the residual enthalpy resulting from heating the partially cyclised product could be established.

The results produced enabled a reaction mechanism to be proposed, and subsequently a kinetic model was applied to the reaction.

It was of interest to discover whether the chemical cyclisation reaction could be used as a substitute for the low temperature oxidation reaction in the production of carbon fibres. If the chemical reaction could introduce sufficient cyclisation to thermally stabilise PAN, at a relatively low temperature, then direct carbonisation to produce carbon fibres would improve the economics of their production.
CHAPTER 4  EXPERIMENTAL PROCEDURES

4.1 Introduction

Polyacrylonitrile (PAN) was produced in the laboratory to ensure that a well characterised polymer was used. Since a low molecular weight polymer was suited to this study, acrylonitrile was polymerised in toluene solution in which a small degree of transfer occurs. The polymerisation was only allowed to continue to 25% conversion to reduce the incidence of side reactions which could lead to structural impurities.

An initial series of experiments was carried out to determine the effect of various additives on the coloration of PAN in N,N'-dimethylformamide solution. Once the coloration reaction had been established, the effect of a particular additive was investigated. A sampling technique was developed to study the reaction at intermediate stages. The products were examined using a variety of solid state and solution techniques. Qualitative and quantitative analyses were made and a reaction mechanism was established.

4.2 Reagents used

(a) Acrylonitrile (AN) (BDH Chemicals Ltd.)

The inhibitor was removed by storage over silica gel in an argon atmosphere. Prior to use, AN was freshly distilled with an argon purge using the continuous distillation apparatus shown in Figure (29).

(b) Toluene (Fisons Ltd.)

Toluene was freshly distilled before use, the fractional distillate with b.p. of 383 K was collected.

(c) α-azo bis-isobutyronitrile (BDH Chemicals Ltd.)

This was used without further purification.

(d) N,N'-dimethylformamide (DMF) (Fisons Ltd.)

DMF was fractionally distilled through a 60 cm Vigreux column with a reflux ratio of 10:1. Generous head and tail fractions were discarded.
Figure (20) The apparatus used for the continuous distillation of acrylonitrile.
Solvent with b.p. of 424 K was collected. Figure (21) shows the apparatus used to store the DMF under vacuum. The solvent was transferred to flask (A), which contained molecular sieves (Linde 3A BDH Ltd.), freshly baked out to a vacuum of less than $10^{-4}$ torr, by heating at 570 K for two days and cooled before reducing the vacuum with argon. The reservoir was closed with a mercury seal (B), and the DMF degassed and refluxed for several hours prior to use. The solvent was dosed by distillation into a vertical burette (C), and transferred to an evacuated reaction vessel (D), by gravity through a "Rotaflo" tap (E).

(e) **n-Butyllithium** (n-BuLi) Koch-Light Laboratories)

The n-BuLi was used without further purification. The solution (15% w/w in hexane) was stored under nitrogen and dispensed using a syringe through a rubber septum.

(f) **Methanol** (BDH Chemicals Ltd.)

This was used without further purification.

(g) **Ethyl iodide** (BDH Chemicals Ltd.)

This was used without further purification.

(h) **Dimethylsulphoxide** (DMSO) (BDH Chemicals Ltd.)

DMSO was used without further purification.

### 4.3 Polymerisation of AN

A variety of techniques have been used for the polymerisation of AN, including bulk, emulsion and suspension methods. Initially bulk polymerisation of AN to about 10% conversion was attempted, using AIBN as a free radical initiator. The exothermicity of the reaction was difficult to control and a product of high molecular weight was produced. For this reason solution polymerisation in toluene, which is a transfer agent ($C_s = 2.63 - 5.83 \times 10^4$ at 333 K) was employed, allowing more control over the polymerisation.
Figure (21) The apparatus used for the distillation of dimethylformamide.
The polymerisation apparatus consisted of a three-necked flask, equipped with a stirrer, condenser, thermometer and argon inlet. The flask was charged with 200 cm$^3$ freshly distilled toluene and 50 cm$^3$ distilled AN. The apparatus was purged with argon and allowed to equilibrate at 343 $^\circ$K. AIBN (concentration=$3.5\times10^{-3}$M) was added with continuous stirring. The polymer began precipitating immediately. The reaction was halted after 3 hrs. at a conversion of approximately 25%, to limit structural impurities. The polymer was isolated by filtration, washed and freeze-dried to constant weight in vacuo. The infrared spectra of the various batches were identical, with absorptions due to impurities absent. The polymer was stored under vacuum and dosed under an argon blanket.

4.4 Molecular weight determination

The molecular weight of PAN was determined by solution viscometry in an Ubbelhode viscometer. A solution of PAN in freshly distilled DMF (concentration= 0.076 mol kg$^{-1}$) was allowed to stand for 24 hrs. to completely dissolve and equilibrate. Viscometry was carried out at 298 $^\circ$ 0.2 K. The intrinsic viscosity [$\eta$] was determined from the intercept of the resulting graph of $\tau - \tau_o$ versus concentration, where $\tau_o$ was the flow time for the solvent and $\tau$ was the corresponding time for the solution at various concentrations.

The molecular weight ($M_w$) was calculated from the Mark-Houwink equation:

$$[\eta] = k(M_w)^a$$

where \( k = 1.66\times10^{-4} \) (dl/g)$^a$(104)
\( a = 0.81(104) \)

A typical intrinsic viscosity value of 0.910 gave an approximate molecular weight of 40,000.
4.5 The qualitative effect of additives.

The qualitative effect of a wide range of additives on the coloration of PAN solutions was investigated. 10% (w/v) solutions of PAN in DMF were dissolved and stabilised at 293K and 323K. The additive of known concentration was added and the colour change recorded. The degree of colour was gauged by comparison with an untreated PAN solution at the same temperature. Table(1) shows a series of additives investigated in this manner.

Inorganic bases were found to be very effective colouring agents. Concentration control proved difficult using bases such as sodium hydroxide, due to their sparing solubility in DMF. Sodium metal produced a similar, more controlled reaction, and was used as a colour initiator in the form of a solution in DMF. Samples were removed at various stages of the reaction, precipitated in an excess of methanol, thoroughly washed and freeze-dried to constant weight in vacuo. The products were examined using solid state and solution techniques, to establish their resultant structures.

Some useful results were obtained by this simple method, however a wide scatter band in the analyses resulted. For this reason the technique was substantially modified to minimise the sources of error, prior to an in-depth study of the effect of a particular additive.

4.6 The reaction of PAN with n-BuLi.

A modified technique was used to investigate the reaction of PAN solutions with n-BuLi. PAN produced as previously described (4.3) was stored under vacuum. Polymer solutions, concentration (c=1.0 mol kg\(^{-1}\)), were produced by the following method. The storage vessel was removed from the vacuum line and let down to argon. The required weight of PAN was placed in section A of the reaction vessel shown in Figure [22]
<table>
<thead>
<tr>
<th>Organic additives</th>
<th>Inorganic additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethylene diamine</td>
<td>alcoholic potassium hydroxide</td>
</tr>
<tr>
<td>glacial acetic acid</td>
<td>concentrated hydrochloric acid</td>
</tr>
<tr>
<td>m-cresol</td>
<td>concentrated sulphuric acid</td>
</tr>
<tr>
<td>n-butyllithium</td>
<td>potassium cyanide</td>
</tr>
<tr>
<td>oxalic acid</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>phenol</td>
<td>sodium metal</td>
</tr>
<tr>
<td>sodium acetate</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>sodium benzoate</td>
<td>sodium thiocyanate</td>
</tr>
<tr>
<td>sodium oxalate</td>
<td>stannic chloride</td>
</tr>
<tr>
<td>succinic acid</td>
<td>titanium tetrachloride</td>
</tr>
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<td>tartaric acid</td>
<td>zinc chloride</td>
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<tr>
<td>thiourea</td>
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</tbody>
</table>

Table (1) Additives used to investigate the colouration of PAN solutions.
Figure (22) The apparatus used for the reaction of PAN solutions with n-BuLi under vacuum.

Figure (23)(inset) The UV absorption cell for the continuous monitoring of reacting solutions under vacuum.
The apparatus was assembled and attached to the vacuum line via socket (C). The reaction vessel was evacuated using both rotary and oil diffusion pumps. Section (B) was isolated by closing "Rotaflo" tap (E). The required volume of DMF, previously distilled under vacuum into the burette (4.2(d)), was run into section (A) under vacuum via "Rotaflo" tap (D). The solution was continuously stirred with a magnetic stirrer and left to ensure complete dissolution. Section (B) remained closed, while argon was introduced into the apparatus. "Rotaflo" tap (D) was closed and the apparatus removed from the vacuum line. The reaction vessel was tipped and "Rotaflo" tap (E) opened. The solution was filtered into section (B) through glass sinter (F). The reaction was initiated by injecting the required volume of n-BuLi into section (B) via rubber septum (G). The solution was mixed vigorously, and this point was taken as \( t_0 \) for the reaction. Samples were removed at various intervals after initiation using a syringe through the rubber septum while bubbling argon across the solution. The samples were precipitated into an excess of methanol. The products were filtered, thoroughly washed in methanol to remove residual solvent and freeze-dried to constant weight in vacuo. A series of reacted polymers was obtained using various combinations of polymer concentration, n-BuLi concentration, reaction temperature and atmosphere.

The structures of the products at various stages of reaction were determined using a series of analytical techniques.

4.7 Infrared spectroscopy

Infrared spectroscopy has been widely applied to the analysis of PAN, in the form of bulk powder, fibre and films. Each application has its advantages, depending on the information required. The major peaks in the spectrum of PAN have been well characterised, and was therefore used as a standard. Structural changes resulting from the reaction of the
polymer with n-BuLi were determined by comparing the spectra obtained with the standard. The spectra were calibrated using the internal standard technique,\(^{(105)}\) to enable the change in nitrile concentration to be calculated.

Powder specimens were examined using the standard potassium bromide disc method. Discs were produced by grinding together 0.3 g spectroscopy grade potassium bromide with 0.003 g dry polymer until a fine dispersion of polymer was achieved. The potassium bromide was stored at 393 K, and was further dried at 433 K immediately prior to use, to minimise water absorption. The mixture was pressed in an evacuated die to produce a disc diameter 8 mm, thickness 0.7 mm, at a pressure of 155 MPa for three minutes. The discs were examined immediately using a Perkin-Elmer 457 diffraction grating infrared spectrometer with scanning range 4000-250 cm\(^{-1}\). Scans were carried out using normal slit mode and medium scan speed. The resulting spectra were analysed qualitatively and quantitatively with respect to experimental conditions.

4.8 Ultraviolet absorption spectroscopy

The reacted polymers were examined using ultraviolet absorption spectroscopy, to establish the presence of chromophoric and/or conjugated species. A dynamic analysis technique was initially investigated, but was ultimately unsuccessful in recording spectral changes under the experimental conditions used. A second arm was attached to the reaction vessel, as shown in Figure (23). A quartz cell with path length 1.0 mm was used. When the solution had been initiated as previously described (4.6), the reaction vessel was tipped and the "Rotaflo" tap opened. The solution was filtered through the glass sinter into the cell which had been previously evacuated. However, spectra were not obtained by this method due to the intense chromophoric nature of the reacting solutions, despite
the short path length of the quartz cell. The concentration of the absorbing species was too great and could not be balanced with the reference solvent.

Therefore spectra were obtained from dilute solutions of redissolved reacted polymer. Spectra were recorded using a Perkin-Elmer 137 Ultra-violet Absorption Spectrometer, scanning the UV-visible regions of the spectrum (190-750 nm). Stoppered quartz cells with path length 10 mm were used. Freshly distilled DMF was placed in the reference beam.

4.9 Gel permeation chromatography

GPC was used to monitor the integrity of the polymer after reaction of PAN with additives. The molecular weight distribution of the homo-polymer was recorded and used as a standard. Changes in structure resulting from the reaction, including chain scission and crosslinking phenomena would be apparent from the change in molecular weight distribution.

The reacted polymer was redissolved in freshly distilled DMF (concentration = 1.03 mol kg\(^{-1}\)). Chromatograms were recorded using a Waters Associates Instrument equipped with a Model R401 Differential Refractometer. The reference solvent, freshly distilled DMF, was pumped through the apparatus at a flow rate of 1.0 cm\(^3\) min\(^{-1}\). Three columns filled with μ-Styragel were used to separate the polymer solution according to the size of its constituent molecules. μ-Styragel with pore sizes 10\(^5\), 10\(^4\) and 10\(^3\) Å were used to achieve the required separation. Solutions (volume = 0.1 cm\(^3\)) were injected directly on to the column for analysis. Elution volume was plotted as a function of the quantity of sample of particular "effective size", observed by differences in refractive indices of the constituents with respect to the reference solvent. The system had been previously calibrated using well characterised polystyrene standards of known molecular weight. The molecular weight at any elution volume could be calculated with
respect to polystyrene. Changes in the molecular weight distribution of the reacted polymers were recorded in this manner.

4.10 H'-Nuclear magnetic resonance spectroscopy.

H'-NMR spectroscopy was employed to determine the proton distribution in the polymer after reaction with n-BuLi. The ratio of the $\beta:\alpha$ protons was calculated indicating whether reaction in the polymer backbone had occurred.

The H'-NMR spectrum of PAN has been well characterised, and is contained in the Staedtler Reference Spectra. This reference spectrum was used to characterise the spectrum of PAN used in the experiment. The technique was found to be susceptible to impurities, particularly water and incompletely deuterated solvent (i.e. $d_5$-DMSO impurities).

Treated polymer was dissolved in deuterodimethylsulphoxide-$d_6$. H'-NMR spectra were recorded using a Brucker WH-90 Pulsed Fourier Transform NMR Spectrometer with H' resonance at 90 MHz. $CH_2:CH$ ratios were calculated from the computed integral step peak heights, and changes in proton distribution were measured with respect to the theoretical value of 2 calculated for PAN.

The technique was also used to detect proton containing terminal groups. However their low concentration in relation to the bulk of the polymer may preclude their detection.

4.11 Thermal analysis.

4.11.1 Differential scanning calorimetry (DSC)

Thermal analysis was used to characterise the reaction of PAN with additives. PAN is known to undergo a vigorous exothermic reaction when heated to 573 K. Therefore structural changes occurring when PAN has been reacted with n-BuLi should alter the characteristic exotherm. Monitoring these
changes enabled the structure produced to be correlated with the residual enthalpy of the reacted polymers.

The temperature difference between the sample and a reference was measured as the temperature of the calorimeter was raised. Therefore an endothermic change in state of the sample would result in the absorption of heat, without a commensurate rise in temperature, so that the sample temperature falls behind that of the reference. An exothermic reaction results in the opposite effect. DSC actually measured the heat required to maintain the sample and the reference at the same temperature, recorded either as an exo- or endo-therm on heating.

A Dupont 990 Thermal Analyser equipped with a DSC cell was used to record the heat of reaction of n-BuLi treated PAN. A few milligrams of finely ground reacted polymer was weighed into a preweighed aluminium pan. An identical pan was used as a reference. A programmed heating cycle was employed, the samples being heated in a stream of oxygen-free nitrogen, (unless otherwise stated) with a flow rate of 50 cm$^3$ min$^{-1}$. The heating rate was 20 K min$^{-1}$ in the temperature range 293-673 K. A two-pen chart recorder was used so that both heating rate and temperature difference could be plotted. From this data a value of residual enthalpy ($\Delta H$) was calculated, since $\Delta H$ is related to the area enclosed by the curve by the following equation:

$$\Delta H = \frac{A}{m} \left( 60BE\Delta q_s \right)$$

where

- $A$ = Peak Area (in$^2$)
- $m$ = Mass of sample (mg)
- $B$ = Timebase setting (min in$^{-1}$)
- $E$ = Cell calibration coefficient at temperature of experiment
- $\Delta q_s$ = Y-axis range (mcal sec$^{-1}$ in$^{-1}$)
4.11.2 **Thermogravimetric analysis (TGA)**

TGA measures the weight change in a sample during a heating programme, and in some cases can be used at the same time as DSC to obtain an overall picture of the thermal stability of a sample. Thermograms were recorded using a Stanton Redcroft TG750 Thermogravimetric Analyser. A few milligrams of finely ground polymer was weighed into a tared platinum pan, which was suspended on a very sensitive balance and lowered into a furnace. Samples were heated in oxygen-free nitrogen at a flow rate of 50 cm$^3$min$^{-1}$, using a heating rate of 20 K min$^{-1}$ in the temperature range 293-673 K. The percentage weight change was recorded as a function of temperature.

4.12 **Elemental analysis**

Elemental analysis was used to monitor changes in the relative proportions of elemental constituents as the reaction of PAN with n-BuLi proceeded. Representative sample from each series of reactions was examined. It is generally difficult to calculate directly the four elements (C, H, N, O), required for analysis using most elemental analysis techniques. Three elements can readily be found, the fourth is calculated by difference. For this reason two techniques were used. Microanalytical elemental analysis calculated the oxygen content by difference, while X-ray photoelectron spectroscopy calculated the hydrogen content in this manner. The latter technique was also used to monitor structural changes as the reaction of PAN with n-BuLi proceeded.

4.12.1 **Microanalytical elemental analysis**

Microanalytical elemental analysis was carried out using a Perkin-Elmer 420 Elemental Analyser. Analyses were obtained from finely ground reacted polymers. Carbon, hydrogen and nitrogen were calculated directly, while the oxygen percentage was found by difference.
4.12.2 X-ray photoelectron spectroscopy

Samples of finely ground reacted polymers were pressed onto small rectangles of indium, which were mounted on to a specimen holder using double-sided Sellotape. The sample holder was loaded into the specimen chamber which was then evacuated to a vacuum better than $10^{-8}$ torr. Specimens were irradiated using Mg K$_{\alpha 1,2}$ radiation (0.7eV), with analyser energy 50eV. Spectra were obtained for the binding energy region 0-1000 eV on a narrow scan. Areas of particular interest were examined more closely using a wide scan (typically 30eV). Spectra of binding energy versus counts were obtained for each sample. Values of peak height were corrected according to their sensitivity factors, and also for an oxygen impurity factor which was apparent from the spectrum of the indium. Values of the percentages of carbon, nitrogen and oxygen were calculated directly, while the hydrogen was found by difference.
5.1 Introduction

A review of the literature indicated that the structure of PAN could be transformed by chemical additives. A solution chemistry technique was used to incorporate the additive into the polymer. The initial experiments involved a qualitative study of the effect of a wide range of additives, as a function of the coloration of PAN in solution. Many additives produced coloured solutions, so a detailed study of the effect of a particular additive was made. Spectroscopic and thermal analysis techniques were used to characterise the reaction. Both qualitative and quantitative analyses were made in order to establish a reaction mechanism.

The reaction of PAN with sodium metal was cursorily investigated, but was complicated by possible side reactions and its sparing solubility in the solvent. Therefore the precise reaction mechanism was difficult to establish. For this reason a technique was developed to initiate the reaction with n-BuLi.

5.2 Qualitative effects of additives on PAN solutions

Freshly dissolved solutions of homopolymer in DMF were transparent and virtually colourless. Table (2) shows a series of additives examined as coloration initiators for PAN in solution. Concentrations have not been quoted because different solubilities of the various additives, in DMF, made exact values difficult to calculate. 10% (w/v) PAN solutions in DMF were examined at the stated temperatures. The colours formed were gauged by comparison with an untreated PAN solution at the same temperature. The table indicates that a wide range of compounds, both acids and alkalis, colour PAN solutions to a greater or lesser extent. The variety of colours produced suggested that there was not a unique coloration mechanism operating. The complexity of the qualitative reaction observed, led to the development
<table>
<thead>
<tr>
<th>Additive</th>
<th>Temperature (K)</th>
<th>Effect observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>alcoholic potassium hyroxide</td>
<td>293</td>
<td>dark orange-brown gel</td>
</tr>
<tr>
<td>diethylene diamine</td>
<td>293</td>
<td>yellow gel</td>
</tr>
<tr>
<td>glacial acetic acid</td>
<td>293</td>
<td>brown gel</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>293</td>
<td>white gel</td>
</tr>
<tr>
<td>m-cresol</td>
<td>323</td>
<td>little effect</td>
</tr>
<tr>
<td>n-butyllithium</td>
<td>293</td>
<td>rapid through yellow to red</td>
</tr>
<tr>
<td>oxalic acid</td>
<td>323</td>
<td>pale yellow</td>
</tr>
<tr>
<td>phenol</td>
<td>293</td>
<td>yellow-brown</td>
</tr>
<tr>
<td>silver nitrate+ sodium hydroxide</td>
<td>323</td>
<td>black treacle-like liquid</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>293 (323)</td>
<td>rapid through yellow to red ultimate gelation</td>
</tr>
<tr>
<td>sodium thiocyanate</td>
<td>293</td>
<td>pale orange</td>
</tr>
<tr>
<td>sodium metal</td>
<td>293</td>
<td>yellow through to red</td>
</tr>
<tr>
<td>succinic acid</td>
<td>293</td>
<td>white-yellow gel</td>
</tr>
<tr>
<td>sulphuric acid</td>
<td>293</td>
<td>little effect</td>
</tr>
<tr>
<td>stannic chloride</td>
<td>323</td>
<td>pale yellow</td>
</tr>
<tr>
<td>titanium tetrachloride</td>
<td>293</td>
<td>little effect</td>
</tr>
<tr>
<td>thiourea</td>
<td>293</td>
<td>orange-brown gel</td>
</tr>
<tr>
<td>urea</td>
<td>293</td>
<td>orange</td>
</tr>
<tr>
<td>zinc chloride</td>
<td>293 (323)</td>
<td>yellow; darker at 323 K</td>
</tr>
</tbody>
</table>

Table (2) The observed effect of some additives on the colouration of PAN solutions.
of a technique to study more closely the particular reaction of one or two additives.

Deep colours were produced when solutions were treated with strong bases. Rapid coloration through yellow, orange to deep red was recorded in a matter of a few minutes, with gelation occurring at long times. An additive was required which produced a vigorous colour change while the rate of coloration had to be sufficiently slow to enable the reaction to be followed. Sodium and potassium hydroxides were suitable in this respect but their sparing solubility in the solvent made the reaction difficult to control. Metallic sodium had a similar effect and was more soluble in DMF, and its reaction with PAN solutions was more thoroughly investigated.

5.3 The effect of sodium solution in DMF on dissolved PAN

5.3.1 Introduction

The solutions of PAN in DMF were prepared and reacted with solutions of sodium in DMF as previously described (4.5). The resultant precipitated polymer ranged in colour from pale yellow to deep red, as a function of reaction time.

