THE OXIDATION OF ACRYLIC FIBRES
FOR THE FORMATION OF CARBON FIBRES.

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SUMMARY.

The chemistry of the thermal reactions of polyacrylonitrile have attracted attention since the use of the polymer as a textile fibre. The discovery that high performance carbon fibres could be easily made from acrylic fibres added another dimension to the scene - the morphology of the fibres during the thermal reactions. This thesis attempts to combine chemical analysis with mechanical analysis in order to determine why acrylic fibres are so suitable for the formation of carbon fibres.

Firstly, apparatus for the heat treatment and carbonisation of acrylic fibres was constructed, and experimental conditions for the production of high performance carbon fibres, from Courtelle fibres, were established and proved. By analysing Courtelle fibres taken from various stages in the production, the pertinence of the work was ensured. The analytical procedures used were elemental, infra-red and mechanical.

Because the spectrum of Courtelle was complicated by the comonomers, which contained oxygenated groups, the homopolymer was synthesised and used for comparison. Additionally, in order to obtain quantitative measurements from the infra-red spectra, films of homopolymer and Courtelle were produced and a technique for correlating fibres and film was developed.

The work was concentrated on the preliminary stages of the heat treatment process where the foundations of the carbon fibre structure are laid. The most important result of this work is that reasons have been described for the necessity of the oxidation stage in the production. These reasons centre on the formation of high energy bonding and the introduction of potential cross-linking ability, both without disruption to the oriented macromolecular structure.

This thesis also points out the more significant anomalies in the theories. Perhaps the least understood area is the relation between the extent of precursor oxidation and the development of high performance properties in the carbon fibres. It seems appropriate to finish this summary on a negative note as although the suggested theories seem basically sound, the anomalies are of such gravity that it would be conceited to say that the process of producing carbon fibres from acrylic fibres, is well understood.
ACKNOWLEDGEMENTS.

I would like to thank the British Aircraft Corporation for showing interest, in relatively academic aspects of carbon fibre technology, by sponsoring the work.

My thanks go also to Professor J.E. Bailey, who has co-ordinated the work, and to Dr. B.C. Stace who made many helpful suggestions and whose equipment was used for all the infra-red analyses.

I should like to take this opportunity to thank my long suffering family and my mother, whose untiring efforts have ensured perfect typing.
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CHAPTER 1.

INTRODUCTION.

1.1. Historical development.

The term "carbon fibres" usually refers to carbon or graphite in filamentary form which has high strength and modulus properties. These fibres, when bonded with a matrix, create a material having outstanding mechanical properties coupled with low density. Therein lies their importance and the reason for their adoption mainly by the aerospace industry.

Although high performance carbon fibres are a modern development, carbon fibres as such have been known for many years. At around the turn of the century natural fibres, (cellulose or protein), were partially carbonised and used as the filament in electric lights. The importance of these fibres was their electrical resistance and thermal stability in an inert environment. Such fibres still have a limited use as a high temperature packing material.

In 1961 Shindo described a method of producing carbon fibres from synthetic textile fibres based on polyacrylonitrile (PAN) (1). His method involved heating the fibres in an oxidative atmosphere at low temperatures ( \(< 300^\circ C\) ) followed by further heating at relatively high temperature ( \(> 1000^\circ C\) ) in an inert or vacuum environment. He produced virtually pure carbon fibres but with little improvement in mechanical properties.

Some years later, Johnson, Phillips and Watt (Royal Aircraft Establishment), were searching for new high temperature filamentary materials, and repeated Shindo's work. They found that, by preventing the shrinkage which normally occurs when PAN fibres are heated through their glass transition, carbon fibres could be produced which had excellent mechanical properties (2). A comparison of the properties of carbon fibres with other materials is shown in Table 1. The process for producing these high performance carbon fibres has become known as the RAE process. According to the final heat treatment temperature, fibres can be produced with either high strength and low modulus (1200-1500°C) or vice versa ( \(> 2000^\circ C\) ) (Table 1).
TABLE 1.

The mechanical properties of carbon fibres and composites compared with other materials (3).