The products were examined using infrared and ultraviolet absorption spectroscopy, gel permeation chromatography and thermal analysis to establish the reaction.

5.3.2 The infrared spectrum of the product

Major spectral changes were observed after very short reaction times. A broad band developed in the region 3700-3100 cm\(^{-1}\), a shoulder became visible on the nitrile stretching band (2400 cm\(^{-1}\)), and peaks appeared at 1660, 1225 and 1180 cm\(^{-1}\), compared with the spectrum of the homopolymer. From the spectral changes it was concluded that the characteristic nitrile absorption had changed in some way, while absorptions in the double bond region of the spectrum had also appeared, although this area was poorly
resolved. No spectra are presented in this section because of the poor resolution. Refinement of the technique produced the better spectra presented in section 5.4.3. Similarly peak assignments will be correspondingly discussed.

5.3.3 The ultraviolet absorption spectrum of the product

UV spectra were obtained from products at intermediate stages of the reaction. Figure (24) shows a series of spectra at various times after initiation with the sodium solution. The spectrum of the homopolymer showed a small peak ($\lambda_{\text{max}}=275 \text{ nm}$). At wavelengths shorter than 270 nm the spectrum was obscured by the cut-off point of the solvent. After treatment with a solution of sodium, the spectrum broadened towards the visible region a peak maximum being observed at $\lambda_{\text{max}}=310 \text{ nm}$. The peak gradually shifted to longer wavelengths as the reaction proceeded. After approximately 1.5 hrs (5.4x10$^3$ s) a second maximum appeared at about 350 nm, whose magnitude increased with time. Figure (25) shows a plot of absorbance at 310 nm as a function of reaction time, compared with similar results obtained for potassium hydroxide and zinc chloride. The curve for sodium treated polymers increased during the first hour but tended towards an asymptote at longer times. The reaction with potassium hydroxide produced a similar trend, although the initial increase was not so rapid. In contrast, the reaction with zinc chloride resulted in a larger magnitude of absorbance at shorter times, only increasing slightly with time. This could be explained by complex formation in the latter case rather than oligomerisation of the nitrile groups.

These results indicated the presence of chromophoric species in the reaction product. The observed increase in the intensity of the absorbance was indicative of an increasing number of absorbing species as the reaction proceeded. Therefore, since the wavelength of maximum absorbance was shifted towards the visible region of the spectrum, an increasingly conjugated system was being developed.
Figure (24) The UV absorption spectra for PAN solutions reacted with sodium/DMF solutions, (1) t=0 (2) t=2700 s. (3) t=12600 s.

Figure (25) Maximum UV absorption as a function of time for the reaction of PAN solutions with various additives.
5.3.4 The gel permeation chromatography analysis of the product

Analysis of the treated polymers was carried to establish whether the reaction with a solution of sodium resulted in a change in molecular weight distribution with respect to the unreacted polymer. Figure (26) shows a series of chromatograms obtained as a function of reaction time. A Gaussian shaped peak centred around an elution volume of 23 cm$^3$ was obtained for the homopolymer, which corresponded to a molecular weight of 180,000 with respect to polystyrene. A small shoulder was apparent at lower elution volumes, indicating the presence of a small amount of a higher molecular weight constituent. A Gaussian shaped peak is indicative of a fairly uniform distribution of molecular weights. The peak at the low molecular weight end of the spectrum was attributed to an impurity in the solvent. Small quantities of impurities with large differences in refractive index compared with the reference solvent will be recorded as a relatively large peak. In this case the molecular weight was approximately 20 with respect to polystyrene and was probably due to dissolved water.

As the reaction time increased, the peak broadened towards smaller elution volumes, i.e. to larger molecular weights with respect to polystyrene. Two or more overlapping peaks developed. The results suggested that the reaction of PAN with solutions of sodium produced a polymer with a larger effective size than the homopolymer.

5.3.5 The thermal analysis of the product

The cyclisation of nitrile groups has been characterised by a vigorous exothermic reaction on heating. DSC was used to monitor the residual enthalpy produced when the reaction products were heated. Figure (27) shows a series of DSC traces obtained as a function of reaction time with solutions of sodium. There was an initial large decrease in the area enclosed by the exotherm, although a quantified change in residual enthalpy was difficult to calculate. However the technique was refined and in a later
Figure (26) Gel permeation chromatograms for PAN solutions reacted with sodium/DMF, (1) t=0, (2) t=900 s, (3) t=2700 s, (4) t=12600 s.

Figure (27) DSC traces recorded for PAN reacted with sodium/DMF (1) t=900 s, (2) t=2700 s, (3) t=12600 s. (sample size 2-5 mg.)
section the relationship between the nitrile concentration and the residual enthalpy was clearly demonstrated.

5.3.6 Summary

The spectral changes reported have demonstrated that structural changes were apparent when PAN was treated with solutions of sodium. A decrease in nitrile concentration was the main inference from the infrared spectra. The ultraviolet absorption spectra indicated the development of a conjugated system, characterised by a shift in absorbance to longer wavelengths. Coincidently the chromatograms recorded the production of species with larger effective size (or higher molecular weight), compared with the homopolymer. These observations, coupled with the decrease in residual enthalpy, led to the conclusion that the nitrile groups had reacted. Since more than one nitrile group was consumed per sodium ion, an oligomerisation process was inferred, producing a chromophoric, conjugated polymer.

A reaction mechanism was required to explain these observations. The evidence suggested that the secondary polymerisation of the pendant nitrile groups, as proposed for the thermal stabilisation reaction in PAN, was the most probable explanation. However elucidation of the mechanism of the reaction with sodium solutions was complicated by a number of factors. The reaction product of sodium on dissolution in DMF was not well defined, so that isolation of the probable initiator complex was difficult. Also the sparing solubility of sodium metal in DMF made the initiation solutions difficult to standardise. Therefore no attempt was made to examine this reaction in more detail and consequently a mechanism is not given.

At this stage of the work modification of the various techniques was made. The examination of the products in the solid state depended strongly on specimen preparation. The results from infrared spectroscopy and thermal analysis proved to be strongly dependent on the particle size of the specimens.
Therefore to achieve consistent results the samples were very carefully ground.

It was important to establish a mechanism for the coloration reaction. It was decided to investigate thoroughly the reaction of PAN with a well-characterised initiator. A number of modifications were made to the reaction technique to ensure reproducibility of the results. The solvent was purified as described (4.2.d), stored over baked-out molecular sieves and freshly distilled in vacuo prior to use. All reactions were carried out either in vacuo, or where necessary in an atmosphere of argon. In this way impurities which could be present in the polymer, solvent or atmosphere were reduced to a minimum.

n-BuLi was chosen as the initiator for a detailed examination for the reaction with PAN since it could be easily dosed and analysed. The initiator was used in the form of a solution in hexane, which itself was found to have no effect on the coloration of PAN solutions.

5.4 The reaction of PAN solutions with n-BuLi

5.4.1 Introduction

The initial survey of the effect of various additives indicated that n-BuLi could initiate the coloration of PAN solutions. A method was developed to sample the reaction at intermediate stages. These samples were analysed by a variety of techniques. From the changes observed in the infrared and ultraviolet spectroscopy, H'-NMR spectroscopy and gel permeation chromatography a reaction mechanism has been proposed.

5.4.2 Coloration of PAN solutions with n-BuLi

The coloration of PAN solutions in the presence of n-BuLi was reported in section (5.2). Using this initiator the experimental conditions could be readily adjusted to allow the coloration to occur at a rate which could be followed by the sampling procedure. Table (3) shows a series
<table>
<thead>
<tr>
<th>n-BuLi-\text{I} (mol kg\textsuperscript{-1})</th>
<th>Time (min)</th>
<th>Temperature (K)</th>
<th>Atmosphere</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1</td>
<td>293</td>
<td>argon</td>
<td>pale yellow</td>
</tr>
<tr>
<td>0.1</td>
<td>10</td>
<td>293</td>
<td>argon</td>
<td>orange</td>
</tr>
<tr>
<td>0.1</td>
<td>60</td>
<td>293</td>
<td>argon</td>
<td>dark orange</td>
</tr>
<tr>
<td>0.1</td>
<td>100</td>
<td>293</td>
<td>argon</td>
<td>red</td>
</tr>
<tr>
<td>0.1</td>
<td>200</td>
<td>293</td>
<td>argon</td>
<td>brown</td>
</tr>
<tr>
<td>0.1</td>
<td>1150</td>
<td>293</td>
<td>argon</td>
<td>dark brown</td>
</tr>
</tbody>
</table>

Table (3) A sequence of colours produced by the reaction of PAN solutions with n-BuLi.
of colour observations for a sample reaction ([n-BuLi] = 0.1 mol kg\(^{-1}\),
T=293 K, in argon). The unreacted PAN solutions were virtually colourless:
and PAN reprecipitated from solution without additives retained its original
white colour. The colours reported in the table referred to the colour of the
precipitate, which was the same as the treated solution prior to termination.
Since the supernatant liquid was also colourless, none of the products remained
in solution. Untreated PAN could be recovered quantitatively by this process.
An immediate yellow colour was observed on addition of n-BuLi, which deepened
more slowly with time, through yellow, orange, red-to-brown. At a given—
time, increasing the n-BuLi concentration produced darker colours. Similar
effects were observed in the case of increased temperatures after constant
periods and n-BuLi concentrations. The reaction was monitored by
spectroscopic analysis of the products.

5.4.3 Qualitative analysis of the infrared spectra

The spectrum of PAN is well resolved, and assignment of the major
peaks has been established. Table (4) shows the assignments of the major
peaks, the good agreement between the calculated values and the observed
wavenumbers at which specific groups absorb was apparent. (106,107)

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed</td>
<td>Calculated</td>
<td>vs</td>
</tr>
<tr>
<td>2940</td>
<td>2935</td>
<td>vs</td>
</tr>
<tr>
<td>2870</td>
<td>2886</td>
<td>m</td>
</tr>
<tr>
<td>2240</td>
<td>2237</td>
<td>vs</td>
</tr>
<tr>
<td>1445</td>
<td>1453</td>
<td>vs</td>
</tr>
<tr>
<td>1355</td>
<td>1357</td>
<td>m</td>
</tr>
</tbody>
</table>

\[ vs = \text{very strong} \quad \gamma_a = \text{asymmetric stretch} \]
\[ m = \text{medium} \quad \gamma_s = \text{symmetric stretch} \]

Table (4) Peak assignments in the spectrum of PAN
Figure (28) shows a spectrum obtained for the unreacted polymer, the major peaks are labelled. Spectral changes observed after reaction with n-BuLi have been determined by comparison of the spectrum of treated PAN with Figure (28). The assignments of the peaks in a modified sample have been obtained by studying those reported in the literature for thermally treated PAN. Clarke\(^\text{(57)}\) has extensively reviewed the literature up to 1976, and the various assignments for both inertly and oxidatively heat-treated PAN are summarised in Table (5). No reference will be made to the techniques used to record these spectra, since details may be obtained by referring to the primary references.

The reaction of PAN produced immediate spectral changes. Figure (29) shows a series of spectra for PAN (concentration = 1.0 mol kg\(^{-1}\)) with 0.1 mol kg\(^{-1}\) n-BuLi for different times. In the region 3700-3000 cm\(^{-1}\) background absorption by residual water in the potassium bromide, because of its hydrophilic nature, used to produce the discs, add to the complexity of the absorption. However these absorbances are mainly attributed to imine and hydroxyl groups. Therefore it was important to ensure that water contamination was minimal. It was minimised by storing the potassium bromide in an oven at 239 K, followed by baking at 423 K and cooling in a dessicator immediately prior to use. The disc was produced, and the spectrum was recorded as rapidly as possible. A blank disc prepared in this manner showed no evidence of water absorption, so significant water contribution to the spectra could be discounted. Since the spectra of polymers recorded immediately after freeze-drying, and after storage for several days in air were essentially the same, and since oxygen was absent during the treatments, hydroxyl absorption was similarly discounted. Therefore the absorption in this region was attributed to the formation of amine, or more likely imine groups.
Figure (28) The infrared spectra of PAN, indicating the assignment of the major peaks.
<table>
<thead>
<tr>
<th>Peak (cm(^{-1}))</th>
<th>Assignment</th>
<th>Peak (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400-3350</td>
<td>N-H</td>
<td>3600-3200</td>
<td>N-H</td>
</tr>
<tr>
<td>3230-3200</td>
<td>N-H</td>
<td>3380-3330</td>
<td>N-H</td>
</tr>
<tr>
<td>2200-2185</td>
<td>conj. C=N</td>
<td>3380-3330</td>
<td>O-H</td>
</tr>
<tr>
<td>2170</td>
<td>RNH(^+_x)</td>
<td>3330-3310</td>
<td>O-H</td>
</tr>
<tr>
<td>2150</td>
<td>or (C=\text{C} \equiv \text{N})</td>
<td>2920</td>
<td>C-H</td>
</tr>
<tr>
<td>1670-1620</td>
<td>C=N</td>
<td>2170</td>
<td>RNH(^+_x)</td>
</tr>
<tr>
<td>1670-1620</td>
<td>conj. C=N</td>
<td>1720</td>
<td>C=O</td>
</tr>
<tr>
<td>1670-1620</td>
<td>NH(_2)</td>
<td>1720</td>
<td>C=N</td>
</tr>
<tr>
<td>1615-1580</td>
<td>C=N</td>
<td>1680-1630</td>
<td>C=O</td>
</tr>
<tr>
<td>1615-1580</td>
<td>conj. C=N</td>
<td>1680-1630</td>
<td>C=(\equiv)</td>
</tr>
<tr>
<td>1615-1580</td>
<td>C=(\equiv)</td>
<td>1620-1585</td>
<td>C=(\equiv)</td>
</tr>
<tr>
<td>1615-1580</td>
<td>N-H(_x)</td>
<td>1620-1585</td>
<td>N-H</td>
</tr>
<tr>
<td>1550-1540</td>
<td>=N-H</td>
<td>1620-1585</td>
<td>C=N</td>
</tr>
<tr>
<td>1550-1540</td>
<td>CO(^\Theta)_2</td>
<td>1550-1540</td>
<td>C=N-H</td>
</tr>
<tr>
<td>1420</td>
<td>C=C arom.</td>
<td>1550-1540</td>
<td>CO(^\Theta)_2</td>
</tr>
<tr>
<td>1370</td>
<td>R(_3)C-OH</td>
<td>1380-1370</td>
<td>=C-H</td>
</tr>
<tr>
<td>1340</td>
<td>CO(^\Theta)_2</td>
<td>1380-1370</td>
<td>R(_3)C-OH</td>
</tr>
<tr>
<td>1160-1150</td>
<td>C-N</td>
<td>1340</td>
<td>CO(^\Theta)_2</td>
</tr>
<tr>
<td>1160-1150</td>
<td>R(_3)C-OH</td>
<td>1290-1170</td>
<td>=N-O</td>
</tr>
<tr>
<td>1160-1150</td>
<td>C=C arom.</td>
<td>1165-1135</td>
<td>R(_3)C-OH</td>
</tr>
<tr>
<td>965-900</td>
<td>-C=C-H</td>
<td>1165-1135</td>
<td>-C=CH(_2)-CH-</td>
</tr>
<tr>
<td>910</td>
<td>&quot;</td>
<td>980</td>
<td>N-O</td>
</tr>
<tr>
<td>810-800</td>
<td>&quot;</td>
<td>810-800</td>
<td>-C=C-H</td>
</tr>
<tr>
<td>740</td>
<td>&quot;</td>
<td>810-800</td>
<td>NH</td>
</tr>
<tr>
<td>650</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (5)  Infrared assignments for heat-treated PAN\(^{(57)}\)
(not including major peaks from Table 4)
Figure (29) The infrared spectra of the products of the reaction of PAN solutions with n-BuLi. (1) t=60 s, (2) t=600 s, (3) t=3600 s, (4) t=6000 s, (5) t=12000 s. ([PAN]=1.0 mol kg$^{-1}$, [n-BuLi]=0.1 mol kg$^{-1}$, T=293 K, in argon.)
The most striking features of the spectra were the development of a broad band in the region 3700-3000 cm\(^{-1}\), a decrease in the nitrile (2240 cm\(^{-1}\)) absorption, the appearance and relative increase in intensity of an adjacent peak at 2200 cm\(^{-1}\), and substantial development of peaks in the region 1700-950 cm\(^{-1}\). As the reaction time increased the resolution of the spectra decreased. A more detailed analysis can be made by considering a typical spectrum, Figure (29), curve 2 shows PAN reacted with n-BuLi for 10 min. Although broad regions of overlapping peaks were developed, peaks were observed at the following wave-numbers: 3420, 3360, 3250, 2200, 1670, 1580, 1510, 1380, 1330, 1300, 1250, 1090 and 660 cm\(^{-1}\). The peaks 3700-3000 cm\(^{-1}\) are typical of those observed for primary amines, or in this case more likely imine groups. The structured nature of the broad band was characteristic of hydrogen-bonded species. As observed for the reaction of PAN with solutions of sodium, there was an immediate reduction in intensity of the CN (2240 cm\(^{-1}\)) with concurrent appearance of peak at 2200 cm\(^{-1}\), whose intensity seemed to reach a limiting value after short reaction times. The shift with respect to the standard nitrile stretching frequency was only 40 cm\(^{-1}\) which is indicative of the formation of nitrile groups in a different environment. A detailed discussion of the assignment of this peak will be made in section (6.3.2.3) since it is central to quantifying the reaction. The overlapping peaks in the region 1700-1400 cm\(^{-1}\) have been assigned to a variety of unsaturated groups, such as (C=N), (C=C) and C=O, and -NH\(_{(x)}\) structures. Their complexity precluded their separation for quantitative analysis, although their presence was indicative of unsaturated species being produced by the reaction. Detailed discussion of 1R assignments will be made in section (6.3.2).

Summary of the infrared spectral results showed that the nitrile groups had reacted in some way, and that imine or amine groups,
which were possibly hydrogen bonded, were produced. In a later section (6.3.2.5) it is proposed that intramolecular hydrogen bonding of an imine group to an adjacent nitrile group is likely. The complex region from 1700 to 1400 cm\(^{-1}\) is evidence for the production of unsaturated groups. Since the nitrile absorption reduces in intensity it is probable that the (C=\(\text{N}\)) assignment is applicable in this case. These observations could be explained in terms of a simple cyclisation reaction through the pendant nitrile groups producing either conjugated or nonconjugated \(\text{C}=\text{N}\)\(_x\) sequences.

As the reaction time increased, the spectra became less well resolved, although still dominated by the doublet nitrile absorption. This is a function of using a conventional dispersive infrared spectroscopy technique for analysing increasingly optically dense samples, a problem similarly accounted for PAN which has been pyrolysed for long times. Interpretation of the spectra becomes increasingly difficult as the reaction proceeds. Therefore the results have to be considered in combination with results from other spectroscopic techniques.

5.4.4. Evidence for hydrogen bonding

The broad structured absorption centered at 3400 cm\(^{-1}\) is attributed to hydrogen-bonded NH groups. Infrared spectroscopy was used to substantiate this assignment. Since the spectra remained unchanged when recorded in DMSO solutions it was concluded that intra-molecular hydrogen-bonding was present, because it is more persistent than intermolecular hydrogen-bonding even in dilute solution. The shift in wavenumber of the second nitrile peak was sufficiently small to suggest that a terminal NH group (on the end of a cyclised sequence) was hydrogen-bonded to an adjacent nitrile group. Dreiding models supported this theory indicating that the correct orientation of the molecule to allow hydrogen-bonding was
In order to establish the concept of hydrogen-bonding, attempts were made to remove its incidence and to examine the resulting spectral changes.

The spectra of reacted polymers were measured in dilute solutions of both DMF and DMSO. Satisfactory spectra were only achieved using calcium fluoride windows and various spacers with path lengths shorter than 0.2 mm. The overtone region of the solvent absorbances however caused a loss of resolution. Therefore solution spectroscopy proved inconclusive, particularly since intramolecular hydrogen-bonding is notoriously persistent even in dilute solution. Two alternative methods were used for its detection.

It was decided to terminate the reaction in a non-solvent which would be unlikely to result in hydrogen-bonding. Samples had previously been prepared by precipitating a reacting solution into an excess of methanol and examining the bulk sample produced. In this experiment a solution was dissolved and initiated as previously described. (PAN concentration = 1.0 mol kg\(^{-1}\), n-BuLi concentration = 0.11 mol kg\(^{-1}\), \(T = 293\) K in argon.) After a given time (24 hrs) half of the solution was precipitated into methanol as usual, while the other aliquot was precipitated into an excess of ethyl iodide. The precipitates were washed, freeze-dried and their spectra recorded by the usual method. The presence of alkyl end-groups in this latter case should prevent hydrogen-bonding so that all residual nitrile groups should be in the same environment, and thus absorb at the same wavelength. Thus the nitrile region of the latter sample should be different from the conventionally prepared sample. The peak at 2200 cm\(^{-1}\) should disappear while the peak at 2240 cm\(^{-1}\) should correspondingly increase in intensity. This change was observed by measuring the intensities of both nitrile peaks and calculating their ratio \(\frac{\text{CN}_{2200\ \text{cm}^{-1}}}{\text{CN}_{2240\ \text{cm}^{-1}}} (R)\). The sample precipitated into methanol had a value of \(R = 1.428\) compared with
a value of $R = 1.417$ for the sample precipitated into ethyl iodide. Although a decrease in the magnitude of the nitrile ratio was observed its magnitude was concluded to be insignificant in terms of evidence for the removal of hydrogen-bonding. It was interesting to note that although the two spectra obtained were substantially the same, visually the samples were different. The sample precipitated into methanol was deep red while the sample precipitated into ethyl iodide was deep yellow. Therefore a species of different chromophoric nature was produced in the latter case. A possible structure to account for this behaviour is

![Structure](image)

As the previous method similarly proved inconclusive, a solution of reacted polymer was treated with a strong inorganic acid. The quaternised product was initially examined directly using infrared spectroscopy. However, to avoid solvent absorptions the quaternised solution was recovered from solution by precipitation, and the freeze-dried sample examined by the potassium bromide disc method. The characteristics of the nitrile region were altered by the addition of the acid. The relative intensity of the $2200\text{ cm}^{-1}$ was reduced, compared with that obtained from the same specimen without acidification. The ratio ($R$) of the nitrile peaks obtained with and without the acidification treatment was calculated. Prior to acidification a value of $R = 1.429$ was calculated. After acidification the values obtained were $R = 0.692$ in solution and $R = 0.523$ for the bulk specimen. The spectrum of the quaternised sample also developed peaks at $2780$ and $1790\text{ cm}^{-1}$ characteristic of $\text{NR}_4^+$ groups. Although an absorption was still present after acidification, its intensity was greatly reduced. This could indicate the presence of a third type of nitrile group, such as an unsaturated group, in the structure. In section (6.3.2.5) arguments against this hypothesis are presented. Furthermore, during the work-up
procedure it was likely that transfer of a proton to the methanol occurred giving rise to the apparent incomplete quaternisation.

Although conclusive evidence for hydrogen-bonding was not apparent, the overall trends of the preceding series of experiments produced strong evidence favouring the concept. A detailed discussion, including evidence from the literature, will be presented in section (6.3.2.5).

5.4.5 Ultraviolet absorption spectroscopy

The ultraviolet spectrum of PAN in dilute DMF solution was previously reported in section 5.3.3. Figure (30) shows a series of spectra obtained from dilute DMF solutions of redissolved treated polymers, for PAN (concentration = 1.0 mol kg\(^{-1}\)), initiated by n-BuLi (concentration = 0.08 mol kg\(^{-1}\)) for various times.

A sharp, intense peak was recorded at approximately 270 nm. The actual shape of the peak was obscured by the cut-off point resulting from the absorption of the solvent. In a solvent which allows analysis at shorter wavelengths, a broader peak with a tail below 250 nm would be expected. The development of colour during the reaction was confirmed by the broadening of the ultraviolet absorption spectrum and a shift to higher wavelengths. As the reaction progressed the intensity at 270 nm decreased, so that the number of species absorbing at this wavelength are less, and therefore must react further. The shift of the absorption to higher wavelengths characterises the development of an increasingly conjugated system. An indication of the number of conjugated sequences can be calculated from the wavelength of maximum absorbance ($\lambda_{\text{max}}$), by using the Kuhn free electron theory for polyene structures.\(^{(108)}\) Table (6) shows the values of $\lambda_{\text{max}}$ calculated for various extents of conjugation of the \(-(\text{C=N})_x\) species.
Figure (30) The UV absorption spectra of the products of the reaction of PAN solutions with n-BuLi, recorded in dilute solutions. (1) t=60 s., (2) t=600 s., (3) t=3600 s., (4) t=6000 s., (5) t=12000 s. ([PAN] = 1.0 mol kg⁻¹; [n-BuLi] = 0.1 mol kg⁻¹; T=293 K, under argon.)
Table (6)  Calculated wavelengths of maximum absorbance for conjugated (C=N)_x sequences.

<table>
<thead>
<tr>
<th>x</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>264</td>
</tr>
<tr>
<td>4</td>
<td>302</td>
</tr>
<tr>
<td>5</td>
<td>333</td>
</tr>
<tr>
<td>6</td>
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<td>380</td>
</tr>
<tr>
<td>8</td>
<td>398</td>
</tr>
<tr>
<td>9</td>
<td>413</td>
</tr>
<tr>
<td>10</td>
<td>427</td>
</tr>
</tbody>
</table>

After 10 mins. a peak with \( \lambda_{\text{max}} \) at approximately 300 nm developed. Its intensity increased with increased reaction time, indicating the presence of an increasing number of chromophoric species. Further broadening occurred in the spectra and after 60 mins. a second peak maximum appeared at \( \lambda = 365-370 \) nm, whose intensity similarly increased with increased reaction time.

The combination of increasing absorbance at any wavelength together with broadening of the spectrum to longer wavelengths indicates the production of chromophoric, conjugated species. Comparing the wavelengths of maximum absorbance with the calculated values using the Kuhn free electron theory for conjugated polyene structures, shown in the previous table, the results are consistent with formation of a conjugated system where \( x=4-8 \).

Figure (30) has shown that a fairly complex spectrum developed during the reaction. The complexity is due to a combination of factors. The decrease in the intensity of the peak at 270 nm is accompanied by an increase in absorbance at any wavelength as the
reaction time increased, which is a function of the increasing number of species with the same extent of conjugation. At the same time, the broadening of the spectrum to longer wavelengths indicates an increasing extent of conjugation present in the polymer as the reaction proceeded. Therefore, the spectra represent a complex mixture of increasing numbers of a specific extent of conjugation, together with an increasing extent of conjugation. Since the spectra could not be readily deconvoluted into its component peaks, an analysis has been carried out at representative points of the spectra. For this reason the nature of the spectra of reacted polymers has been demonstrated by analysing the two peaks apparent at 300 and 365 nm. Table (7) tabulates the values of absorbance for these peaks as a function of experimental conditions, for the reaction with n-BuLi. Figure (31) is an illustrative plot of absorbance versus reaction time for both these peaks. It can be seen that the absorption at 300 nm occurs first, and at all times is more intense than the absorption at 365 nm. Both peaks tend towards a limiting value after approximately 100 mins. This feature would be expected because the initiation mechanism on the addition of an additive produces a finite length of linear polymer between initiation sites, which is a function of the concentration.

A similar analysis was used to determine the effect of the reaction temperature on the ultraviolet spectra of the products. Qualitative infrared analysis of the samples produced at different temperatures were ostensibly the same (5.4.3) while the corresponding quantitative analysis will show the differences in terms of the extent and degree of nitrile reaction (5.4.3). However, despite the apparent similarities in the infrared spectra, the reaction products produced at elevated temperatures (313, 333 K) were no long soluble in DMF.
<table>
<thead>
<tr>
<th>[n-BuLi] (mol kg⁻¹)</th>
<th>Time (s)</th>
<th>Atmosphere</th>
<th>$\lambda=300$ nm</th>
<th>$\lambda=365$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>60</td>
<td>Argon</td>
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</tr>
<tr>
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<td>600</td>
<td>Argon</td>
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</tr>
<tr>
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<td>6000</td>
<td>Argon</td>
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</tr>
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<td>Argon</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
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<td>Argon</td>
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</tr>
<tr>
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<td>Argon</td>
<td>0.42</td>
<td>0.28</td>
</tr>
<tr>
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<td>6000</td>
<td>Argon</td>
<td>0.61</td>
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</tr>
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<td>12000</td>
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</tr>
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<td>Argon</td>
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</tr>
<tr>
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<td>Argon</td>
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<td>0.38</td>
</tr>
<tr>
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<td>6000</td>
<td>Argon</td>
<td>0.64</td>
<td>0.43</td>
</tr>
<tr>
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<td>12000</td>
<td>Argon</td>
<td>0.69</td>
<td>0.46</td>
</tr>
<tr>
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<td>60</td>
<td>Argon</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>0.08</td>
<td>1200</td>
<td>Oxygen</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
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<td>2400</td>
<td>Oxygen</td>
<td>0.15</td>
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</tr>
<tr>
<td>0.08</td>
<td>3600</td>
<td>Oxygen</td>
<td>0.18</td>
<td>0.10</td>
</tr>
<tr>
<td>0.08</td>
<td>6000</td>
<td>Oxygen</td>
<td>0.145</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table (7) The values of absorbance at $\lambda=300$ nm. and $\lambda=365$ nm. as a function of n-BuLi concentration and time, for the reaction with PAN ([PAN]=1.0 mol kg⁻¹, $T=293$ K).
Figure (31) Absorbance as a function of reaction time for the products of the reaction of PAN with n-BuLi
(1) = 300 nm., (2) = 365 nm. ([PAN] = 1.0 mol kg⁻¹, [n-BuLi] = 0.1 mol kg⁻¹, T = 293 K, under Argon)
Therefore ultraviolet spectroscopy of these samples could not be carried out. Heating, to effect dissolution would negate the fact that the samples had been produced at relatively low temperatures. It was also interesting to note that although the precipitated product was insoluble in DMF, it had remained in solution for the duration of the reaction. The solubility properties of the products must change as the reaction temperature increased, such that DMF was initially a good solvent and apparently becomes a non-solvent for the reaction products produced at higher temperatures.

The presence of oxygen in the reaction medium had been shown to inhibit the reaction which had been initiated in an inert atmosphere, as shown by the lack of colour development as the reaction proceeded in the presence of oxygen. The inhibition of the reaction by oxygen was confirmed by the ultraviolet absorption spectra, which showed little development in the absorbances at either 300 or 365 nm.

These results can be used in conjunction with the spectroscopic data generated by other techniques to determine a mechanism for the reaction of PAN with n-BuLi. A detailed discussion of the structure and mechanism will be given in section (6.3.3).

5.4.6 H'-nuclear magnetic resonance spectroscopy

Qualitative spectroscopic evidence has so far indicated that the reaction of PAN with n-BuLi reduces the nitrile concentration, producing a conjugated system. The cyclisation reaction through the pendant nitrile groups was thought to produce a conjugated \((\text{C} = \text{N})_x\) system, from the evidence reported in the previous two sections. However, the production of a conjugated sequence by a different mechanism could not be ignored. Reaction in the polymer backbone, either at the \(\alpha\)- or \(\beta\)-hydrogen position could produce a conjugated system without necessarily causing the cyclisation reaction to occur. Therefore a
method was needed to establish whether any such reaction had occurred. H'-NMR was used to clarify this point. If a reaction of either the α- or β- hydrogens occurred, a change in proton ratios would be recorded. For this reason H'-NMR was employed as a service technique for further elucidation of the structure of PAN treated with n-BuLi.

Figure (32) shows the H'-NMR spectrum obtained for the homopolymer. Comparison with the Standard Staedtler Reference spectrum for PAN, shown in Figure (33) enabled the peaks recorded to be identified. The chemical shifts for PAN in d₆-DMSO showed a broad band centred at δ = 2.1 ppm, which correspond with the CH₂ protons, and a complex peak at δ = 3.15 ppm, corresponding to the CH protons. In a well resolved spectrum this peak should appear as a resolveable quintet. The peak attributed to the methylene protons should resolve into a triplet. The reference spectrum shows the presence of impurities in the polymer. Typically these are the peaks at δ = 2.52 ppm, due to non-deuterated impurities in the d₆-DMSO solvent, at δ = 3.3 ppm, due to a trace of water in the solvent, and at δ = 3.72 ppm which has been attributed to an impurity of unknown origin. Similar impurities were observed in the spectrum of the PAN used in this experiment, probably due to traces of both water and residual solvent.

A series of spectra were obtained for PAN treated with n-BuLi under various experimental conditions, and a representative spectrum is shown in Figure (34). Contamination peaks were noted as previously described. The proton ratios (CH₂/CH) were calculated, using the integrated curve. Various CH₂/CH ratios are shown in Table (8). The theoretical value of
Figure (32) The H'-NMR spectrum of PAN recorded in d₆-DMSO.

Figure (33) The H'-NMR spectrum of PAN from the Staedtler Reference Spectra, recorded in d₆-DMSO.
Figure (34) A typical H'-NMR spectrum of a product of the reaction of PAN solution with n-BuLi, recorded in d$_6$-DMSO, ([PAN]=1.0 mol kg$^{-1}$, [n-BuLi]=0.05 mol kg$^{-1}$, T=293 K, t=600 s., under Argon).
<table>
<thead>
<tr>
<th>Concentration (mol kg(^{-1}))</th>
<th>Time (min)</th>
<th>Temperature (K)</th>
<th>(\text{CH}_2/\text{CH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>n-BuLi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.08</td>
<td>200</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.05</td>
<td>1</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.05</td>
<td>10</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>1</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>10</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>60</td>
<td>293</td>
</tr>
<tr>
<td>1.0</td>
<td>0.08</td>
<td></td>
<td>273</td>
</tr>
</tbody>
</table>

**Table (8)** Proton ratios calculated for samples from the reaction of PAN solutions with n-BuLi under various conditions.
CH$_2$/CH calculated from the empirical formula of PAN is equal to 2.00. The experimental value of 2.05 was very close to this value. The ratios calculated for treated PAN did not deviate greatly from this value, and there was no obvious trend to indicate that reaction of these groups had occurred. It was concluded that under the reported experimental conditions no reaction through the polymer backbone had taken place.

An addition point of interest in some of the spectra of the treated polymers was a doublet at $\delta = 2.91$ ppm due to traces of occluded DMF. In the preparation of samples, the polymers had been freeze-dried under high vacuum. It was apparent that residual DMF was bound in the polymers making its total removal difficult. Solvent residues are notoriously difficult to remove from the homopolymer without prolonged heating, which was not desired in this case.

From these results it was concluded that the conjugated sequences observed by the other spectroscopic techniques were attributable to segments of cyclised polymer, produced by the secondary polymerisation of the pendant nitrile groups initiated by the addition of n-BuLi. No evidence for the production of a conjugated polyene structure, which would be the result of reaction in the polymer backbone was observed. Furthermore, a shift in the CH$_2$ spectrum which would be the result of a change in the chemical environment of the CH$_2$ protons on the formation of a condensed pyridine structure was not observed.

5.4.7 Gel permeation chromatography

An important factor when considering the reaction of PAN with n-BuLi was the importance of maintaining structural integrity. Stabilisation of the polymer would not be enhanced if molecular breakdown was brought about by the reaction. Consequently the products were examined by GPC in order
to detect any chain scission or fragmentation during the treatment.

Chromatograms were obtained from solutions of reacted polymers, redissolved in distilled DMF. Calibration of samples with respect to polystyrene (PS) standards of known molecular weight in DMF was made. Figure (35) shows the calibration curve, with log(molecular weight) plotted versus elution volume. The molecular weight of a sample at a given elution volume could then be calculated with respect to PS. Figure (36) shows a typical series of chromatograms for PAN initiated with n-BuLi (concentration =0.08 mol kg\(^{-1}\)), at 293 K for various times. Observation of the peak maxima positions show considerable changes compared with the chromatogram of the homopolymer. In all the chromatograms peaks at elution volumes greater than 35 cm\(^3\) have been ignored, since they are caused by impurities such as water and dissolved gases in the solvent. The chromatogram recorded for PAN shows a symmetrical peak centred around elution volume of 23.5 cm\(^3\) which equates with a molecular weight of 140,000 with respect to PS. 

\[ \tilde{M}_n = \frac{\sum H}{\sum HM/M} \]

where \( H \) = peak height at any elution volume

\[ \tilde{M}_w = \frac{\sum HM}{\sum H} \]

\( M \) = molecular weight at same elution volume w.r.t. PS.

Values obtained for the homopolymer were

\[ \tilde{M}_n = 140,000 \]
\[ \tilde{M}_w = 250,000 \]

Similar values were not calculated for treated polymers since their solution properties change continuously as the reaction proceeds.

Analysis of the chromatograms from the reacted polymers was complicated by a number of factors. In the case of a monomeric or simple material, a Gaussian shaped curve would be obtained. A symmetrical peak would be
Figure (35) The calibration curve for GPC obtained using polystyrene standards.
Figure (36) A series of chromatograms recorded for the products of the reaction of PAN solutions with n-BuLi. (1) t = 0, (2) t = 60 s., (3) t = 600 s., (4) t = 6000 s., (5) t = 12000 s. ([PAN] = 1.0 mol kg\(^{-1}\), [n-BuLi] = 0.08 mol kg\(^{-1}\), T = 293 K, under Argon)
indicative of a statistically uniform distribution of molecules. The position of the peak maximum is dependent on the molecular weight of the constituent molecules, while the enclosed area is proportional to the weight and concentration of the sample in solution. For a polydisperse material the resultant curve is a composite of Gaussian curves of all its components. The total area under the curve is proportional to the concentration but the height of the individual peaks is not then proportional to the relative abundance of the components at the corresponding elution volume, since it will also depend on the abundance of the neighbouring components. Specific analysis of the traces recorded, in terms of the amount of the various components and their molecular weights is difficult because the curves cannot be readily deconvoluted. Therefore a comparative analysis was used.

As the reaction proceeded major changes in the chromatograms with respect to the homopolymer were observed. The residual peak recorded initially was shifted to slightly lower elution volumes. Concurrently secondary overlapping peaks developed at smaller elution volumes. In some cases a sharp peak developed at 15 cm due to exclusion of the molecules with the longest dimension from the gel. Since the excluded polymer peak disappears early in the reaction, polymers with small extents of cyclisation have an apparently decreased effective size. At larger extents of cyclisation the apparent effective size is increased. This is explained by the change in the thermodynamics of the ladder polymer solution. These results support the formation of a ladder polymer with an effective average molecular dimension in DMF solution, which is dependent on the extent of cyclisation.

The apparent trend to larger elution volumes (or smaller effective size) cannot be explained by chain scission because the limiting osmotic pressure of both the homopolymer and a cyclised polymer (extent=0.632) in DMF solution were found to be the same. Since $M_n$ remained constant intra-
molecular chain reactions must have taken place, rather than chain scission or intermolecular crosslinking.

5.4.8 Elemental analysis

Elemental analysis was used to monitor the reaction of PAN with n-BuLi, in terms of changes in its elemental constituents as the reaction proceeded.

5.4.8.1 Microanalytical analysis

This technique was not used as a continuous monitoring technique, but was used to examine representative samples after their reaction with n-BuLi. Table (9) shows that the experimental analysis of the homopolymer was in good agreement with the theoretical values calculated from the empirical formula of PAN ($C_3H_3N$). Incomplete analysis was apparent, however the small percentage difference is attributed to oxygen, which cannot be determined directly. A small quantity of water could have been adsorbed on to the surface of the polymer prior to testing, which could account for the presence of oxygen. Alternatively, it is possible that the argon used as the purging atmosphere in the production of the polymer was not completely oxygen free.

Table (10) shows a series of analyses obtained for treated polymers with respect to their experimental conditions. A change in elemental composition with respect to PAN was apparent. The major change was the increased oxygen content. The fraction of hydrogen also slightly increased. These changes can be explained in a number of ways. Firstly the factors outlined for the presence of oxygen in the starting polymer also exist after reaction with n-BuLi, although this explanation probably does not account for the fairly substantial increase in percentage of oxygen. Secondly the H'-NMR results in section 5.4.6 indicated that small quantities of occluded DMF remained in the reacted polymers despite extensive freeze-drying. Such an impurity would effect the elemental analysis. Similarly
<table>
<thead>
<tr>
<th>Element</th>
<th>% calculated</th>
<th>% found</th>
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<td>67.92</td>
<td>67.52</td>
</tr>
<tr>
<td>nitrogen</td>
<td>26.42</td>
<td>26.00</td>
</tr>
<tr>
<td>hydrogen</td>
<td>5.66</td>
<td>5.16</td>
</tr>
<tr>
<td>oxygen (by difference)</td>
<td>-</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table (9) The theoretical and experimental values for the elemental analysis of PAN.

<table>
<thead>
<tr>
<th>Concentration (mol kg(^{-1}))</th>
<th>Time (min)</th>
<th>Temperature (K)</th>
<th>Elements</th>
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</thead>
<tbody>
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<td>BuLi</td>
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<td>C</td>
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<td>293</td>
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Table (10) Elemental analyses for PAN treated with n-BuLi under various conditions.

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Table (11) Elemental analyses for PAN treated with n-BuLi at 293 K for various times, obtained by x-ray photoelectron spectroscopy.
methanol not removed on freeze-drying could be present, although this is less likely because of the high vapour pressure of methanol relative to DMF.

5.4.8.2 X-ray Photoelectron spectroscopy

The reasons for using this technique were twofold. It had been hoped to use this method to monitor structural changes in the treated polymers directly. Secondly the spectra could be used to confirm the elemental analysis obtained by the microanalytical technique. Spectra were obtained from powder specimens, and since XPS is mainly a technique for the examination of the specimen surface, information about the bulk of the sample was not obtained. In the first instance, therefore, XPS was used as a confirmatory analysis technique. Carbon, nitrogen and oxygen were determined directly from the recorded spectra while hydrogen was calculated by difference. Figure (37) shows a typical spectrum obtained from PAN. The C (1S), N (1S) and O (1S) were recorded at their respective binding energies, and were then corrected by their sensitivity factors, as is common practice. A noticeable feature of the spectrum was a doublet attributable to indium. Thus the method of specimen mounting posed problems in the elemental calculations. Values were therefore corrected using the following method. The spectrum of PAN showed a much higher oxygen concentration than was recorded using the microanalysis technique. The spectrum of a blank indium specimen holder was therefore recorded, and produced a similar peak in its spectrum, indicating the presence of an oxygen impurity on the indium. A constant oxygen impurity level was therefore assumed for all the indium sample holders, and an oxygen correction factor was calculated from the In (1S) and O (1S) ratios. All succeeding oxygen percentages were corrected using this factor.

Elemental percentages were calculated from the peak heights, which were computed from the 30 eV scans of the regions pertaining to the
Figure (37) The x-ray photoelectron spectrum of PAN.
Figure (38) The x-ray photoelectron spectrum recorded for PAN treated with n-BuLi (concentration = 0.08 mol kg$^{-1}$) for 6000 s.
specific peaks. Figure (38) shows a typical spectrum for a treated polymer. Table (11) shows a series of elemental analyses for samples treated with 0.08 mol kg\(^{-1}\) n-BuLi at 293 K for various times. Figure (39) shows a plot of the change in elemental components with respect to reaction time. The percentages of carbon and hydrogen remain substantially constant, while the nitrogen concentration decreases with time.

The presence of oxygen apparent in this technique was thought to be a function of adsorbed water vapour on the surface of specimens. This conclusion was drawn from the fact that oxygen concentrations using this technique were less than those determined by microanalysis. ESCA determines surface characteristics while microanalysis is a function of bulk properties. Since the oxygen value in the latter case is higher than the former, it is more likely to be attributed to occluded DMF, while oxygen at the surface is due to water vapour. In the case of oxidation occurring during storage, it would be expected that oxygen levels would be higher using ESCA since the surfaces are the most susceptible to oxidation.

It was not possible to use this technique to observe structural changes occurring as the reaction proceeded. The peaks recorded for each elemental component on a 30 eV scan were Gaussian in shape for unreacted polymers. While the corresponding peaks for the reacted polymers became more structured, their components could not be deconvoluted. Although this technique indicated a change in bonding as the reaction proceeded, specific analysis of the types of bonds present was not possible. The spectra were therefore used as a confirmatory elemental analysis technique.

5.4.8.3. Summary of elemental analysis

Determination of the elemental percentages present in the homopolymer using both analysis techniques gave good agreement. Both
Figure (39) Elemental constituents calculated from XPS, for products of the reaction of PAN with \( n\text{-BuLi} \) as a function of time, \([n\text{-BuLi}]=0.08 \text{ mol kg}^{-1}, T=293 \text{ K, under argon}\)
techniques also demonstrated the presence of oxygen in some of the samples. There are a number of possible sources for the oxygen, including small oxygen impurities in the oxygen-free nitrogen, adsorbed water, retained methanol, which is unlikely because of its low vapour pressure, and residual DMF which was not removed despite extensive freeze-drying.