<table>
<thead>
<tr>
<th>Material</th>
<th>UTS (GN/m²)</th>
<th>Youngs Modulus (GN/m²)</th>
<th>Specific UTS (GN/m²)</th>
<th>Specific Youngs Modulus (GN/m²)</th>
</tr>
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<tr>
<td>(Filaments)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Fibre (2500°C)</td>
<td>2.0</td>
<td>400</td>
<td>0.8</td>
<td>200</td>
</tr>
<tr>
<td>Carbon Fibre (1500°C)</td>
<td>2.7</td>
<td>300</td>
<td>1.6</td>
<td>165</td>
</tr>
<tr>
<td>Boron Fibre</td>
<td>2.8</td>
<td>420</td>
<td>1.1</td>
<td>168</td>
</tr>
<tr>
<td>Steel Wire</td>
<td>4.0</td>
<td>210</td>
<td>0.4</td>
<td>27</td>
</tr>
<tr>
<td>E Glass</td>
<td>3.5</td>
<td>63</td>
<td>1.4</td>
<td>25</td>
</tr>
<tr>
<td>(Bulk Materials)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Fibre Composite (2500°C)</td>
<td>1.0</td>
<td>190</td>
<td>0.6</td>
<td>120</td>
</tr>
<tr>
<td>Carbon Fibre Composite (1500°C)</td>
<td>1.4</td>
<td>130</td>
<td>0.9</td>
<td>87</td>
</tr>
<tr>
<td>G R P</td>
<td>1.1</td>
<td>40</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Steel</td>
<td>1.0</td>
<td>210</td>
<td>0.1</td>
<td>27</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.4</td>
<td>70</td>
<td>0.1</td>
<td>25</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.9</td>
<td>112</td>
<td>0.2</td>
<td>25</td>
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1.2. Structure of Carbon fibres.

The physical structure of carbon fibres is still the subject of controversy. There seems little doubt that the predominant method of chemical bonding is $sp^2$ hybridisation, as in graphite. There, the resemblance between carbon fibres and graphite ends, for their crystalline structures are quite different. Carbon fibres are said to have a turbostratic crystal structure: while the length and breadth of the unit cell are invariant, the third dimension, i.e. the distance between graphite planes, varies. However, in spite of this fundamentally non-crystalline behaviour, early papers referred to the structure of carbon fibres in terms of crystallites, the dimensions of which have been deduced from wide angle x-ray measurements. The high performance character of carbon fibres has been attributed to two unique properties of the crystallites, i.e. they are very small, and are aligned along the fibre axis.

It is probably more accurate to think of the structure of carbon fibres in terms of macromolecules of graphite, contained in ribbons. More precisely, the graphite planes are several hexagons wide, but so long that they may be considered almost infinite on an atomic scale. Several planes are stacked to form the ribbon. The ribbons lie approximately parallel to the fibre axis but twist and branch. In this interpretation of the x-ray data, the stacking height of the ribbon corresponds to the thickness of the so-called crystallite ($L_0$), while the concept of crystallite length does not exist. There is no discontinuous change in structure at boundaries. The parameter which has been interpreted as crystallite length ($L_0$) probably relates to a perfectly straight and ordered section of ribbon.

It is the orientation of the ribbons along the fibre axis which accounts for the high modulus and in part, the high strength of carbon fibres. It is most probable that this structure is derived directly from the precursor structure, which also consists of macromolecules aligned along the fibre axis. The reason for not allowing the fibres to shrink during thermal treatment is simply to preserve the molecular alignment. However, there is x-ray and electron diffraction evidence suggesting that disorientation occurs even when the fibres are restrained during the heat treatments (4, 5).
This interpretation is arguable because it is difficult to suggest reasons for the realignment of the molecules if disorientation does occur.

There are significant differences in structure between the high strength and the high modulus fibres. In a high strength fibre (1300°C) $L_c$ has been measured at approximately 1 nm and $L_a$ at 2 nm, i.e. the ribbon consists of about 4 layers of hexagons (6). The corresponding high modulus fibre (2350°C) has $L_c = 4.4$ nm and $L_a = 7.1$ nm. The density also increases during the heat treatment which probably accounts for the increase in $L_c$. The increase in $L_a$ can be attributed to further straightening of the ribbons.

The reason for the fall in strength with heat treatment after 1500°C is not known with certainty. It has been suggested that the actual strength is related mainly to the presence of imperfections such as voids or impurities. It has been shown that large voids appear at temperatures greater than 1800°C (7). These may originate from metallic impurities. Certainly the strength values are improved by ensuring purity in the precursor fibres (8).
1.3 Precursors and processing routes.

It is an understatement that the extrusion of graphite presently creates unsurmountable difficulties. Therefore it is necessary to start with an organic filament and remove elements other than carbon by pyrolysis. There are four fundamental requirements of precursors for carbon fibres.

A. Good carbon yield on pyrolysis.

Of the many carbon compounds which have high carbon contents, few pyrolyse in such a way that carbon remains in good yield. Compounds containing oxygen tend to lose carbon as the monoxide or dioxide during pyrolysis.

B. Fibre forming.

The term fibre forming does not mean to imply the necessity of long linear macromolecules which are oriented along the fibre axis. All that is required is that at some time prior to carbonisation it is possible to form a filament. However, if the material does not contain oriented macromolecules, the final carbon fibre will have isotropic properties and a high temperature (> 2500°C) stretch process would be necessary to produce orientation and high performance properties.