The fraction of oxygen was less in the XPS analysis than in the microanalytical technique. Since the former is a surface technique, the presence of oxygen is probably due to adsorption of impurity oxygen or water. The oxygen observed in the bulk technique was probably due to occluded DMF. Taking both these factors into account, it was calculated that between 5-10% occluded DMF could account for the fraction of oxygen observed in the analyses.

The effect of DMF on the results presented will be discussed in section (6.3.)

5.5 Quantification of the cyclisation reaction

5.5.1. Introduction

The cyclisation reaction for BuLi treated PAN was established from spectroscopic evidence. The spectra obtained were then analysed to calculate the degree and extent of the cyclisation, by quantitative analysis of infrared spectra, with reference to values calculated from other techniques. It was difficult to standardise the spectra obtained from potassium bromide discs containing dispersed solids. Therefore it was necessary to employ a method of quantitative analysis, dependent on a number of assumptions which will be discussed as they arise. All results presented are a consistent series based on a relative absorbance at a specific wave number. The baseline density method was used to calculate peak intensities from the absorption spectra. When using the potassium bromide disc method as a continuous monitoring technique, it was difficult to ensure identical reproduction of sample
size, dispersion and thickness, despite efforts to minimise these discrepancies. For this reason spectra were calibrated with respect to a standard. Possible standardisation methods can be summarised as follows:

(i) incorporating an additive of known absorbance into the polymer. Such an additive must have a well defined, characteristic absorbance in a region of the spectrum which would not interfere with sample absorbances. This method introduces similar sources of error as using an uncalibrated spectrum, since the additive must be added reproducibly.

(ii) using an internal standard. The obvious advantage of this method is the constancy of the proportion of the particular absorption irrespective of slight fluctuations in absolute sample size. The chosen absorption must represent a group which remains unreacted throughout the reaction.

The latter method was used to calibrate the spectra. The strong CH\textsubscript{2} (2940 cm\textsuperscript{-1}) peak was thought to be a suitable internal standard, although this presumes that no reaction of the polymer backbone occurs. H\textsuperscript{1}-NMR spectra reported in section (5.4.6) indicated that the ratio CH\textsubscript{2}/CH remained constant throughout the reaction. It was therefore concluded that no reaction in the polymer backbone had occurred, thus establishing the validity of using the CH\textsubscript{2} (2940 cm\textsuperscript{-1}) peak as an internal standard. Using this method the need for exact reproducibility of specimen size in a potassium bromide disc was reduced, although care was taken to achieve consistency. It was found that variation of sample size in the range 2-6 mg of PAN in a standard disc gave constant CN(2240 cm\textsuperscript{-1})/CH\textsubscript{2}(2940 cm\textsuperscript{-1}) ratios. All values of absorbance quoted in the succeeding section are calculated using the internal standardisation technique.
5.5.2. The effect of n-BuLi concentration on the degree and extent of the cyclisation reaction in PAN

To calculate the degree and extent of the cyclisation, the total nitrile concentration at any point in the reaction had to be calculated. Section (5.4.3) indicated that two absorptions in the spectra of reacted polymers were attributable to nitrile groups, at 2240 cm\(^{-1}\) and 2200 cm\(^{-1}\). Figures (40) and (41) show typical plots of the relative absorbance of both nitrile peaks as a function of reaction time. A rapid decrease in the absorbance at 2240 cm\(^{-1}\), which corresponds with a rapid increase in the 2200 cm\(^{-1}\) peak was observed in the first 10 mins. of the reaction. At longer times, the relative intensities of both absorptions reached limiting values. In order to calculate the total nitrile concentration at any time, the relative contributions of each nitrile peak to the total was determined. The Beer-Lambert Law was shown to apply to the nitrile absorption at 2240 cm\(^{-1}\) with respect to the nitrile concentration in a potassium bromide disc. Figure (42) shows the linearity of the plot of relative nitrile absorbance, versus nitrile concentration.

Using the relationship

\[ A = \varepsilon c L \]

where \( A \) = absorbance
\( \varepsilon \) = extinction coefficient
\( c \) = molar concentration
\( L \) = path length (cm)

the gradient gave a value of extinction coefficient for CN (2240 cm\(^{-1}\)) such that

\[ \varepsilon_{2240} = 30.5 \text{ kg mol}^{-1} \text{ cm}^{-1} \]

The corresponding extinction coefficient for the second nitrile peak \( \varepsilon_{2200} \) was determined by considering the 2200 cm\(^{-1}\) peak immediately after initiation with various concentrations of n-BuLi. By assuming
Figure (40) Relative absorbance of the CN(2240) cm$^{-1}$ peak as a function of reaction time for the reaction of PAN solutions with n-BuLi, ([n-BuLi]=0.10 mol kg$^{-1}$, T=293 K, under Argon)

Figure (41) Relative absorbance of the CN(2200) cm$^{-1}$ peak as a function of reaction time for the reaction of PAN solutions with n-BuLi, ([n-BuLi]=0.10 mol kg$^{-1}$, T=293 K, under Argon)
Figure (42) Relative absorbance of the CN(2240) cm$^{-1}$ peak as a function of nitrile concentration.

Figure (43) Relative absorbance of the CN(2200) cm$^{-1}$ peak as a function of n-BuLi concentration.
that directly after initiation, one CN (2200 cm\(^{-1}\)) group is produced for each initiator ion, a plot of the relative nitrile absorbance at 2200 cm\(^{-1}\) versus the BuLi concentration could be made. Figure (43) shows this to be a linear plot, whose gradient gives

\[ \varepsilon_{2200} = 352 \text{ kg mol}^{-1} \text{ cm}^{-1} \]

In order to calculate the total nitrile concentration at any time in the reaction, the peak at 2200 cm\(^{-1}\) was corrected to allow for the large differences in extinction coefficients of the two nitrile absorbances.

Therefore Table (12) quantitatively analyses the reaction of PAN with n-BuLi in terms of the relative absorbance of the nitrile peaks, extent of cyclisation (as a mole fraction) and the degree of cyclisation, as a function of n-BuLi concentration, at constant temperature. The degree of cyclisation \( (C_\chi) \) is an average value computed by dividing the extent of reaction by the n-BuLi concentration. Figure (44) shows a typical plot of the fraction of unreacted nitrile groups with respect to time for n-BuLi concentration of 0.1 mol kg\(^{-1}\). Typically there was an initial rapid decrease in nitrile concentration in the first 10 mins. of the reaction. At longer times the curves tended towards a limiting value, which was relatively independent of n-BuLi concentration. A constant ultimate value of 60-65% reacted nitrile groups was observed.

The extent of reaction increased as the reaction proceeded, tending to a limiting value at longer times. Similar trends were observed for the degree of cyclisation, since the latter was dependent on the n-BuLi concentration. However, the degree of cyclisation also decreased with increased n-BuLi concentration. The length which cyclised sequences can attain is clearly a function of the distance between initiation sites, which depends on the initiator concentration. The lower the concentration is, the further apart the initiation sites are, and so the cyclised length can be correspondingly longer. In the absence of any molecular
| [n-BuLi] (mol kg\(^{-1}\)) | Time (s) | P\(_{CN}\) | C\(_x\)  | R \(
\frac{CN(2200)}{CN(2240)}\) |
<table>
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**Table (12)** The extent (P\(_{CN}\)) and degree (C\(_x\)) of the cyclisation reaction as a function of n-BuLi concentration and time, ([PAN]=1.0 mol kg\(^{-1}\), T=293 K, under Argon)
Figure (44) Mole fraction of unreacted nitrile groups as a function of reaction time, for the reaction of PAN solutions with n-BuLi, (1) [n-BuLi] = 0.10 mol kg⁻¹, (2) [n-BuLi] = 0.01 mol kg⁻¹ (T=293 K, under Argon)
restriction the reaction can proceed along the polymer chain between
initiation sites. The actual ladder length may be reduced if growing
sequences oppose one another. At the other extreme, at the high n-BuLi
concentration, the initiation sites are much closer together. In this
case sequences of only limited length can occur before hinderance from
other growing ends occurs. Degrees of cyclisation up to 23 were observed.

5.5.3. The effect of reaction temperature on the extent and degree of
the cyclisation reaction in PAN

Values of the extent and degree of the cyclisation reaction as
a function of reaction temperature were computed as previously described.
The results obtained are tabulated in Table (13). Figure (45) illustrates
the reaction with a plot of unreacted nitrile groups as a function of time
for reaction temperatures of 293 K and 313 K.

The characteristics of the plots are similar to the graphs plotted
for the effect of n-BuLi concentration on the extent of cyclisation.
There is an initial rapid decrease in nitrile concentration followed by
a more gradual decrease as the reaction proceeds.

The initial rate of decrease in nitrile concentration is higher as
the reaction temperature is increased. However the bulk of the reaction
takes place in the first 10 minutes at the higher reaction temperature,
and the limiting fraction of reacted nitrile groups is reached faster.
Increasing the reaction temperature therefore appears to result in a
higher limiting residual nitrile concentration. At 273 K there was a
rapid initial reaction of the nitrile groups, on addition of the
initiator, but little further increase in the extent of reaction was
observed. At reduced temperatures the chain mobility is reduced, and
rotation about the polymer backbone cannot readily occur, thus
preventing the limiting value of extent of reaction from being reached.
<table>
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<th>[n-BuLi] (mol kg(^{-1}))</th>
<th>Time (s)</th>
<th>Temperature (K)</th>
<th>(P_{\text{CN}})</th>
<th>(C_x)</th>
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**Table (13)** The extent (\(P_{\text{CN}}\)) and degree (\(C_x\)) of the cyclisation reaction, as a function of temperature and time ([PAN]=1.0 mol kg\(^{-1}\), under Argon).
Figure (45) Mole fraction of unreacted nitrile groups as a function of reaction time for PAN solutions reacted with [n-BuLi]=0.08 mol kg−1, (1) T=293 K, (2) T=313 K.
By employing low temperatures for these reactions the possibilities of side reactions, which could obscure the cyclisation reactions is minimised. It has been shown that the cyclisation reaction can be initiated by n-BuLi at temperatures as low as 273 K, although at this temperature energy considerations makes propagation increasingly difficult.

5.5.4. The effect of atmosphere on the extent and degree on the cyclisation reaction in PAN

Carbon fibres with improved mechanical properties are produced when the low temperature thermal treatment is carried out in an oxidising atmosphere. Therefore the effect of oxygen on the reaction of PAN with n-BuLi was studied.

The cyclisation reaction was initiated by n-BuLi (concentration = 0.08 mol kg\(^{-1}\)) in an inert atmosphere, in the normal manner. After approximately 5 minutes the solution was flushed with oxygen. Sampling of the reaction continued as previously described, in an oxygen atmosphere. This method was used because impurities such as oxygen are known to inhibit ionic reactions, and therefore an inert atmosphere was used to ensure that initiation occurred.

On addition of the initiator the solution was immediately coloured yellow. Observation of the colour in the presence of oxygen however showed very little further change with increased reaction time.

Quantitative analysis of the spectra showed an initial decrease in nitrile concentration, for the sample removed prior to flushing with oxygen. However, this value remained virtually constant for samples removed from the oxygen contaminated solution. It was therefore concluded that the cyclisation reaction, which had been initiated in an inert atmosphere, was inhibited by the presence of oxygen. This fact is also evidence confirming that the reaction of PAN with n-BuLi is an ionic reaction.
5.5.5 The effect of polymer concentration on the extent and degree of the cyclisation reaction in PAN.

The effect of polymer concentration on the extent of the cyclisation reaction in PAN was investigated. The aim of the experiment was to determine the limiting extent of cyclisation, in order ultimately to determine the possible ceiling temperature effect for the reaction. A sampling technique was therefore not employed. Polymer solutions were dissolved in the normal manner. The reaction was initiated with n-BuLi (concentration = 0.11 mol kg\(^{-1}\)), at 293 K under argon, for different polymer concentrations. The reaction continued for 24 hr. to ensure that a limiting nitrile concentration was reached. The products were isolated, and the spectra were recorded in the usual way. Table (14) correlates the extent of the nitrile reaction with the initial polymer concentration. Figure (46) is a plot of the residual nitrile fraction as a function of initial nitrile concentration, indicating the proportionality of the relationship.

The large nitrile : n-BuLi concentrations, however, precluded the determination of a ceiling temperature effect for the reaction.

5.5.6 Summary

A method has been developed to calculate the extent of the cyclisation reaction, for a variety of experimental conditions, using the infrared spectra of the products. The results have indicated that extents of cyclisation between 0-0.6 can be achieved. By considering the n-BuLi concentration the average degree of reaction was also computed. Cyclised lengths between 2-23 monomer units were calculated, depending upon the experimental conditions used.

This technique could therefore be used to incorporate cyclised sequences of known length into PAN.
Table (14) The extent of cyclisation as a function of polymer concentration, ([n-BuLi] = 0.11 mol kg\textsuperscript{-1}, T=293 K, under Argon.)

<table>
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<th>[CN]\textsubscript{o} (mol kg\textsuperscript{-1})</th>
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<th>(1-P)\textsubscript{CN} (%)</th>
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Figure (46) Residual nitrile concentration as a function of polymer concentration, ([n-BuLi] = 0.11 mol kg\textsuperscript{-1}, T=293 K, under Argon)
5.6 Thermal analysis of cyclised PAN

5.6.1 D.S.C analysis of PAN

The exotherm observed when PAN is heated in a controlled manner, in the temperature range up to 650 K, in an inert atmosphere, is directly associated with the thermally induced cyclisation reaction. D.S.C. analysis of the homopolymer was carried out in order to compare the enthalpy of the thermal reaction of the nitrile groups with the corresponding enthalpy values obtained when the partially cyclised products of the reaction of PAN with n-BuLi are heated.

When PAN was heated in an inert atmosphere a sharp, vigorous exotherm was recorded. A peak maximum temperature of 548 K was observed. The enthalpy of the thermally induced cyclisation reaction was 20.1 kJ mol\(^{-1}\), calculated from the enclosed area of the curve, as described in section (4.11.1). The corresponding curve recorded when PAN was heated in an oxidising atmosphere was similar in shape, however the peak maximum temperature was displaced to higher temperature, (598K). Figure (47) demonstrates the respective traces obtained for PAN heated in both inert and oxidising atmospheres.

The results for the homopolymer can be used as a baseline, to determine the effect of partial cyclisation on the characteristic exotherm. Therefore, partially cyclised polymers, produced by the reaction of PAN with n-BuLi were similarly examined. The relationship between the residual enthalpy and the extent of cyclisation was determined.

5.6.2 D.S.C. of partially cyclised PAN

D.S.C. traces were recorded for all n-BuLi treated specimens in the temperature range 273-648 K. Major changes in the exotherm characteristics were apparent even for very small extents of cyclisation
Figure (47) DSC traces for PAN recorded in (1)N₂, (sample size=2.5 mg.), (2)O₂, (sample size=270 mg.)
Figure (48) shows a typical series of traces recorded for samples reacted with n-BuLi for various times. The sharp exotherm associated with PAN was drastically reduced in intensity even when the extent of cyclisation was as low as 0.28. The exotherm initiation temperature ($T_i$) was also reduced, resulting in a broadening of the curves. The residual enthalpy was calculated as described in section (4.11.1).

Table (15) tabulates the residual enthalpy as a function of experimental conditions. The temperature at which the exotherms were at a maximum remained relatively constant, irrespective of the extent of cyclisation, and was 540 ± 10 K. Figure (49), curve (1), shows a typical plot of residual enthalpy as a function of reaction time, for the reaction where n-BuLi concentration 0.08 mol kg$^{-1}$, reaction temperature 293 K, under argon. For all concentrations, at constant temperature, there was a rapid decrease in residual enthalpy after short reaction times, with a more gradual subsequent decrease at longer times. At the lowest concentration the initial large decrease was less apparent, although the overall shape of the curve was similar. At the highest concentration the residual enthalpy tended towards a limiting value as the reaction time increased. The effect of increasing the n-BuLi concentration was to correspondingly decrease the residual enthalpy.

The residual enthalpy was similarly calculated as a function of reaction temperature. Table (16) reports these values with respect to reaction time and extent of cyclisation, while Figure (49), curve (2), demonstrates the nature of these results as a function of reaction time, at 313 K, for n-BuLi concentration of 0.08 mol kg$^{-1}$. The shape of the curve is similar to curve (1). Generally the effect of increasing the reaction temperature was to correspondingly decrease the residual enthalpy.
Figure (48) DSC traces recorded for the products of PAN solutions with \([\text{n-BuLi}] = 0.08 \text{ mol kg}^{-1}\) at 293 K. 
(1) \(P_{\text{CN}} = 0.28\), (2) \(P_{\text{CN}} = 0.395\), (3) \(P_{\text{CN}} = 0.519\), (4) \(P_{\text{CN}} = 0.584\).
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Table (15) Residual enthalpy as a function of [n-BuLi] and reaction time (T=293 K), (Tᵢ=exotherm initiation temperature, Tₘₐₓ=peak maximum temperature.)
Figure (49) Residual enthalpy recorded for the products of the reaction of PAN solutions with $[\text{n-BuLi}] = 0.08$ mol kg$^{-1}$ as a function of reaction time, (1) $T = 293$ K, in nitrogen, (2) $T = 313$ K, in nitrogen, (3) $T = 293$ K in oxygen.
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Table (16) Residual enthalpy for partially cyclised PAN as a function of experimental conditions.
The specimens produced in an oxygen atmosphere were similarly examined. Figure (49), curve (3) shows a plot of the results as a function of reaction time, for n-BuLi concentration of 0.08 mol kg\(^{-1}\), at 293 K. It was noted that the residual enthalpy apparently decreased in the same manner as for the inertly produced samples. At all reaction times, the residual enthalpy is higher for specimens produced in oxygen, than the corresponding inertly produced specimens. Section (5.4.4) has shown that in spectroscopic terms the presence of oxygen has apparently inhibited the cyclisation reaction, whereas the thermal analysis results indicate that the residual enthalpy does not remain constant. The samples produced in oxygen were initiated in an atmosphere of argon. The terminal imine groups resulting from precipitating the product into methanol to effect recovery, can initiate the thermal reaction on heating. It has been shown from elemental analysis that occluded DMF is present in the samples, despite extensive freeze-drying. This may affect the residual enthalpy to some degree, since an endothermic reaction would be expected on distillation. This would reduce the apparent residual enthalpy due to the cyclisation of the nitrile groups on heating.

The relationship between the nitrile concentration and the residual enthalpy was determined. Figure (50) shows a plot of mole fraction of residual nitriles versus residual enthalpy. The proportionality between the number of residual nitrile groups, calculated from the infrared spectra, and the residual enthalpy is clearly demonstrated. The calculated value of 24.2 kJ mol\(^{-1}\) for the enthalpy of cyclisation of the residual nitrile groups compared favourably with the value of 31.0 kJ mol\(^{-1}\) reported by Grassie\(^{28}\) for the thermal reaction, in an inert atmosphere. From this result it was concluded that the structure produced chemically was substantially the same as thermally
Figure (50) Mole fraction of residual nitrile groups as a function of residual enthalpy.

Residual nitrile (mole fraction)

ΔH (Jg⁻¹)(x10²)
stabilised PAN. The intercept value of 0.20 mole fraction of unreacted nitrile groups implied that under any experimental conditions, there will always be 20\% of the nitrile groups which cannot participate in the cyclisation reaction. This is in agreement with the value of 19.2\% calculated for the thermal reaction\(^{(20)}\). Thus the thermal initiation of reacted samples must be associated with the end-groups on the cyclised sequences, and not the self initiation process.

5.6.3 Thermogravimetric analysis of PAN

The weight loss characteristics were recorded for PAN in the same programmed heating range used for the D.S.C. analysis. Figure (51) shows the thermogram recorded for PAN, which showed that PAN was thermally stable at temperatures up to the exotherm initiation temperature (approximately 510 K), the weight loss observed being only 1\%. Above this temperature, rapid weight loss occurred as the exothermic reaction proceeded. At the finish of the exothermic reaction the total weight loss was approximately 5\%, although on further heating the weight loss increased rapidly.

5.6.4 Thermogravimetric analysis of partially cyclised PAN

Thermograms were recorded for n-BuLi treated samples, in the same temperature range as used in the D.S.C. analysis. A typical series of thermograms are shown in Figure (52), for the experiment where n-BuLi concentration = 0.08 mol kg\(^{-1}\), at 293 K, under argon. The corresponding extents of cyclisation have also been quoted. At the lowest extent of cyclisation (0.28) samples were apparently thermally stable up to approximately 523 K. Above this temperature an increase in the weight loss was observed. This rate was less rapid than the steep weight loss recorded during the exothermic
Figure (51) The thermogram for PAN recorded in nitrogen.
Figure (52) Thermograms recorded for the products of the reaction of PAN solutions with \([n{-}\text{BuLi}] = 0.08\) mol kg\(^{-1}\), (1)\(P_{\text{CN}} = 0.28\), (2)\(P_{\text{CN}} = 0.395\), (3)\(P_{\text{CN}} = 0.519\), (4)\(P_{\text{CN}} = 0.584\), (5)\(P_{\text{CN}} = 0.671\).
reaction in PAN. At larger extents of cyclisation, although increased weight loss was observed compared with PAN, at lower temperatures, the vigorous weight loss associated with the exotherm was less apparent. The implication of these results is that low extents of cyclisation are sufficient to thermally stabilise PAN with respect to weight loss. The thermal stability appeared not to improve for larger extents of cyclisation, and/or increased initiator concentration. As the extent of cyclisation is increased, the temperature at which the onset of the weight loss occurs, was reduced. Extents of cyclisation as high as 0.584 did not result in catastrophic weight loss. Above this, a weight loss was apparent from ambient temperature. It was likely that at higher extents of cyclisation, with correspondingly longer cyclised sequences, the possibility of degradation reactions increases, since there would be little scope for further cyclisation to occur.

If the residual DMF observed in section (5.4.8) is taken into account, then a marked difference would be observed in the thermograms of partially cyclised PAN. In the presence of retained solvent, there would be a weight loss on heating, which could be attributed to the solvent being distilled out. Figure (53) shows a plot of approximate DMF concentration plotted as a function of extent of cyclisation. As the extent of cyclisation increases, the possible percentage of occluded DMF also increases. This relationship can be used to explain the apparent reduced thermal stability of the products with the highest extents of reaction. If the contribution of occluded DMF to the thermograms is removed, the increased thermal stability of the partially cyclised products, in the exotherm temperature range, is demonstrated, even for the largest extents of cyclisation.

The thermal stability of a partially cyclised product in the carbonisation temperature range was also investigated. Figure (54) shows
Figure (53) Percentage occluded DMF as a function of the extent of cyclisation.
Figure (54) Thermograms (1) for PAN stabilised at 498 K for 1.5 hrs. in nitrogen prior to carbonisation, (2) for partially cyclised PAN ($P_{CN}=0.584$) directly carbonised.
a comparison between the homopolymer, preheated in nitrogen at 493 K for 1.5 hr., and then programme heated (20 K min\(^{-1}\)) to 1220 K, in nitrogen; and a partially cyclised polymer (extent of cyclisation =0.584) carbonised directly under the same conditions, In the former case, little weight loss (2\%) was recorded during the low temperature treatment. After carbonising to 1220 K a steady-state carbon yield of approximately 40\% was achieved. In the latter case similar weight loss characteristics were observed in the first part of the heating curve, (up to 800 K) up to which point approximately 20\% weight loss was observed. Further weight loss for the partially cyclised product was substantially less than recorded for the conventionally stabilised polymer, and at 1220 K approximately 70\% of the original sample was left. However, a steady-state condition was not achieved in the same time as the thermally stabilised homopolymer, and the yield was slightly higher than the theoretical carbon yield for PAN. The results however suggest that an improved carbon yield may be possible from a carbonised, partially cyclised polymer, but that the nature of the product reduces the rate at which non-carbon atoms are expelled on carbonisation, increasing the required carbonisation time. This is an area which requires further work, since only a cursory examination of the carbonising potential of the partially cyclised product has been made.

5.6.5 Separation of the cyclisation and oxidation reactions in PAN.

5.6.5.1 Introduction

When PAN is thermally treated in an inert atmosphere a simple cyclisation mechanism is generally accepted. Heating in an oxidising atmosphere, in contrast, results in competing cyclisation and oxidation reactions. The overall shape of the exotherms for PAN heated in an oxidising atmosphere was found to be similar to that of
inertly treated PAN, except that the peak maximum temperature was displaced to higher temperature, with a corresponding increase in the enthalpy recorded. It was therefore of interest to try and separate the cyclisation and oxidation reactions in PAN. This was done initially by investigating the thermal properties of PAN under a variety of heating conditions. A similar investigation of the chemically cyclised polymers, with varying extents of reaction was made, and conclusions as to the nature of the oxidatively produced exotherm were made by comparing the two sets of data.

5.6.5.2 Thermal analysis of PAN under a variety of heating conditions

As previously reported (section 5.5.1) inert thermal treatment of PAN (273-623 K), produces a sharp exotherm with peak maximum temperature 548 K. Identical treatment in an oxidising atmosphere results in a shift of the peak temperature to 598 K, while the exotherm shape remains basically the same. In the production of carbon fibres, the heat evolved during the thermal reaction must be dissipated, to prevent major disruptions to the fibular structure. For this reason, the stabilisation process is carried out under isothermal conditions. The fibres are held at 498 K, to reduce the rate of heat output, thus dissipating the exotherm, without damaging the fibre. In an oxidising atmosphere, the resultant extent of cyclisation is sufficient to stabilise the polymer, and enable the fibre to withstand the carbonisation process.

In order to assess the contribution of the various thermal reactions to the exotherm, a variety of heating schedules were employed. PAN was heated in both nitrogen and oxygen (heating rate=20 K min⁻¹). PAN was heated to 500 K and held at temperature for 20 min. This short isothermal treatment was used since Clarke (57) has already shown that sufficient
stabilisation can be brought about under these conditions. The resultant polymer was quenched to 273 K, and reheated in oxygen, under the standard heating conditions. In comparison to this treatment, PAN was heated through the exotherm in nitrogen, quenched and reheated in oxygen. Figure (55) a series of exotherms produced under these conditions.

It was apparent that little heat was evolved when isothermally heating PAN at 500 K. Thus by holding at temperature just below the exotherm initiation temperature the heat produced could readily be dissipated. Curve (4) shows the results obtained by reheating the isothermally treated specimen in oxygen. A definite peak maximum at 598 K was recorded, although its intensity was substantially less than the corresponding value for the oxidised polymer. The broadening occurred at lower temperatures, in the range 423-548 K. A discernable maximum is apparent at approximately 538 K. The area enclosed by the exotherm probably corresponds with the cyclisation of any residual nitrile groups remaining after the isothermal treatment. Oxidation can take place over a wider temperature range, since parts of the structure have already been cyclised. Competition between the cyclisation and oxidation reactions was still apparent. Curve (5) shows the effect of heating through the exotherm in nitrogen, prior to oxidising the sample. The trend previously discussed was reversed. The peak broadening was still apparent, but in this case, a peak maximum at 498 K was observed, with a shoulder at 598 K. The conclusion drawn for this observation was that once the cyclisation reaction had occurred, the oxidation reaction could be induced at a much lower temperature.

To take the investigation one stage further, the effect of the isothermal treatment time was studied. Figure (56) shows a series of exotherms for PAN heated in oxygen, as a function of the time of the prior isothermal treatment. The dominant peak maximum at 598 K remained
Figure (55) DSC traces for (1) PAN in nitrogen, (2) PAN in oxygen, (3) PAN isothermally held at 498 K in nitrogen for 20 mins., (4) PAN in oxygen after isothermal hold in nitrogen at 498 K for 20 mins., (5) PAN in oxygen after heating through the exotherm in nitrogen.
Figure (56) DSC traces of PAN heated in oxygen after isothermal hold at 498 K. for 20 mins. in nitrogen for (1) t=0, (2) t=5 mins., (3) t=14 mins., (4) t=25 mins., (5) t=55 mins., (6) after heating to 575 K. in nitrogen.
constant. As the isothermal treatment time increased, the peaks broadened. The magnitude of the components with peak maximum temperature at 598 K decreased. After an isothermal treatment time of 20 min. a definite shoulder had developed on the main exotherm (temperature approximately 500 K). The decrease in magnitude of the peak at 598 K was accompanied by an increase in intensity of the shoulder.

A similar series of experiments was investigated for partially cyclised PAN, with varying extents of cyclisation. Figure (57) shows a series of traces obtained for PAN heated in nitrogen, after the reaction with n-BuLi (concentration = 0.08 mol kg\(^{-1}\), at 313 K). As previously observed, the intensity of the exotherm decreased with increasing extent of cyclisation. The residual enthalpy decreased correspondingly. Figure (58) shows the corresponding traces obtained when similar samples were heated in oxygen. Whereas a distinct, decreasing exotherm was observed on heating in nitrogen for all extents of cyclisation, a similar, well defined peak was only observed on heating in oxygen for small extents of cyclisation. As the extent of cyclisation increased, the curves became less well resolved. A distinct exotherm was not apparent, rather a gradual shift of the baseline was more obvious.

Figures (59) and (60) show the traces obtained when partially cyclised PAN has been programme heated in oxygen after previous isothermal treatment at 498 K in nitrogen, and after heating through the exotherm, respectively. The poor resolution of the traces made calculation of the enthalpies of reaction impossible. When heating the samples in oxygen, after prior isothermal treatment, the onset of heat evolution was not appreciably evident, but occurred at approximately 473 K. In contrast, reheating the samples in oxygen after previously heating through the exotherm in nitrogen, resulted in heat evolution at temperatures below 373 K. In this latter case, heating of the partially cyclised polymer
DSC traces for the products of the reaction of PAN solutions with \([\text{n-BuLi}] = 0.08 \text{mol kg}^{-1}\), at 313K, recorded in nitrogen for (1) \(P_{\text{CN}} = 0.406\), (2) \(P_{\text{CN}} = 0.439\), (3) \(P_{\text{CN}} = 0.541\), (4) \(P_{\text{CN}} = 0.559\), (5) \(P_{\text{CN}} = 0.565\), (6) \(P_{\text{CN}} = 0.592\), (7) \(P_{\text{CN}} = 0.635\). (sample size = 2.0 mg.)
Figure (58) DSC traces for the products of the reaction of PAN solutions with [n-BuLi] = 0.08 mol kg⁻¹ at 293 K.
(1) P_{CN}=0.28, (2) P_{CN}=0.395, (3) P_{CN}=0.519, (sample size = 2.0 mg.)
Figure (59) DSC traces for the products of the reaction of PAN solutions with \([n-\text{BuLi}] = 0.08\text{mol kg}^{-1}\) at 313 K. recorded in oxygen (1)\(P_{\text{CN}} = 0.406\), (2)\(P_{\text{CN}} = 0.439\), (3)\(P_{\text{CN}} = 0.541\), (4)\(P_{\text{CN}} = 0.565\), (5)\(P_{\text{CN}} = 0.635\). (Sample size=2.0mg.) after isothermal hold at 498 K. for 20mins. in nitrogen.
Figure (60) DSC traces for the products of the reaction of PAN solutions with $[\text{n-BuLi}] = 0.08\text{mol kg}^{-1}$ at 313 K. recorded in oxygen after previously heating through the exotherm in nitrogen for (1) $P_{\text{CN}} = 0.406$, (2) $P_{\text{CN}} = 0.439$, (3) $P_{\text{CN}} = 0.541$, (4) $P_{\text{CN}} = 0.635$. (Sample size = 2.0 mg.)
through its exotherm, should consume all the reactable nitrile groups. Thus reheating in oxygen was solely attributed to oxidation, which could be initiated at a lower temperature.
6.1 Introduction

The preceding chapter has presented a series of results indicating that PAN can be cyclised in the presence of additives. The cyclisation reaction in PAN induces thermal stability and is extremely important to the production of carbon fibres. Therefore, the reaction of PAN with n-BuLi must be considered both in terms of the reaction mechanism, deduced from the identification of the intermediate structures, and the suitability of the process as an alternative to thermal stabilisation reaction, at 498 K. The thermal reaction in an inert atmosphere, is better characterised than that under oxidative conditions, and the structure is considered to consist of short sequences of condensed naphthyridine rings produced by the additional polymerisation of the pendant nitrile groups. The effect of oxygen, comonomers, additives and any impurities present in commercial acrylonitrile polymers are complex, and thus the structure is less well characterised.

Many workers have studied the stabilisation reaction, under a variety of experimental conditions, and most make use of PAN in the form of powders, fibres or films. In contrast, solution studies were favoured by Kubasova (109), Berlin (110) and Yakobashvili (111). The different experimental techniques may be responsible for the variety of degradation mechanisms proposed.

In order to study the reaction of PAN with additives the reaction medium and experimental techniques had to be carefully considered. It was important to use experimental conditions which would ensure reproducible results. The PAN used throughout was made by radical polymerisation in the presence of a solvent with mild transfer properties, so that the average degree of polymerisation was controllable.
In addition, the side reactions responsible for abnormal structures in the polymer were limited by terminating the reaction at conversions of 25%. Therefore a well characterised polymer was used throughout this investigation.

Two methods of incorporating additives into the polymer were considered

(1) by addition to the bulk polymer
(2) by addition to polymer solutions

The rate of reaction is controlled by the rotation about the skeletal bonds of the polymer backbone, to bring the adjacent nitrile group into a reactable position. A solution technique was therefore chosen since a low reaction temperature could be used, due to the increased chain mobility in solution. Furthermore, a low reaction temperature reduces the incidence of side reactions, with high activation energies, from obscuring the cyclisation reaction. The incorporation of additives into a polymer solution also ensures uniform dispersion and reproducible results.

In contrast to the solution technique, Grassie(29), who investigated the effect of a wide range of additives, used a bulk technique, which relied upon the intimate mixing of an additive with the solid polymer. A nonuniform reaction could result, since the additive could react preferentially at particle surfaces, rather than in the bulk of the material.

In conclusion, solution studies were thought to be more suitable for studying the reaction of chemical initiators of the cyclisation of PAN. By catalytically reacting PAN with additives in solution, at relatively low temperatures, the reaction was more readily controlled and reproduced. The resultant products were then characterised using a combination of techniques. Sampling the reaction at various intermediate
stages enabled the reaction mechanism to be established.

Although solution chemistry was suitable for studying the chemical reaction, it must be acknowledged that reactions in this medium are likely to be substantially different from those which occur in stretched fibres. This fact must therefore be remembered when considering the suitability of using a chemically stabilised PAN fibres as precursors to carbon fibre formation.

6.2 Qualitative effect of additives

The results reported in section (5.2) showed that a wide variety of additives coloured PAN solutions, producing a similarly wide variety of colours. Sodium metal was found to colour PAN solutions rapidly. Marked spectral changes were also observed even after very short reaction times. As the reaction progressed, the nitrile concentration and the residual enthalpy, recorded on reheating, both decreased. Since more than one nitrile group per sodium ion disappeared, oligomersation of the nitrile groups was concluded. However the initiation mechanism was difficult to identify. In the first instance, a simple ionic mechanism was hypothesised. This simple approach was complicated by the possible reactions on dissolution of sodium in DMF, to produce the initiation solution. It has been reported that DMF behaves as an aldehyde\(^{(112)}\) in many of its reactions, with the carbonyl group undergoing nucleophilic attack\(^{(113)}\). A possible reaction is suggested in Figure (61) which is the conventional "ketyl" reaction of DMF with potassium and sodium. Although no study of this reaction was made, any such reaction would obscure the identity of the initiating species. Therefore a reaction mechanism was not developed for the reaction of sodium solutions in DMF on the cyclisation of PAN.
Figure (61) A possible mechanism for the reaction of sodium with DMF.

Figure (62) A termination reaction to produce cyclic end-groups in the polymerisation of AN (114).
Subsequent reactions were carried out using a well characterised ionic initiator, whose chemistry was less obscure. Anionic polymerisations tend to be less complex than cationic or free radical reactions in which transfer is more likely. n-BuLi has been used to polymerise AN anionically at low temperature in polar solvents, and the resultant polymer is reported\(^{61,62}\) to be yellow in colour, of low molecular weight and sometimes soluble in acetone. Termination involved cyclisation of the growing anion with the adjacent nitrile group\(^{114}\) to produce a chromophoric end-group. The proposed termination reaction with n-BuLi for this process can be seen in Figure (62). Overberger et al.\(^{115}\) proposed a similar termination mechanism for PAMN. However, Miller\(^{116}\) was able to prepare samples of PAN with a wide range of molecular weights, all of which were white in colour.

The fact that n-BuLi produces cyclised chromophoric species on reaction with AN led to the conclusion that it could probably initiate the cyclisation reaction in PAN. It had already been shown that n-BuLi successfully colours PAN solutions (section 5.4.2).

Other organometallic compounds have also been used to study coloration and degradation in PAN/DMF solutions. Friedreich\(^{94,95}\) produced coloured polymers by the reaction of PAN with tributyltinmethoxide, the reaction mechanism is shown in Figure (17) (section 2.5.4).

Thus it was concluded that organometallic compounds are effective cyclisation initiators. Table (3) (section 5.4.2) has shown that n-BuLi effectively colours PAN at a rate which could be recorded using a sampling technique. It was therefore used to initiate the production of cyclised polymers, whose structures could be elucidated at various stages of the reaction, enabling a reaction mechanism to be proposed.
6.3 Structure produced by the reaction of PAN with n-BuLi

6.3.1 Introduction

The structures of the polymers produced by the reaction of PAN with n-BuLi were determined using a combination of spectroscopic techniques. An isolated spectroscopic method, such as infrared, could not be relied upon to unambiguously establish the structure of the reacted polymer. The possible unsaturated groups which could result from the reaction absorb in the same spectral region. For this reason infrared spectroscopy was used in conjunction with ultraviolet absorption spectroscopy and H'-nuclear magnetic resonance techniques in order to determine the structures produced. Gel permeation chromatography was used to monitor the integrity of the resultant polymers, while elemental analysis established to elemental proportions throughout the reaction.

6.3.2 Qualitative infrared spectroscopy

6.3.2.1 Introduction

The results presented in section (5.4.3) indicated that noticeable spectral changes occurred when PAN solutions were treated with n-BuLi, as compared with the spectrum of the homopolymer. The major regions of interest in the spectra recorded, as far as structural elucidation is concerned, are the broad band developed between 3700-3100 cm\(^{-1}\), the peak which appeared at 2200 cm\(^{-1}\), and the series of overlapping peaks in the 1700-1200 cm\(^{-1}\) region. Therefore, in order to identify structures produced by the reaction, the absorbing species at these various wavenumbers must be established.

Clarke\(^{(57)}\) extensively reviewed the various assignments of the peaks produced when PAN is heated in both inert and oxidising atmospheres. Table (5) has already listed a summary of assignments made for the peaks developed during the thermal reaction. For simplicity, Table (17) summarises the assignments of the peaks of particular interest to this
## INFRARED PEAK ASSIGNMENTS

<table>
<thead>
<tr>
<th>INERT</th>
<th>OXIDISING</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400-3200 NH</td>
<td>3600-3200 NH</td>
</tr>
<tr>
<td>1670-1540 C=N*</td>
<td>3380-3100 OH</td>
</tr>
<tr>
<td>NH₂</td>
<td>1720-1540 C=O</td>
</tr>
<tr>
<td>C=C</td>
<td>C=N</td>
</tr>
<tr>
<td>NHₓ</td>
<td>C=C</td>
</tr>
</tbody>
</table>

* non conjugated or conjugated

### Table (17) Summary of the major IR peak assignments.

## INFRARED PEAK POSITIONS

<table>
<thead>
<tr>
<th>OBSERVED</th>
<th>OBSERVED (51)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3420</td>
<td>3390</td>
</tr>
<tr>
<td>3360</td>
<td>3356</td>
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<td>2200</td>
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<td>1670</td>
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</tr>
<tr>
<td>1090</td>
<td>1150</td>
</tr>
<tr>
<td>660</td>
<td>750</td>
</tr>
</tbody>
</table>

### Table (18) Comparison of peaks observed for PAN reacted with n-BuLi, and PAN reacted at 473 K under reduced pressure (51).
discussion, although no reference was made in Clarke's(57) summary to the peak observed 2200 cm\(^{-1}\).

Since Clarke's(57) review, more detailed infrared studies of the thermal reaction have been carried out. Stupp and Carr(117) studied the infrared response of heat treated PAN films, while Coleman and Petcavich(51) have reported superior spectra using the more sensitive Fourier Transform infrared spectroscopy technique for a similar analysis.

Before entering into a detailed discussion of peak assignments for the regions of the spectra of interest, it is interesting to compare a typical spectrum produced by the reaction of PAN with n-BuLi, with a spectrum reported by Coleman and Petcavich(51) for PAN thermally degraded under reduced pressure. Table (18) summarises the new peaks developed during both reactions. The similarities in the spectra are immediately apparent. It is therefore useful to use this as a basis for discussing the structure produced by the chemical reaction, in relation to the thermal degradation of PAN.

6.3.2.2 The 3700-3000 cm\(^{-1}\) band

Table (17) shows that the absorptions in this region have been attributed to -NH and OH groups. Section (5.4.3) has shown that OH contribution to the spectral of n-BuLi treated PAN was minimal. Therefore it was concluded that this absorption was due primarily to NH groups. Clarke(118) and Koenig(119) have similarly assigned such absorptions, also proposing significant intermolecular association of the -NH groups (possibly imines). Coleman and Petcavich(51) detected a doublet in this region, at 3390 and 3356 cm\(^{-1}\), for thermally degraded PAN under reduced pressure. This band is purported to be typical of primary amines(120), and so they assign this absorption to both NH and NH\(_2\) stretching modes.
The model compound $\Delta(8,9)$-oct-hydro-7-quinoline$^{(121)}$ has been used to study this region of the spectrum. The N-H absorption is reported at \(3405 \text{ cm}^{-1}\). Since no band is observed at \(3600 \text{ cm}^{-1}\) a keto-enol tautomerisation has been proposed. For this reason it was concluded that the absorption centered at approximately \(3230 \text{ cm}^{-1}\) for thermally degraded PAN was unlikely to be associated with an imine type structure$^{(51)}$. Brown et al.$^{(122)}$ summarised the behaviour of 5 and 6 membered ring compounds and proposed that the enamine structure, rather than the exocyclic imine structure, would be favoured for thermally degraded PAN. Further evidence to support this assignment was obtained by exposing degraded films to \(D_2O\). The doublet previously observed centred at \(3370 \text{ cm}^{-1}\), was eliminated, while the peak at \(3230 \text{ cm}^{-1}\) was considerably reduced. These observations were concluded to be consistent with the assignment of this peak to primary and secondary amines, because deuteration treatment should affect the absorptions of amines. The structure produced by the reaction with n-BuLi was not appreciably oxygen sensitive, as indicated by reproducibility of the spectra after extended storage in the atmosphere. Therefore the imine-enamine tautomerisation was considered to be less likely, based on the oxygen sensitivity of the enamine group, which is reported to react to produce the pyridone-type structure.$^{(51)}$ The reaction with n-BuLi has been killed by precipitation into methanol. Termination occurs by hydrogen transfer to the growing anion, to produce an NH group. Therefore in the absence of tautomerisation imine groups will be produced. No evidence of a change in proton distribution which could account for tautomerisation was observed in the H'$^\prime$-NMR spectra.

Finally the nature of the broad band at \(3230 \text{ cm}^{-1}\) is thought to be typical of an absorption in which H-bonding is significant. While
Coleman and Petcavich\textsuperscript{(51)} report a doublet at 3390 and 3356 cm\textsuperscript{-1} for thermally degraded PAN, the spectrum of n-BuLi treated PAN shows two distinct peaks at 3420 and 3360 cm\textsuperscript{-1}. The fine structure observed could be explained by the presence of inter- or intra-molecular H-bonding. This possibility is discussed in greater depth in section (6.3.2.4).

6.3.2.3 The 1700-1200 cm\textsuperscript{-1} band

This highly developed region of the spectrum has been variously assigned by workers on the basis of a variety of experimental results. The peaks in the 1800-1500 cm\textsuperscript{-1} region have been assigned to C=C, C=N and C=O stretching modes and to NH in the plane bending mode. Apart from the proposed structures of Schurz et al.\textsuperscript{(43,44)} and Conley et al.\textsuperscript{(36)} all the others contain conjugated \pi bonds (either C=C or C=N), and the broad intense band in the range 1600-1560 cm\textsuperscript{-1} is assigned to their stretching frequencies.\textsuperscript{(120)} However it is very difficult to distinguish between (C=C) and (C=N) absorptions. Stupp and Carr\textsuperscript{(117)} have reported that the absorptions near to 1600 cm\textsuperscript{-1} appeared progressively when PAN was heated rapidly to 200°C, prior to any reduction in the absorbance of the nitrile groups. A similar observation was reported by Conley et al.\textsuperscript{(36)}

Since it is generally accepted that (C=N) stretching absorptions occur above 1600 cm\textsuperscript{-1} \textsuperscript{(120,123)}, Stupp and Carr\textsuperscript{(117)} assigned the absorption observed between 1625 and 1610 cm\textsuperscript{-1} to the (C=N) stretching mode. The broad peak recorded near 1600 cm\textsuperscript{-1}, observed prior to any detectable nitrile reaction was presumably attributed to unsaturated (C=C) bands. This led to the conclusion that thermally degraded PAN, probably consists of a mixture of (C=N) and unsaturated (C=C) bonds. However, their paper does not report a heating rate from which this latter conclusion was drawn. It is possible that very rapid heating
could induce preferential chain scission, rather than promoting nitrile polymerisation. Since no change in the CH₂:CH proton ratio was detected for the n-BuLi initiated reaction, the assignment of absorptions in this region to unsaturated (C=C) bands was discounted. Coleman and Petcavich (51) observed an intense doublet at 1610 and 1575 cm⁻¹, which was significantly affected in the presence of D₂O, for PAN thermally degraded under reduced pressure. Further investigations (124) using α-d PAN confirmed that the NH bending mode was responsible for the 1585 cm⁻¹ peak, which agreed with the assignment made by Grassie and McGuchan (71). Danner (65) also reported the doublet and concluded that it resulted from the heterocyclic structure produced by the cyclisation reaction. He therefore assigned the peak at 1610 cm⁻¹ to the conjugated (C=N) double bond. Grassie and McGuchan (71), in contrast, did not distinguish between the conjugated (C=C) and (C=N) bonds when assigning the peak at 1610 cm⁻¹.

Stupp and Carr (117) also observed peaks at 1610 and 1575 cm⁻¹, which they distinguished from their previously discussed absorption between 1625 and 1610 cm⁻¹. The peak at 1610 cm⁻¹ was assigned to a mixed mode, predominantly C=O stretching, in conjugation with a C=C stretching vibration. The 1575 cm⁻¹ peak was also a mixed mode, predominantly C=C stretching and, as previously discussed, NH bending vibrations. The infrared spectrum of the enamine Δ(8,9)-octohydro-7-quinoline (121) was again used as evidence to confirm these assignments, since C=O and C=C stretching frequencies were recorded at 1610 and 1585 cm⁻¹ respectively. In the absence of oxygen in the reaction medium, however, the C=O assignment can be ignored.

Retained DMF can also influence this region of the spectrum. Its characteristic absorptions are the carbonyl group at 1660 cm⁻¹ and methyl groups at 1385 cm⁻¹. These were apparent in Stupp and Carr's (117) results
who thermally degraded PAN films from which it was difficult to remove all the DMF. Therefore it is also possible that the peak observed at 1670 cm\(^{-1}\) in n-BuLi treated specimen is a result of the presence of a small amount of occluded DMF, despite extensive freeze-drying. Removal of the solvent molecules from a matrix of PAN is difficult owing to the strong molecular interactions between the DMF, a highly polar molecule, and PAN macromolecules which contain the strong nitrile dipole.

In conclusion, the absorptions in this region are predominantly assigned to (C=\(\text{N}\)) stretching, and NH bending modes. The (C=C) assignment is improbable considering the evidence from the H'\(^{-}\)-NMR since section 5.4.6 indicated that the proton ratio (\(\text{CH}_2:CH\)) remained constant throughout the reaction. A change in this ratio is a prerequisite to reaction of the backbone to produce (C=C) bonds.

6.3.2.4 The 2200 cm\(^{-1}\) peak

The results in section 5.4.3 indicated that an absorption developed at 2200 cm\(^{-1}\) in the infrared spectrum of n-BuLi treated PAN, immediately after initiation. The intensity of the peak increases as the reaction proceeds, and ultimately tends to a limiting value. In contrast, although Coleman and Petcavich\(^{(51)}\) reported a similar absorption, Table (18), its intensity was reportedly weak. The shift in the absorption wavenumber is only 40 cm\(^{-1}\) with respect to the standard nitrile stretching frequency and is probably a result of an environmental change affecting some of the unreacted nitrile groups during the reaction. In fact Clarke\(^{(57)}\) concluded that this peak was due to nitrile groups affected by adjacent cyclised sequences. Clarification of the assignment of this peak is important since its intensity and calculated extinction coefficient have been used to quantify the
cyclisation reaction (section 5.4).

A variety of suggestions have been made in the literature, for
the assignment of the peak at 2200 cm\(^{-1}\).

Stupp and Carr\(^{(117)}\) concluded that cyanide ions could be
generated during the thermal reaction, particularly in the presence
of DMF, which was thought to catalyse their production. However, it
was not clear whether the absorption was attributed to a cyanide ion
which had initiated a cyclisation reaction or an unsaturated nitrile.
They argued that the magnitude of the shift with respect to the 2240 cm\(^{-1}\)
peak was indicative of a change in state of the nitrile groups.
Frequency shifts for the nitrile stretching absorption ranging from
25-35 cm\(^{-1}\) have been reported\(^{(125)}\) for small molecules, as a result of
the nitrile groups being conjugated with C=C groups. Therefore nitrile
groups conjugated with species resulting from dehydrogenation of the
backbone could be a possible explanation. Other workers also suggest
that such conjugated nitriles are characterised by satellite bands at
2200 cm\(^{-1}\) \(^{\footnotesize{(32,109)}}\) and 2215 cm\(^{-1}\) \(^{\footnotesize{(36)}}\) particularly in the spectra of PAN
films degraded in air. Since the shift in absorption for the second
peak in this study was larger than the shifts reported above, the
assignment was not considered to be applicable to the reaction of
PAN with n-BuLi. When Johnson et al.\(^{(72)}\) observed a similar peak at
2185 cm\(^{-1}\) on treating PAN films with excess NaCN, its presence was
assigned to a conjugated nitrile group. Cyanide end-groups result
from the reaction and would be conjugated with the developing
cyclised sequence, as shown in the following diagram:
In the absence of saturated nitrile species in the reaction with n-BuLi, this assignment was also discounted.

Other species which could be responsible for this absorption are isocyanides, or nitriles in highly electronegative environments. Some enamionitriles have been reported to absorb at 2180 cm⁻¹(48), and ammonium salts of tricyanomethyl anions, where 3 nitrile groups, which substitute the same carbon atom, cause a strong nitrile band at 2180 cm⁻¹(125). In both of these cases, the intensity of the 2185 cm⁻¹ peak suggested that cyanide ions were generated during degradation. However, the mild experimental conditions used for the reaction of PAN with n-BuLi is unlikely to lead to the catalytic production of cyanide ions.

Protonated imine groups (immonium salts) are also characterised by several bands in the triple bond region of the spectrum (2200 - 1800 cm⁻¹)(127). Although imine groups (>C = N-H) absorb in this region, and are thought to terminate the cyclised sequences, no evidence for protonated imine groups was observed. Protonated ladder polymer which would contain protonated conjugated imines should absorb at 2500-2325 cm⁻¹. Inorganic isocyanate ions also absorb in the region 2220-2130 cm⁻¹. The reaction of organic nitriles in the presence of oxygen in a basic medium could produce a species of this type.(84) However, the absence of oxygen in the reaction medium precludes the formation of similar species in cyclised PAN.

When PAN is thermally degraded over the temperature range 473-723 K small amounts of hydrogen cyanide have been detected.(36,55,128-130) Also if the thermal reaction is not controlled, low molecular weight nitrile containing fragments can be produced. However the GPC results have shown that fragmentation has not occurred during the reaction of PAN with n-BuLi. Therefore absorptions due to species of this nature can be discounted.
Simple inorganic cyanides absorb at 2100 cm$^{-1}$(120,131). However, under certain conditions these absorptions can occur at higher wavelengths, depending on the degree of covalency of the bond, i.e. nearer the organic nitrile region. Copper, mercury and nickel salts are reported to absorb at 2160 cm$^{-1}$, 2180 cm$^{-1}$ and 2176 cm$^{-1}$ respectively. However, these species are absent from the reaction environment, and this assignment can similarly be discounted. Coleman and Petcavich(51) assign the 2200 cm$^{-1}$ peak to the cyclic iminonitrile structure which Grassie(19) previously proposed in the self initiation mechanism of thermal cyclisation. The implication is that tautomerisation produces the $\beta$-amino unsaturated nitrile which could absorb at 2200 cm$^{-1}$. Cuncliffe (132) et al. similarly reported an absorbance when AN was polymerised with sodium diglycidyl ether of Bisphenol 'A' copolymer with isoprene. The absorption was assigned to an enaminonitrile, because a similar result is observed when propionitrile is reacted with n-BuLi and was absent when copolymerised with methacrylonitrile. It is an example of the Thorpe reaction, which occurs via proton abstraction from the $\alpha$-carbon, followed by carbanion attack at a second nitrile. For propionitrile the tautomeric enamine results

$$\text{CH}_3\text{-CH-C-C}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{-C}\equiv\text{C-C}_2\text{H}_5$$

If a conventional ionic initiation mechanism is proposed for the reaction of PAN with n-BuLi (see section 6.4), with termination brought about by the addition of methanol, then imine end-groups would be
expected by the following reaction

\[
\begin{align*}
\text{Li-Bu} & \quad \text{MeOH} \\
\text{CH}_2 & \quad \text{CH} & \quad \text{CH}_2 \\
\text{N} & \quad \text{N} & \quad \text{N}
\end{align*}
\]

In this case the environment of the adjacent nitrile could be affected if intramolecular association (hydrogen-bonding) is present in the polymer chain. Intermolecular association would not produce two distinct absorptions in the spectrum.

Therefore, by considering all the proposed assignments for this peak made in the literature, it was concluded that the terminal imine group produced is associated with the adjacent nitrile group by hydrogen-bonding, resulting in two distinct nitrile peaks in the spectrum. This conclusion was particularly applicable considering the relatively mild experimental conditions used to initiate the cyclisation reaction. Possible catalytic reactions would be more likely at higher temperatures. Clarke's\(^{(57)}\) conclusion that the nitrile environment affects its absorption was confirmed. The environment, in this case, is the proposed presence of intramolecular hydrogen-bonding.

6.3.2.5 The hydrogen bonding argument

Although spectral evidence favoured the presence of intramolecular hydrogen-bonding, in practice this proved difficult to substantiate conclusively.

The presence of the broad, structured bond in the 3700-3000 cm\(^{-1}\) indicates the possible presence of hydrogen-bonded NH groups. Hydroxyl groups which are similarly hydrogen-bonded are reportedly characterised by broadening in this region.\(^{(133,134)}\) Hydrogen-bonding may be present either as inter- or intra-molecular bonding. However, when the spectra
of treated polymers were recorded in dilute solution (section 5.4.4) the peak at 2200 cm⁻¹, the broad NH bond were both still present. As intermolecular hydrogen-bonding is less persistent, using dilute solutions should either reduce its effect or remove it altogether. Since this was not the case the more persistent intra-molecular H-bonding is therefore favoured.

Intramolecular H-bonding occurs when one proton donor and one proton acceptor, on the same molecule, are in a favourable spatial configuration. The distance between such a donor and acceptor must be between 1.4 and 2.5 Å. Dreiding models confirm that the proposed structure of an NH group hydrogen bonded to an adjacent nitrile group is possible since the distance between the donor and acceptor is within this range. For a typical value of hydrogen-bond length the ladder molecule will be bent out of plane at this point.

The possible effects of hydrogen bonding on the infrared spectrum can be briefly summarised (135). A proton donor (A-H) and an acceptor (B) produce H-bonded complex A-H...B. The absorption due to the A-H stretching vibration is shifted to lower frequencies, 30-several hundred cm⁻¹, because of the lower force constant for the A-H bond. These absorption bonds are much broader. On the other hand, the A-H deformation modes are shifted to higher frequencies but to a lesser extent. New vibrational modes corresponding to H...B stretching and deformation are found at lower frequencies in the far infrared region.

Experimental proof for the presence of H-bonding proved very difficult, since it is present immediately after initiation. Therefore the only suitable method of establishing its presence was to eliminate the structure responsible.

The most successful technique proved to be quaternisation of a solution of reacted polymer with a strong inorganic acid. This
technique should cause the disappearance of the 2200 cm\(^{-1}\), and a corresponding increase in absorbance at 2240 cm\(^{-1}\). The increase will be small, however, because of the difference in the extinction coefficients (section 5.5.1). The 2200 cm\(^{-1}\) peak did not disappear completely (section 5.4.4), although its intensity was greatly reduced compared with the untreated specimen. Peaks also developed at 2780, and 1790 cm\(^{-1}\). A shift in the broad peak centred at 1660 cm\(^{-1}\) to lower wavelengths. These peaks indicated that quaternisation of the imine/amine groups had occurred, since they are assigned to species such as ammonium NR\(^{+}\) groups. The presence of the small peak at 2200 cm\(^{-1}\) could be explained by a number of factors. The extinction coefficient of the 2200 cm\(^{-1}\) peak was shown to be 11.5 times larger than that of the peak at 2240 cm\(^{-1}\) (section 5.5.1). Therefore it could be attributed to a very small concentration of unaffected nitrile groups. Complete quaternisation of terminal imines may not have been achieved because some proton exchange could have resulted from precipitation into methanol for bulk analysis, which could also account for a small absorption. Examination of the acidified solution was not possible due to the intense solvent absorptions.

In conclusion, there is evidence favouring the proposed intramolecular hydrogen-bonding affecting the absorption of an adjacent nitrile group. Spectra from these polymers strongly support the presence of terminal imine groups. Consequently hydrogen-bonding between them, and the adjacent nitriles seems most likely.

6.3.3 **UV Absorption spectroscopy**

Ultra-violet absorption spectroscopy has been used widely to characterise conjugated and chromophoric systems. Conjugation in a molecule results in a shift in the characteristic absorption towards the visible region compared with the simple unconjugated system.
The ultraviolet absorption spectrum of PAN has been discussed in the literature. Conclusions about the structural changes in PAN treated with n-BuLi were made by direct comparison of the spectrum with that from untreated PAN. The spectra were recorded from solutions in DMF, which begins to absorb at 270 nm. The untreated polymer solution was transparent down to this wavelength. The absorptions reported for PAN are generally at shorter wavelengths. Treiber et al. reported an absorption band in the region 265-275 nm which was absent in rigorously purified nitrile compounds, and in PAN prepared by ionic-coordinate catalysts of the type reported by Chiang et al. (Schurz et al. also observed an absorption at 270 nm, superimposed on a strong peak whose $\lambda_{\text{max}}$ was below 200 nm, which is attributed to CN chromophore (rep. $\lambda_{\text{max}} = 180$ nm). Talat-Erben and Bywater attributed it to ketene-imine impurities in the polymer, although corresponding absorbances were not recorded in the IR spectrum. The ketene-imine structure has characteristic absorbance at 290 nm. Kirby et al. similarly reported an intense peak at 265 nm, for PAN produced in organic solvents. Short contact of the polymer with acid shifted the peak to 275 nm. The former peak was assigned to acid sensitive enamine groups, which can readily be hydrolysed to $\beta$-ketonitrile groups accounting for the shift in wavelength. Since the standard polymer used in this experiment did not absorb above 275 nm, the development of the spectrum at longer wavelengths was directly attributed to structural changes resulting from the reaction with n-BuLi.

The spectra of the products reported in section 5.4.5 showed a broadening towards longer wavelengths as the reaction time increased, indicative of the formation of a progressively conjugated structure. A variety of unsaturated groups could produce a conjugated structure either by reaction of the nitrile groups or of the polymer backbone. Ferguson has reported characteristic absorptions for such
unsaturated groups: \( C=C \) \( (\lambda_{\text{max}} = 200 \text{ nm}) \), \( C=N \) \( (\lambda_{\text{max}} = 230 \text{ nm}) \), and \( N=N \) \( (\lambda_{\text{max}} = 347 \text{ nm}) \). Incorporation of these groups into a conjugated sequence would cause shifts in absorbance to longer wavelengths.

Therefore two reactions could account for the conjugation observed in the spectra:

1. the production of cyclised sequences
2. the formation of a conjugated polyene structure.

The latter reaction was favoured by Kubasova\(^{(142)}\) who reported an average chain length of 5-6 double bonds.\(^{(143-144)}\) Increased intensity of the spectra was attributed to accumulation of sequences of similar length. Berlin et al.\(^{(39)}\) thermally degraded PAN and recorded its ultraviolet absorption spectrum in dilute DMF solutions, and observed two absorptions maxima at 267 nm and 377 nm. The absorbance of both maxima continuously increases, although the rate of change for the second maximum (377 nm) is substantially smaller than for the former.

By comparing this result with the curve presented in Figure (33) for n-BuLi treated PAN, a difference in the nature of the two reactions is apparent. Berlin\(^{(39)}\) concluded from his results that a conjugated polyene structure was produced when solutions of PAN were heat treated, because no corresponding decrease in nitrile concentration was observed in the infrared spectra.

In contrast section (5.4.2) showed that the total nitrile concentration decreased as the reaction of PAN with n-BuLi proceeded, indicating reaction of the pendant nitrile groups. Also since the peaks in the ultraviolet absorption spectra could not be deconvoluted into its components, it was concluded to be a complex mixture of various extents of conjugated \( \{C=N\}_x \) sequences containing various numbers of the respective sequences. Direct evidence against the polyene structure resulting from the reaction of PAN with n-BuLi was apparent
from the H'-NMR results, which indicated that the $\text{CH}_2/\text{CH}$ ratios were constant throughout the reaction. Takata and Hiroi\textsuperscript{(46)} used model compounds to establish the ultraviolet absorption characteristics of thermally treated nitrile compounds, which are summarised in Table (19). PAN was also treated with bases.\textsuperscript{(46)} The spectra were compared with values obtained for model compounds, from which he proposed a series of conjugated cyclised structures to account for the observed absorption maxima, Figure (63). Structures II and III absorb in the region of the spectrum where absorptions for n-BuLi treated PAN were recorded and are further evidence for the proposed cyclisation reaction. Further support is reported by Grasselli et al.\textsuperscript{(145)} who used ultraviolet absorption spectroscopy to study the thermal degradation of PAN. They concluded that the absorption at 352 nm, which increased in intensity as the reaction continued, was attributable to the condensation of nitrile groups to form conjugated sequences of 3-5 heterocyclic rings containing C=N groups.

In conclusion the spectral characteristics observed for PAN treated with n-BuLi were consistent with the formation of a cyclised ring structure, containing conjugated $\overline{(\text{C}=-\text{N})_x}$ groups. Table (6) (section 5.4.5) indicated that values of $x = 4$-$8$ would account for the degree of broadening observed in the spectra. The final structure probably consists of sequences with different degrees of conjugation, with an increasing number of such species produced as the reaction proceeds.

6.3.4 Summary

It is generally accepted that when PAN is heated in an inert atmosphere a cyclisation reaction occurs.\textsuperscript{(31-35)} Spectroscopic techniques were used to discover whether the condensed naphthyridine structure proposed for the former reaction was duplicated by the chemical reaction with n-BuLi.
<table>
<thead>
<tr>
<th>Formula</th>
<th>solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\log \varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{CH} - \text{CHCH}_3$</td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>254.5</td>
<td>4.33</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>209</td>
<td>3.89</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH} - \text{CCHCH}_3$</td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>212</td>
<td>3.59</td>
</tr>
<tr>
<td>$\text{CH}_2 - \text{CH}_2$</td>
<td>$\text{H}_2\text{O}$</td>
<td>227</td>
<td>4.31</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C} = \text{CCHCH}_3$</td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>268</td>
<td>3.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>275</td>
<td>3.41</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH} - \text{CHCH}_3$</td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>300</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>211.5</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>265.5</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>306</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>311.5</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>319</td>
<td>3.88</td>
</tr>
<tr>
<td>$\text{NC} - \text{CH}_2 - \text{C} - \text{CH}_3$</td>
<td>hexane</td>
<td>257</td>
<td>4.28</td>
</tr>
<tr>
<td>$\text{CH}_3 - \text{C} - \text{OC}_2\text{H}_5$</td>
<td>$\text{CH}_3\text{OH}$</td>
<td>253</td>
<td>4.10</td>
</tr>
</tbody>
</table>

Table (19) The UV absorption characteristics of various model compounds (46).
Wavelength of absorbance (nm)

233-45

286-300

336

Figure (63) Structures proposed to account for absorptions in the UV spectrum of heat treated PAN (46).
The infrared and ultraviolet absorption spectra of the reaction products, obtained under a variety of experimental conditions, indicate that a conjugated system was produced. The constant CH₂/CH ratio observed in the H'-NMR spectra offers indirect evidence for the condensed naphthyridine structure proposed, containing terminal imine groups. The infrared spectra are best interpreted by this structure. The nitrile peak at 2200 cm⁻¹ was concluded to result from intramolecular hydrogen-bonding between a terminal imine group and the adjacent nitrile group. Confirmation of this structure was also apparent from the ultraviolet absorption spectra, which agreed well with those reported in the literature, for both model compounds, and thermally and alkali degraded PAN.

Results from both GPC and osmometry indicated no evidence for either crosslinking or chain scission reactions. Therefore the reaction of PAN with n-BuLi was concluded to produce a condensed naphthyridine structure, with terminal C=N groups produced by the reaction of the growing anion with methanol, on precipitation. The imine group was concluded to be intramolecularly bonded to the adjacent nitrile group. The proposed reaction mechanism is given in the following section.

6.4 The reaction mechanism

Analysis of the results was initially concerned with the structure produced at intermediate stages of the reaction of PAN with n-BuLi. A mechanism was required to explain the changes observed.

A mechanism for the reaction of PAN with n-BuLi was hypothesised from the qualitative spectroscopic observations reported in section (5.3). Figure (64) demonstrates the proposed mechanism. Initiation occurs by nucleophilic attack at the pendant nitrile groups and is followed by oligomerisation by an intramolecular ionic propagation reaction to produce a cyclised six-membered ring. Precipitation of the reaction
Figure (64) The mechanism proposed for the reaction of PAN with n-BuLi.
product brings about termination of the growing ladder sequence by reacting with the growing anion to produce a terminal imine group. Transfer mechanisms would probably involve backbone hydrogen abstraction, which was not apparent from the results presented for H'-NMR analysis.

This proposed reaction mechanism is similar to the first three stages of the mechanism proposed by Coleman and Petcavich \(^{(51)}\) for the thermal degradation of PAN under reduced pressure. (see Figure (5)). Cyclised sequences are produced, containing terminal imine groups, by nucleophilic attack at the nitrile group, and propagated by the subsequent cyclisation reaction. However, they concluded from infrared spectroscopy in isolation, that the imine structure tautomerises to produce an enamine structure. This reaction is summarised in Figure (65), which also indicates that the oxygen sensitive enamine group reacts further, producing a pyridone-type structure (III), since heterocyclic enamines are thought to be extremely sensitive to oxidation.\(^{(53,54)}\) Although small quantities of oxygen were present in polymers produced by the reaction with n-BuLi, this was attributed to residual DMF. Oxygen sensitivity was also discounted because the infrared spectrum of n-BuLi treated samples immediately after freeze-drying, and after storage in air were ostensibly the same. If the tautomeration and subsequent oxidation reactions illustrated in Figure (65) occurred when PAN was reacted with n-BuLi then a change in CH\(_2\):CH ratio would be apparent. This however was not the case, so the tautomeration reaction was thought to be unlikely.

A similar, but more complex mechanism resulting in a pyridone-type structure was proposed by Johnson et al.\(^{(72)}\) However in both these cases the experiments from which the reactions were proposed were carried out at elevated temperatures. It is possible that if the chemical cyclisation reaction was carried out at substantially higher temperatures, then a
Figure (65) The final three stages in the scheme proposed for the reaction of PAN at 473 K. under reduced pressure (51).
change in the final stages of the reaction may result.

In conclusion, a simple ionic initiation and propagation mechanism leading to the production of a condensed naphthyridine structure is proposed for the reaction of PAN with n-BuLi, under the experimental conditions investigated.

6.5 Quantification of the cyclisation reaction

As in most polymerisation processes it is important to measure the average length of the molecules produced. In this type of reaction, a direct method for such a calculation is not applicable and indirect estimations are required. It is particularly important in carbon fibre technology since the properties of a carbon fibre may depend on the degree and extent of cyclisation which has been introduced into the fibre. Indeed Clarke\(^{(57)}\) has carried out similar calculations for thermally treated and oxidised polymer films. One of the intentions of this study was to discover ways of incorporating cyclised sequences of known length into the polymer and to look for any compatible size in the final carbon fibre.

Since it has been shown that the secondary nitrile peak at 2200 cm\(^{-1}\) is linearly dependent on the initiator concentration, and appears to be associated with the end of a cyclised sequence, as postulated previously by Clarke\(^{(57)}\), the cyclised lengths can be estimated in the following manner. The total nitrile concentration was determined by considering the contribution of both nitrile peaks in the infrared spectra, after correcting the secondary peak to allow for the large difference in extinction coefficients. This was determined as a mole fraction giving a value for the extent of reaction of the nitrile groups at any time. The average length of the cyclised sequences, or the average degree of
cyclisation, was calculated from the appropriate n-BuLi concentration.

There has been little attempt in the literature to determine the length of cyclised sequences for either thermal or chemical reactions in PAN. Grassie et al (15) and Noh and Yu (20) concluded that the kinetic cyclised length must be short. Clarke (57), in contrast, described a principle by which the length of cyclised sequences could be calculated from the decrease in nitrile absorbance at 2240 cm⁻¹ and the coincident appearance of the second nitrile peak at 2200 cm⁻¹, which indicated that cyclised lengths could be much longer (24-32 in inert atmospheres, and 10-16 in oxidising atmospheres).

In the chemical cyclisation reaction the total nitrile concentration for any reaction time has been calculated from the intensity of both the nitrile absorptions, after correcting for their respective extinction coefficients. (section 5.5.2) If it is considered that the initiator concentration is one hundred percent efficient, then one imine group will be produced for each initiator ion, on initiation. Section (5.5.2) demonstrated the linear relationship between the intensity of the peak at 2200 cm⁻¹ and the initiator concentration, shown in Figure (43). The slope of the graph produced a value of 352 kg mol⁻¹cm⁻¹ for the extinction coefficient of the peak. This value is 11.5 times larger than the corresponding extinction coefficient calculated for the primary nitrile stretching absorption. It was therefore concluded that the apparently intense peak at 2200 cm⁻¹ was caused by relatively small concentrations of imine groups present after initiation, and was observable because of the difference in the magnitude of their respective extinction coefficients.

The results showed that the average number of condensed rings ranged between 2 and 23, and depends mainly on the relative concentrations and temperatures at which the experiments were carried out. The absorption
at 2200 cm⁻¹ was produced immediately on addition of the n-BuLi, and rapidly increased in the first 60 s. After complete initiation, rapid reaction to high oligomers had taken place, demonstrated by the degree of cyclisation after 60 s calculated to be between 3.5 and 6. However, the intensity of this absorption continued to increase over the next 10 min. Whereas the initial absorbance at 2200 cm⁻¹ was linearly proportional to the n-BuLi concentration, the final absorbance at 2200 cm⁻¹ although still linear, no longer passed through the origin, but gave an unlikely negative intercept value of -0.05 mol kg⁻¹ on the concentration axis. This observation can only be explained in three ways:

(1) some further nitrile groups were produced, independent of n-BuLi concentration, as a result of side reactions. A change in the number of CH protons could also produce a similar effect. No evidence for this possibility was detected.

(2) that initiation was not as rapid, or completely one hundred percent efficient as previously assumed. This was considered to be unlikely, since an ionic reaction normally has a very rapid initiation stage.

(3) The most likely explanation is that as the degree of cyclisation increases, the extent of conjugation within the condensed ring structure affects the electron distribution within the hydrogen-bond between the terminal imine group and the adjacent nitrile group, resulting in a further change in extinction coefficient. Figure (66) shows a plot of absorbance at 2200 cm⁻¹ divided by the n-BuLi concentration (A₁₂₂₀₀/[n-BuLi]) versus the degree of cyclisation, indicating that the absorbance becomes asymptotic at a degree of cyclisation of approximately 10, irrespective of n-BuLi concentration. This suggests that the extinction coefficient of the nitrile groups is dependent on the degree of cyclisation of the preceeding ladder sequence.

In conclusion, a method of calculating the average lengths of
Figure (66) The ratio of the absorbance at 2200 cm$^{-1}$ to n-BuLi concentration as a function of the degree of cyclisation.
cyclised sequences from infrared spectroscopy data has been developed for the reaction of PAN with n-BuLi. The average length of cyclised sequences was dependent on the n-BuLi concentration and the reaction temperatures. The results presented in the preceding chapter agreed with the average degree of conjugation in the reacted polymer, calculated from the characteristic wavelengths in the ultraviolet absorption spectra. Cyclised samples with longer cyclised lengths produced at higher temperatures were no longer soluble in DMF. Therefore a corresponding degree of conjugation could not be calculated for these samples.

Therefore a method has been developed by which cyclised sequences of known average length could be chemically produced in PAN, stabilising the polymer and thus enabling it to withstand carbonisation. Using a similar approach to produce a precursor fibre may enable a relationship to be determined between the initial degree of cyclisation and the crystallite size in the resultant carbon fibre.

6.6 Thermal analysis

The observations reported in the literature for the behaviour of PAN heated in an inert atmosphere were confirmed in this investigation. A sharp, intense exotherm occurred when PAN was heated under controlled conditions in an inert atmosphere. The results from the thermal analysis of PAN reacted with n-BuLi (section 5.6) indicated that the residual enthalpy decreases as the extent of cyclisation increases. However, the enthalpy of the thermal cyclisation of the residual nitrile groups was found to be independent of n-BuLi concentration. Therefore the exotherm must be a function of the reaction of the nitrile groups. In this case, the thermal cyclisation of the residual nitrile groups must be initiated by the terminal imine groups, produced as a result of the
chemical cyclisation reaction, otherwise different initiator concentrations would lead to different numbers of isolated nitrile groups. While the magnitude of the exotherm decreased as the extent of cyclisation increased, the maximum peak temperature remained substantially constant throughout. There was also evidence that the exotherm initiation temperature was lower, causing a broadening effect on the shape of the exotherm. This was in marked contrast to the effect of additives on the thermal behaviour of PAN observed by Grassie, who observed that broadening of the exotherm occurred and was accompanied by a reduction in the peak maximum temperature. This contrast, however, may be explained fairly readily, since it is likely to be a function of the experimental method used for observing the effect. In these experiments the additive was reacted directly with the polymer in solution, so that cyclisation was induced prior to the thermal treatment. In Grassie's case, the effect of the presence of additives on the thermal reaction was recorded. In his experiments the additives were intimately mixed with the polymer in a volatile solvent medium, which was evaporated prior to the thermal treatment. However occluded solvent could be evolved during heating, causing the more marked broadening of the exotherms. Similarly the effect of heat on any unreacted additive could contribute to the exotherm, and preferential reaction of the additive at the polymer particle surfaces could have such an effect.

The proportionality of the relationship between the residual enthalpy and the extent of cyclisation was demonstrated in Figure (50) (section 5.6.2). The intercept value inferred that whatever the reaction conditions, 20% of the nitrile groups could never participate in the cyclisation reaction. This value is in close agreement with similar values observed by Noh and Yu and Johnson et al for the thermal reaction in PAN. In this case the fact that 20% of the nitrile groups cannot be cyclised...
was explained by the self initiation mechanism, similarly used to explain the thermal cyclisation reaction, (see Figure (2)), which results in isolated nitrile groups. The conventional anionic initiation mechanism which has been proposed for the reaction of PAN with n-BuLi would not necessarily result in isolated nitrile groups. However propagation of the cyclisation reaction can occur in either direction along the polymer chain, thus increasing the likelihood of producing isolated nitrile groups. Therefore the majority of residual nitrile groups in the case of heat treated, partially cyclised polymers are probably isolated between two terminal imine groups, as shown in Figure (67). The further reaction of an isolated nitrile group would then depend on the stereochemistry of the ladder polymer. The rotational angles will be such that the nitrile and imine groups would be in different planes, making further reaction difficult. An analogous reaction was considered by Flory\(^{146}\) and Wall\(^{147}\), who calculated the number of residual side groups present in thermally condensed poly(methyl vinyl)ketone. Condensation in different directions along the polymer chain leads to two methyl or ketone groups which are unable to react. A value of 18.4\% was calculated for the percentage of residual side groups for the reaction, which is close agreement with the value of 20\% observed for the thermal reaction of partially cyclised PAN. Therefore the condensation reaction model of Flory\(^{146}\) and Wall\(^{147}\) can also be applied to the cyclisation of PAN with n-BuLi. This model is further supported by the appearance of a shoulder on the second nitrile peak (2200 cm\(^{-1}\)), at 2150 cm\(^{-1}\), in the infrared spectrum of a highly cyclised polymer. The infrared spectrum of a sample of thermally cyclised homopolymer was recorded, in order to calculate the percentage of residual nitrile groups remaining after thermal stabilisation. The nitrile absorbance was substantially reduced, but the overall resolution of the spectrum was too poor to allow a
Figure (67) A mechanism demonstrating the production of isolated nitrile groups during the cyclisation of PAN.
quantified calculation to be made.

The thermogravimetric analysis of partially cyclised PAN has indicated that a small extent of cyclisation is sufficient to stabilise the polymer as effectively as the thermal treatment. The onset of serious weight loss occurs at 60 K above the corresponding temperature observed for PAN, which is comparable with the increased thermal stability in oxidised PAN. However, since it appeared that continuing improvement in stability after long reaction times, and increased initiator concentration is not observed, it is concluded that thermal cyclisation is sufficiently rapid to stabilise the polymer. Thus the treatment described here enables rapid initiation of the cyclisation reaction, while self initiation on thermal treatment of the homopolymer is not so effective. It follows therefore that the imine groups produced in the chemical reaction are able to initiate the thermal reaction when the partially cyclised products are heated. However it appears from section (5.5.4) that the concentration of residual DMF is larger for greater extents of cyclisation, and that the apparent instability observed by thermogravimetric analysis is a function of distilling DMF on heating. If this factor is taken into consideration then the thermal stability of the ladder polymer is greatly improved for all extents of cyclisation.

It is interesting to compare the thermal stability of the products from the reaction of PAN with n-BuLi to those of Grassie\(^{(29)}\) and Johnson et al\(^{(72)}\) for their additive reacted polymers. Figure (68) demonstrates this comparison. The results of Johnson et al\(^{(72)}\) show that the thermal stability of PAN cyclised by cyanide ions is comparable to oxidised PAN. Similarly the polymers from this study have comparable thermal stabilities. In contrast Grassie's additive treated polymers are less thermally stable in the temperature range under consideration.
Figure (68) Thermograms recorded for PAN reacted with various additives:
(1)DPPH (29)
(2)Bisphenol (29)
(3)Potassium cyanide (29)
(4)Experimental PAN
(5)Experimental PAN (72)
(6)Sodium cyanide/DMF (72)
(7)n-BuLi ($P_{\text{CN}}=0.28$)
(8)Oxidised PAN (72)
In Johnson's experiments some reaction occurs in solution before the product is heated, whereas in Grassie's experiments the additive reacts with the polymer on heating. Thus, in the latter case, the additive would appear to modify the mechanism of the thermal reaction so that the lower thermal stability may be a function of side reactions.

The thermal analysis of the partially cyclised polymers produced by the reaction of PAN with n-BuLi therefore confirms that the exotherm is a function of the nitrile polymerisation reaction. The proportionality of the relationship between the residual enthalpy and the previously introduced extent of cyclisation is demonstrated. Subsequent thermal initiation of the partially cyclised sequences is brought about by the terminal imine groups. The broadening of the exotherms indicates that as the extent of cyclisation is increased, the resultant heat generated in the subsequent thermal reaction can be dissipated more readily. The partially cyclised polymers are comparably stable with the oxidised homopolymer. This suggests that programmed heating of a partially cyclised product to the carbonisation temperature should not result in catastrophic disintegration of the polymer. This was shown to be the case (section 5.5.4). When the homopolymer was heated to approximately 1200 K, after previous stabilisation at approximately 490 K for 1.5 hrs., a constant weight was achieved after a few minutes at temperature. An approximate carbon yield of 40% was recorded. The partially cyclised polymer when similarly examined under carbonising conditions had a substantially higher corresponding carbon yield, approximately 70%. However in this latter case a constant weight was not achieved in the same time as the thermally stabilised polymer. This infers that although the partially cyclised polymer is thermally stable under these conditions, reactions to promote the expulsion of non-carbonaceous elements is slower.
In conclusion, partially cyclising the polymer prior to carbonisation introduces sufficient thermal stability to enable the polymer to withstand carbonisation without drastic weight loss. A carbon yield better than that observed for homopolymer thermally stabilised in an inert atmosphere prior to carbonisation was recorded. Therefore it is possible that if partially cyclised polymer fibres could be produced by chemical means prior to carbonisation, improved carbon yields could result. This in turn could improve the mechanical properties of the resultant fibres by increasing their density.

6.7 Kinetics of the reaction

6.7.1 The reaction model

The infrared spectroscopy results presented in chapter 5, which were analysed both to elucidate the structure produced, and to calculate the extent of the reaction of the nitrile groups, were also used to formulate a kinetic model for the reaction of PAN with n-BuLi. However the data available for the analysis had a number of deficiencies, which required some assumptions to be made in the development of this model. These will be discussed as they arise.

The results in chapter 5 were obtained using a sampling technique, initially intended to allow structural elucidation. However a kinetic analysis enabled a further interpretation of the results to be made.

There are a number of suitable models which could be applied to the reaction of PAN with n-BuLi. In its simplest terms, the starting homopolymer could be equated with monomer in a conventional polymerisation reaction, while the subsequent secondary polymerisation of the nitrile groups could be seen simply as a linear polymerisation reaction, where initiation is brought about by the addition of n-BuLi.
Alternatively, the reaction could be compared to a crystallisation reaction, where the unreacted monomer units correspond to the amorphous phase, while the six-membered rings correspond to the formation of crystallites. Cyclisation could therefore be visualised as a one-dimensional crystallisation of the amorphous phase. The applicability of both these models will be considered in this section.

The theoretical kinetic chain length was established as a function of initiator concentration, by assuming that one nitrile group has been consumed per initiator ion. Then the average distance between the possible initiation sites can be computed by considering the initiator concentration ([PAN]/[n-BuLi]). The average chain length \( L_{\text{CA}} \) is tabulated in Table (20). Therefore the maximum degree of cyclisation possible is given by \( L_{\text{CA}} \). Figure (69) shows the degree of cyclisation as a function of reaction times for various n-BuLi concentrations, at constant temperature. Comparing the curves with the limiting degree of cyclisation listed in the previous table, it is apparent that the limiting value of the degree of cyclisation \( C_x \) is never achieved. This observation is not surprising, since it was shown in section (5.6.2) that 20% of the nitrile groups can never participate in the cyclisation reaction. This factor is reflected in Table (20) where the figures in parentheses take this value of 20% into account.

The results shown in section (5.4) indicate that there is a rapid decrease in nitrile concentration immediately on initiation, followed by a stage during which most of the colour change occurs. This reaction can be represented by the diagram shown in Figure (70). However, using the sampling technique, the rapid change represented by stage (1) cannot be easily examined.

In anionic reactions, under ideal conditions, rapid 100% efficient initiation should occur, i.e. one butyl anion should consume one nitrile
Table 20  The theoretical distance ($L_{CA}$) in monomer units as a function of n-BuLi concentration.

<table>
<thead>
<tr>
<th>$[\text{PAN}]_1$ (mol kg$^{-1}$)</th>
<th>$[\text{n-BuLi}]_1$ (mol kg$^{-1}$)</th>
<th>$L_{CA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.025</td>
<td>40(32)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.05</td>
<td>20(16)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.08</td>
<td>12(9.5)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>10(8)</td>
</tr>
</tbody>
</table>

Table 21  Nitrile absorbance immediately after initiation ($A_i$) and after 60 s. with the corresponding degree of cyclisation.

<table>
<thead>
<tr>
<th>$[\text{n-BuLi}]_1$ (mol kg$^{-1}$)</th>
<th>$A_i$</th>
<th>$A_{60}$</th>
<th>$C_{X(60)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>2.15</td>
<td>1.85</td>
<td>6.52</td>
</tr>
<tr>
<td>0.05</td>
<td>2.10</td>
<td>1.53</td>
<td>6.12</td>
</tr>
<tr>
<td>0.08</td>
<td>2.02</td>
<td>1.59</td>
<td>3.50</td>
</tr>
<tr>
<td>0.10</td>
<td>1.99</td>
<td>1.39</td>
<td>3.72</td>
</tr>
</tbody>
</table>
Figure (69) The degree of cyclisation as a function of reaction time for the reaction of PAN solutions with n-BuLi for concentrations: (1) 0.025 mol kg\(^{-1}\), (2) 0.05 mol kg\(^{-1}\), (3) 0.08 mol kg\(^{-1}\), (4) 0.10 mol kg\(^{-1}\).
Figure (70) A schematic representation of the proposed two stage reaction for the cyclisation of PAN.
group. The decrease in nitrile concentration which corresponds solely to initiation could be calculated, i.e. a butyl anion reacting with a nitrile group to produce an imine group. Therefore the relative nitrile absorbance \( A_i \) attributed to initiation was calculated, assuming complete reaction. These values are tabulated in Table (21), where \( A^60 \) represents the absorbance at 60 s after initiation, while \( C_x(60) \) is the corresponding value of degree of cyclisation. From these values it was apparent that even at very short reaction times (60 s) propagation to a certain extent has already occurred.

A two stage reaction model was proposed to define the reaction;

Stage (1): initiation and short range propagation

Stage (2): propagation

Using the experimental conditions n-BuLi concentration = 0.1 mol kg\(^{-1}\), temperature 293 K as an example, the reaction was considered as follows.

The reaction can be written in general terms as:

\[
\text{CN} + \text{n-BuLi} \rightarrow \text{products}
\]

The limit of stage (1) under these conditions is defined where \( C_x = 3 \).

Therefore the reaction can be written as follows:

\[
\begin{align*}
\text{CN} + \text{n-BuLi} & \rightarrow k_i \rightarrow \text{CN}(1) \\
\text{CN} + \text{CN}(1) & \rightarrow k_i \rightarrow \text{CN}(2) \quad \text{rapid} \\
\text{CN} + \text{CN}(2) & \rightarrow k_i \rightarrow \text{CN}(3) \\
\text{CN} + \text{CN}(3) & \rightarrow k_p \rightarrow \text{CN}(4) \quad \text{slower}
\end{align*}
\]

then;

\[
\begin{align*}
\text{CN} + \text{CN}(3) & \rightarrow k_p \rightarrow \text{CN}(4) \\
\end{align*}
\]

where

\[
\begin{align*}
k_i & = \text{initial or stage (1) rate constant} \\
k_p & = \text{propagation rate constant}
\end{align*}
\]

\( k_i \) could be calculated approximately from the plot of \( \ln \left( \frac{A_i}{A^\infty} \right) \) versus time graphs for different n-BuLi concentrations. Figure (71) shows a series of plots for this function. \( A^\infty \) was found to be independent
Figure (71) A first order plot for the first stage of the reaction of PAN solutions with n-BuLi, for concentrations: (1) 0.025 mol kg\(^{-1}\), (2) 0.05 mol kg\(^{-1}\), (3) 0.08 mol kg\(^{-1}\), (4) 0.10 mol kg\(^{-1}\).

Figure (72) The rate constant for stage 1 of the reaction of PAN with n-BuLi as a function of n-BuLi concentration.
of n-BuLi concentration at constant. By interpolating, these straight lines the initial rate constants were approximately calculated for stage (1). The proportionality of the plot of these values as shown in Figure (72) enabled the overall rate constant for stage (1) to be calculated, giving a value of $7 \times 10^{-2}$ s$^{-1}$. However there are inherent large errors on the values calculated for this stage of the reaction, because there are insufficient data points on this early section of the curve, as a result of the sampling technique. At the lowest n-BuLi concentration there was a much larger deviation from the straight line, than at higher concentrations. At the lowest concentration the limiting absorbance value may not have been reached because of the decreased reaction rate. However the plot must intercept the origin, since under the experimental conditions used, if there is no initiator present, there will be no change in nitrile concentration.

Stage (2) of the reaction was similarly examined. Figure (73) shows a plot of $\ln\left(\frac{(A_t - A_\infty)}{A_\infty}\right)$ versus time, in which first order kinetics are indicated. The rate constants for various initiator concentrations were calculated from the gradients of these plots and are plotted as a function of n-BuLi concentration in Figure (74). This is a linear plot intercepting the origin. Therefore the following relationship must describe the reaction:

$$k_i = k [n\text{-BuLi}]$$

This method of analysis indicated that stage (2) was a conventional addition oligomerisation where:

$$\text{Rate} = k [\text{CN}][n\text{-BuLi}]$$

Therefore the analysis suggests that both stages of the reaction show first order reaction kinetics with respect to the decrease in nitrile concentration.

For an initiator concentration of 0.1 mol kg$^{-1}$, assuming 100%
Figure (73) A first order plot for the second stage of the reaction of PAN solutions with n-BuLi at 293 K for concentrations (1) 0.025 mol kg$^{-1}$, (2) 0.05 mol kg$^{-1}$, (3) 0.08 mol kg$^{-1}$, (4) 0.10 mol kg$^{-1}$.

Figure (74) The rate constants for stage 2 of the reaction of PAN with n-BuLi plotted as a function of n-BuLi concentration.
efficiency, the average distance between initiation points is 10 monomer units. Therefore stage (1) consists of initiation, followed by rapid, unrestricted oligomerisation to an average degree of cyclisation of 3, the rate constant for this stage being $7 \times 10^{-2}$ s$^{-1}$. Stage (2) is the much slower conventional propagation reaction, indicated by the calculated rate constant of $2.6 \times 10^{-3}$ s$^{-1}$. The propagation reaction is hindered by a number of factors. Once the short range cyclisation reaction has occurred the major factor preventing propagation is the problem of rotation about the skeletal bonds to bring the nitrile groups into reactable positions. Stage (1) introduces short cyclised sequences into the polymer, at regular intervals along the previously flexible chain. These sequences are much stiffer, therefore rotation about the polymer backbone becomes hindered. This effect becomes more apparent as the initiator concentration increases, reducing the inter-initiation site distance, thus further increasing the rigidity of the polymer chain.

A similar analysis was carried out to find the effect of temperature on the kinetics of the reaction. The value of limiting absorbance was found to be temperature dependent, in contrast to its independence of initiator concentration. Table (22) tabulates the limiting values of absorbance for various temperatures, and these values were used to plot the graphs of $\ln\left(\frac{A_t - A_\infty}{A_\infty}\right)$ versus time shown in Figure (75), for stage (2) of the reaction. The corresponding rate constants have also been tabulated, and are plotted as a function of reciprocal temperature in Figure (76). The graph shows the linear relationship between $\ln$(rate constant) and reciprocal temperature, and using the least squares analysis for the best straight line fit, the gradient was calculated to be $-\left(5 \times 10^3\right)$. From the temperature dependence of the rate constants, the Arrhenius equation was used to obtain an activation energy value for the reaction, which was calculated to be $41.5$ kJ. The simple Arrhenius
<table>
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<th>Temperature K</th>
<th>$A_\infty$</th>
<th>K (s$^{-1}$ x10$^{-3}$)</th>
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<tr>
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</table>

Table (22) Effect of temperature on the rate constant as calculated from the limiting absorbance ($A_\infty$).
Figure (75) A first order plot for the second stage of the reaction of PAN solutions with n-BuLi =0.08mol kg\(^{-1}\) for temperatures, (1) 273 K, (2) 293 K, (3) 313 K, (4) 333 K, (0.025mol kg\(^{-1}\)).

Figure (76) Arhenius plot for stage 2 of the reaction of PAN with n-BuLi =0.08mol kg\(^{-1}\).
approach gave good agreement with the activation energy calculated by Noh and Yu\(^{(20)}\) for the thermal cyclisation reaction.

The reaction is schematically represented in Figure (77). The rate constants have been shown to be more than an order of magnitude larger in stage (1) than in stage (2). In summary, the reaction is visualised in terms of rapid initiation followed by simple unrestricted addition oligomerisation to produce cyclised sequences of short kinetic chain length. Above a certain value of \(C_x\), dependent on the number of growing centres, the reaction becomes restricted and propagation is limited by a number of factors:

1. the rigidity of the polymer chains, due to the presence of cyclised sequences, makes rotation about the polymer backbone increasingly more difficult.

2. the distance between the growing chain end (after stage (1)) and the next initiation site.

At high \(n\)-BuLi concentrations, the theoretical propagation length is severely limited by the preceding reaction, and the maximum mole fraction of reactable nitrile groups possible.

The possibility of termination of the propagation reaction, or of establishing an equilibrium, had to be considered. In the latter case the equilibrium could be written as follows:

\[
\text{CN}_3 + n\text{CN} \xrightarrow{\frac{k_p}{k_{dp}}} \text{CN}_{3+n}
\]

However, under the experimental conditions investigated, the reverse reaction was impossible to detect. At elevated temperatures, depropagations are more likely, but results by Johnson et al\(^{(72)}\) for experiments at higher temperatures suggest that the chemistry may be different, so that attempts to establish depolymerisation at higher temperature may not be possible.

The kinetics of the reaction of nitrile polymerisation initiated
Figure (77) A schematic representation of the model.
by n-BuLi has been shown to have two stages, both of which are first order with respect to nitrile concentration. Whereas Noh and Yu\(^{20}\) considered that cyclised lengths must be very short, the values obtained in this study are somewhat larger. The reaction kinetics in the bulk and in solution would not be expected to be the same. However, the similarities in the calculated activation energies for the two reactions suggests that the role of IMF in the latter case, increases the chain mobility, to achieve the same effect as heating the polymer.

In contrast to this analysis, Clarke\(^{57}\) plotted his data for the thermal treatment of films and fibres in the form of a second order rate equation, which produced a linear relationship as a function of reaction time. However, second order plots for the chemical reaction were more scattered and did not show either a linear relationship or the distinct two stage reaction previously described. It was therefore concluded that the change in the first order rate constant can be explained as a change in the rate determining step for the reaction in each of its stages, from the fairly rapid anionic reaction to the slower conformational change in the second stage. The similar activation energies for stage (2) and for thermally degraded PAN suggests that for solid polymers the rate controlling step is the rate of flexing of the partially cyclised polymer.

In contrast to this model, Noh and Yu\(^{20}\) applied a simple crystallisation theory to the thermal polymerisation of the nitrile groups. The nucleation stage was considered to be analogous to the initiation stage in the thermal reaction, while crystal growth was thought to correspond to the propagation stage. The linear secondary polymerisation was therefore considered to correspond to the crystallisation of a one-dimensional amorphous phase. Using the simple Avrami approach, the kinetics of crystallisation relies on establishing the relationship between the
density of the crystalline (cyclised) and melt (linear polymer) phases, and the reaction time, to establish the rate of crystallisation.

The Avrami equation is given by the following relationship:

$$W_L = \frac{W_0}{\exp (-kt^n)}$$

where $k =$ the rate constant  
$W_L =$ the mass of the melt at time $t$  
$W_0 =$ the mass of the melt at time zero  
$n =$ the Avrami integer

The Avrami integer provides information on the geometric form of the growth. If the nucleation rate is rapid, then it is a zeroth-order reaction and for one-dimensional growth the Avrami relation reduces to $n = 1$, which is a first order equation for the kinetic reaction. Noh and Yu \(^\text{20}\) found that their results for the thermal reaction obeyed first-order reaction kinetics. However it is unlikely that heating will induce rapid nucleation (initiation), compared with the addition of an anionic initiator which should result in immediate initiation. Therefore, although their results demonstrates first-order kinetics, the crystallisation theory, as represented by the Avrami equation would not appear to be the best model to apply to the reaction of PAN with n-BuLi.

In conclusion, a two stage reaction model was applied to the kinetics of the chemically induced cyclisation reaction. Stage (1) was initiation followed by short range propagation, and stage (2) was the conventional propagation reaction. Both stages were first-order with respect to nitrile concentration.

6.7.2 The initiation and propagation reactions

The preceeding kinetic analysis has shown that a two stage reaction occurs when PAN is treated with n-BuLi. The components of these
stages, i.e. initiation and propagation, can also be discussed in terms of their chemical reactions.

The mechanism proposed for the reaction, in section (6.4) is a conventional ionic reaction. Anionic initiation at a nitrile group is brought about by a butyl anion, and is subsequently followed by propagation of the growing anion via the pendant nitrile group.

In solution n-BuLi ionises, with varying degrees of association, depending on the polarity of the solvent. Therefore in DMF it ionises to produce free ions, or solvated free ions, which makes initiation at the positively charged carbon of the nitrile group the most likely possibility. However, the possibility of other initiation mechanisms must also be considered.

Wakefield (148) has discussed the behaviour of alkyllithium reactions and concluded that in non-polar solvents coordination centres are established. However this reaction is unlikely to occur in DMF.

An alternative initiation mechanism could involve proton abstraction at the α-carbon, to form a carbanion, which subsequently initiates the polymerisation of the nitrile groups. This process could lead to crosslinking by intermolecular initiation, or to the formation of isolated nitriles, incapable of further reaction, thermally or chemically. Since GPC and osmosis studies failed to reveal any evidence of crosslinking, and since the thermal analysis results indicated that 80% of the nitrile groups could react, this type of reaction is thought to be unlikely. Furthermore, sodium is more likely to be prone to abstraction reactions and this may explain the difference in the GPC results for the two initiators. The sodium initiated products showed a tendency to larger effective size even at low extents of reaction.

Grassie's (19) self initiation reaction for the thermal cyclisation process was also thought to be unlikely. Infrared analysis of the
products after initiation with n-BuLi has shown that a conjugated imine system is produced immediately. The cyclic initiation residues within the polymer structure after self initiation cannot tautomerise to produce such an effect on the infrared spectrum. Also if this type of reaction occurred on the addition of n-BuLi, the number of residual nitrile groups produced would be expected to be a function of the initiator concentration. This has already been shown not to be the case, as shown in Figure (50) (section 5.6.2).

n-BuLi has been used to initiate reactions with other nitriles, such as fumaronitrile. In this case the proposed initiation mechanism involves a radical anion, which could lead to crosslinking and simultaneous ionic or radical cyclisation. No evidence for crosslinking was observed in the GPC results. Therefore this mechanism does not seem to apply to the reaction under consideration.

DMF is reported to react with n-BuLi\(^{149}\), therefore its participation in the reaction must be considered. The behaviour of DMF as an aldehyde, and its effect when sodium is used as an initiator, has been discussed in section (5.1). The reaction of a lithioimine with DMF has been reported by Lwowski\(^{149}\). A ketone, a secondary amine and lithium cyanide are produced. Cyanide ions could then react with the pendant nitrile groups by nucleophilic attack. Evidence of ketone formation would be observed in the infrared spectrum, by an absorption at 1700 cm\(^{-1}\) whose intensity would be proportional to the n-BuLi concentration.

The absorption due to the ketone group should appear at longer wavelengths than for a carbonyl group present as a result of residual DMF, (i.e. 1700-1650 cm\(^{-1}\)). Only small residual DMF peaks were recorded in the infrared
spectra, and no evidence for the ketone absorption was apparent. Similarly no obvious differences in the spectrum was noticed for large n-BuLi:PAN ratios, and catalytic quantities. Also Lwowski et al. used more vigorous experimental conditions (343-353 K for 4-6 hrs.) than those used in this study, which could explain the differences in the reactions proposed. The possibility of n-BuLi reacting preferentially with the DMF cannot be discounted, in which case the following anion could be produced:

\[ \text{Bu}^\text{--} \text{C} \equiv \text{N(CH}_3\text{)}_2 \]

The proposed anionic initiation reaction would still be valid in this case, but the actual initiating species would be different.

In conclusion a conventional anionic initiation mechanism via the pendant nitrile group is the most favourable for the experimental conditions investigated.

The kinetic analysis has shown that the propagation reaction has two stages, rapid growth to short kinetic chain length, followed by slower propagation to longer lengths. The spectroscopic results have indicated that a conjugated imine structure is produced by the reaction of PAN with n-BuLi. This is direct evidence favouring the conventional ionic propagation reaction. If propagation occurred via proton abstraction then a conjugated \(-\{\text{C}==\text{C}\}\- system would be observed in the spectroscopic data. Similarly a change in proton ratios would be recorded in the H'-NMR spectra. Since direct evidence against both of these possibilities has been presented, propagation via the pendant nitriles is concluded. Grassie\(^{(29)}\) has reported a "backbiting" type of propagation mechanism for the thermal reaction, as shown in Figure (10) (section 2.4 ). Extensive transfer occurs in this type of reaction, and since transfer
predominately involves hydrogen abstraction, which has not been observed in this study, this mechanism was also discounted.

A conventional anionic propagation mechanism was therefore concluded, resulting in the secondary polymerisation of the pendant nitrile groups. Both stages of the propagation reaction, as defined by the kinetic analysis, produce the same structure, since no qualitative differences in the spectra were observed. The rapid propagation of ladder sequences with short kinetic chain length occurs when the chain mobility in solution is high. As the number and the length of these sequences increases the rate of propagation, which is controlled by the rate of rotation about the skeletal bonds, decreases, because steric hinderance increases the difficulty of further reaction. Therefore propagation to longer cyclised lengths is slower.

6.8 Comparison of chemically and thermally produced cyclised lengths

Many workers have applied a "rule of thumb" calculation to their experimental results for cyclised PAN, and have generally concluded that only short (<5 heterocyclics) cyclised sequences are produced thermally. Clarke(57) developed a method to calculate the length of cyclised sequences produced in PAN, on heating in both inert and oxidising atmospheres. The maximum degree of cyclisation for Courtelle heated at 498 K in inert atmospheres was 24-32, and correspondingly 10-16 in an oxidising atmosphere. Since these values are substantially larger than any previously reported in the literature, the degree of cyclisation calculated for the chemically cyclised product was compared with those conventionally thermally stabilised.(57)

The peak in the infrared spectrum at 2200 cm⁻¹ has been attributed to a nitrile group environmentally affected by the presence of an adjacent
cyclised sequence. Therefore there will be one of these groups present for every cyclised sequence. Clarke\textsuperscript{(57)} used the ratio of the absorbances of the two nitrile peaks ($A_{\text{CN2200}}/A_{\text{CN2240}}$ (R)) as the basis for his calculation. Values of R were similarly calculated for the n-BuLi initiated products. Figure (78) shows these values plotted as a comparison to Clarke's\textsuperscript{(57)} values calculated for thermally degraded films and fibres. The different nature of the curves is immediately apparent.

Thermally treated Courtelle produces a substantially linear relationship for both inert and oxidising treatments, although the R values in the oxidising atmosphere are between 5 and 10 times greater than the corresponding inert value. In contrast, the chemical reaction produces an immediate, rapid increase in R, tending to a limiting value at longer times. The value $R=1$ (i.e. when both nitrile peaks are the same intensity) is reached for PAN treated with n-BuLi (concentration=0.1 mol kg\textsuperscript{-1}) for 3.3 hr., while the same value is produced after oxidising Courtelle for 10 hr. The inference from the different characteristics of these curves is that initiation is the rate determining step in the thermal reaction, and that oxygen acts as an initiator for the free radical reaction.

It was shown in section (5.5.1) that the extinction coefficients for the two nitrile groups were considerably different. Clarke\textsuperscript{(57)} similarly acknowledged a difference between the extinction coefficients of the two nitrile absorptions. However, he did not actually calculate a value, but introduced a factor of 2.5 into his cyclisation calculation, which was inferred from extinction coefficient values for a saturated alkyl compared with that for an unsaturated nitrile. The example quoted is methylaminodiacetonitrile ($\epsilon=0.007$ l g\textsuperscript{-1}), and aminoacrylonitrile ($\epsilon=0.018$ l g\textsuperscript{-1})\textsuperscript{(151)} If the extinction coefficients differ by a factor of 11.5, as calculated in this study, and this value is substituted
Figure (78) The ratio, $R$, $CN(2200\text{cm}^{-1})/CN(2240\text{cm}^{-1})$ plotted as a function of reaction time, comparing chemically cyclised PAN with heat treated PAN.
into Clarke's equation, then all his calculated values are increased by a factor of 4. This would appear to indicate that the kinetic cyclised chain length could be substantially longer than appreciated in the literature. This therefore implies that oxidised Courteille has an average degree of cyclisation of 52 instead of 14, while corresponding values for the inert case increase from 28 to 112. The apparent reduction in the average value for sequence lengths achieved is indicative of shorter lengths towards the end of the reaction, which is progressively sterically hindered, and also of continuous initiation.

6.9 Relevance to carbon fibre production

A major aim of this work was to establish whether a chemically induced cyclisation reaction could produce stabilised PAN fibres as suitable precursors to carbon fibre formation. The problems associated with such an approach are broadly twofold;

(1) the fibre must have sufficient thermal stability to maintain its integrity on carbonisation.

(2) assuming criterion (1) is fulfilled, the fibre must produce a good carbon yield, and the resulting fibres must have comparable properties to fibres prepared by the conventional route.

A brief examination of the thermal stability of partially cyclised polymer (section 5.6.4) has shown that such products carbonised directly are as thermally stable up to 1200 K, as a sample of homopolymer which has been thermally stabilised at 493 K prior to carbonising.

While studying the bulk properties of these polymers gives an indication of their behaviour under carbonising conditions, it would be of more benefit to study the properties of partially cyclised PAN fibres, and thus evaluate their potential as carbon fibre precursors.
An attempt has been made to produce partially cyclised PAN fibres. Three techniques have been primarily considered.

(1) PAN was initially reacted with n-BuLi in solution. The reaction was killed at the required extent of reaction, calculated from the previous series of experiments. The polymer was precipitated into an excess of methanol. Redissolution of the freeze-dried product subsequently produced a spinning solution, using the wet spinning technique. Alternatively instead of adding an excess of methanol to the reacting solution, only a slight excess relative to the n-BuLi concentration was added. The solution could then be spun directly, since the reaction product remained in solution.

(2) The spinning of "live" polymer solutions was also considered. In this case the doped spinning solution was allowed to react for the required time, after which it could be spun directly. The major disadvantage of this technique would be the changing extent of reaction during the spinning process.

(3) The third possibility was to incorporate the additive (n-BuLi) into spun PAN (or Courtelle) fibres produced by wet spinning, which could be done by incorporating the additive into the coagulation bath. Gump and Steutz(88) used this method, although the problems associated with this technique include maintaining the activity of the n-BuLi in the coagulating bath, to initiate the cyclisation reaction, and to ensure that a uniform reaction throughout the fibre cross-section occurred.

Initial attempts by the author to spin reacted polymers proved difficult, mainly as a result of the low viscosity of the polymers in DMF solution. The technique was latterly modified to use a small quantity of a high molecular polymer as a carrier for the cyclised polymer. Initial experiments were undertaken with spinning solutions doped with small quantities of high molecular weight polyethylene oxide, as a carrier.
The polyethylene oxide is water soluble, therefore it is removed in the coagulating bath, leaving the partially cyclised polymer fibre. The initial series of experiments however, was largely unsuccessful, and further investigations of this type would be extremely interesting. Having produced the partially cyclised fibre it could be evaluated as a precursor to carbon fibre production. Chemical stabilisation of the precursor may obviate the need for an oxidation stage, or reduce the time required for oxidation since oxygen containing groups may be a prerequisite for promoting the dehydrogenation reaction during carbonisation. A possible advantage of producing carbon fibres by this route could be the absence of the sheath-core structure observed in conventionally prepared fibres. This structure is a result of the non-uniform oxidation reaction, which relies on diffusion of oxygen into the bulk of the fibre. Chemically stabilising the polymer should produce a more uniform structure.

Any method which can be used to reduce the energy requirements for the production of carbon fibres could reduce the cost, and make their use in non-specialised applications more attractive.
(1) Qualitative experiments indicated that many additives could irreversibly colour PAN solutions. Initial studies indicated that n-BuLi rapidly coloured PAN solutions, at a rate which could be followed using a sampling technique.

(2) Spectroscopic analysis of the products of the reaction of PAN with n-BuLi indicated that a chromophoric, conjugated polymer was produced. The conjugated species \(-\left\langle \text{C=N} \right\rangle_x^x\) was formed. The data confirmed the proposed secondary polymerisation reaction via the pendant nitrile groups, to produce cyclised sequences. The simple anionic reaction model proposed a structure consisting of short lengths of cyclised sequences separated by linear, unreacted polymer. Termination of the chemical cyclisation reaction produced terminal imine groups, which were hydrogen-bonded to the adjacent nitrile groups.

(3) Quantitative analysis of the reaction products showed that cyclised sequences with kinetic chain length between 2 and 23 monomer units were produced. The values were dependent on the n-BuLi concentration, and the reaction temperature. The cyclisation reaction was inhibited in the presence of oxygen.

(4) The residual enthalpy of the thermal reaction of partially cyclised polymer decreased with increased extent of cyclisation. The residual enthalpy was directly proportional to the number of residual nitrile groups, determined by infrared spectroscopy. Since the residual enthalpy was independent of n-BuLi concentration it was concluded that the terminal imine groups, produced during the chemical reaction, can initiate the thermal cyclisation of the remainder. The enthalpy of the reaction of the residual nitrile groups was calculated to be 24.4 kJ mol\(^{-1}\). Under all
experimental conditions, 20% of the nitrile groups must remain unreacted. The partially cyclised product was found to be potentially as thermally stable under carbonising conditions, as homopolymer thermally stabilised in an inert atmosphere, in the conventional manner.

(5) The conversion curve was found to have two distinct stages, both of which were first order with respect to the decrease in nitrile concentration. Stage (1) consisted of initiation followed by rapid unrestricted oligomerisation to produce cyclised sequences of short kinetic chain length. The rate constant at 293 K, for this stage, was calculated to be $7 \times 10^{-2} \text{ s}^{-1}$. Stage (2) was the propagation reaction, which was restricted by factors including the rate of rotation around the skeletal bonds, steric hinderance and changing solution properties. The second stage rate constant at 293 K was calculated to be $2.6 \times 10^{-3} \text{ s}^{-1}$. The temperature dependence of the reaction obeyed the simple Arrhenius equation. The activation energy for the n-BuLi initiated cyclisation reaction was calculated to be 41.5 kJ.
(1) The kinetics of the reaction need to be examined continuously to enable a more representative model to be proposed, particularly for the first stage of the reaction. The ionic nature of the reaction has not been confirmed, and would be useful in order to confirm the 100% efficiency assumed in the kinetic study.

(2) The reaction should be examined at higher temperatures for possible structural rearrangements, which may explain the results reported by Johnson et al\(^{72}\). Furthermore at higher temperatures low concentrations of initiator could be examined, and the optimum cyclised sequence lengths achieved.

(3) If known numbers of initiating sites can be incorporated into the polymer using the chemical reaction, or by low temperature initiation, then the crystallite size of the final carbon fibre may be shown to correlate to the number and length of cyclised sequences produced in the conventional thermal stabilisation reaction.

(4) The next stage is to confirm, or otherwise, the possibility of producing carbon fibres from these chemically reacted precursor polymers.

(5) Vinylidene dicyanide would appear to be a suitable carbon fibre precursor. However, stabilisation can not be thermally induced since preferential degradation occurs. If chemical initiation of the nitrile groups could be achieved, then carbonisation to produce a dense carbon fibre may be possible.
CHAPTER 9 REFERENCES

60. K. Hidehiko et al, Japan 72 26,978 (1972).
(Available as R.A.E. translation).
98. R.Lockheed, Private communication.
100. M.Akio and M.Takani, Japan 72 26,974 (1972).