C. Non-melting.

Obviously, the fibre must not melt during the pyrolysis but this does not mean the precursor must be thermally stable. It is quite possible to start with a thermoplastic fibre and treat this at low temperatures to produce non-melting character. Such treatments include cross-linking and ring closure reactions.

D. Non-graphitising.

Finally, it is necessary to choose a material which carbonises in such a way that discrete, large graphite crystallites are not produced. The subtle difference between the crystalline structure of carbon fibres and graphite has been explained (section 1.2). The parameters controlling the final crystal structure are not fully understood and few organic materials satisfy this last criterion.

A recent literature review revealed 22 published precursors for carbon fibre production (9). Of these 21 were organic polymers, natural and synthetic, and the remaining one was pitch. A Japanese commercial process for the production of high performance carbon fibres from pitch
has recently been introduced. As previously stated, a high temperature stretch is necessary due to the amorphous, isotropic nature of pitch. More important in the U.S.A., is the use of Rayon as a precursor. These fibres have a $\beta (D) +$ glucose repeat unit which carries a $C-O-C$ group in the main polymeric chain. Consequently pyrolysis causes molecular degradation and disorientation. Therefore, these fibres also have to be given a high temperature stretch to induce high performance properties.

The most important precursor is at the present time acrylic fibre, based on polyacrylonitrile. Although a comparatively expensive precursor, PAN has the advantage of a simple processing route.

1.4. Acrylic fibre precursors.

Polyacrylonitrile is a linear, atactic macromolecule, but the existence of short isotactic or syndiotactic sequences cannot be ruled out. Rarely is the homopolymer used for textile fibres. The material has to be dyed and a copolymeric dye site is usually employed. The highly polar nitrile groups cause such strong intermolecular attractions that the polymer has high density, high $T_g$, degrades before melting and is soluble only in highly polarising solvents. Thus for textile use PAN is usually copolymerised with vinyl monomers having bulky side groups. These cause steric hindrance between molecules, reduce the intermolecular forces and allow easy access of dyes and easier processing. The textile fibre currently employed in Britain for the commercial production of carbon fibres is Courtelle. This contains $6\%$ methyl acrylate comonomer and the dye site is believed to be itaconic acid ($<1\%$). The chemical structure of Courtelle is shown in Figure (1). The role that these ancillary materials play in the degradation, will be discussed later in this thesis.

The physical structure of acrylic fibres has not been studied greatly because of the difficulty in understanding the x-ray fibre diagram. Like carbon fibres themselves, PAN fibres exhibit only 2 dimensional order. They are not crystalline in the ordinary sense but the molecules can be oriented along the fibre axis. PAN fibres show more order laterally than longitudinally. This has been attributed to the nitrile groups: the very strong dipole interactions are the dominant force and in an oriented fibre, fix the position of the molecules laterally. It is not known whether this unusual structure has a direct bearing on the production of carbon fibres. The only known influence of the structure
FIGURE 1  CHEMICAL STRUCTURE
OF COURTELLE

A  ACRYLONITRILE
B  METHYL ACRYLATE
C  ITACONIC ACID

WEIGHT RATIO  A:B:C  93:6:1
MOLAR RATIO,  A:B:C  25:1:0.1
is that the lack of crystallinity allows serious shrinkage when the polymer is heated above its $T_g$; hence the need to restrain the fibres until a thermally stable structure is formed.

The first stage in the carbonisation process is referred to as oxidation because the fibres are heated in air. There may be many heating conditions which would be satisfactory, but it is usual to heat Courtelle fibres at 220-5°C for periods up to 5 hours. The chemical reactions occurring during oxidation result in a thermally stable structure. The character of these fibres has been known for some time. Originally prepared from Orlon acrylic fibres, the thermally stable product was known as Black Orlon. Their exceptional stability is demonstrated in a convincing manner, at lectures, by boiling an egg in a saucepan of water heated over a bunsen with Black Orlon between the bunsen and the pan. After 4 minutes boiling there is no noticeable change in the fibres.

By virtue of this degree of stability, it is possible to heat the fibres under inert conditions to very high temperatures. The strength and modulus of the fibres increases steadily during the process to 1200°C when the strength value reaches a limit. Further heating to 2500°C produces a fibre with greater modulus, but lower strength. The relation between heat treatment temperature and mechanical properties is shown in Figure (2).

1.5 The development of this study.

It has been stated that acrylic fibres need to be oxidised before the carbonisation treatment in order that high performance carbon fibres can be produced, and that oxidation is the process whereby thermal stability is conferred to the acrylic fibres. But it is not the only method of achieving this. Simply heating the fibres in the absence of oxygen does impart a degree of thermal stability and attempts have been made to produce high performance carbon fibres without the oxidation stage, (10, 11). Although carbon fibres can be produced in this way, their mechanical performance is poor.

At the time this study was initiated there were no published works describing the relationship between the chemistry of oxidation and the mechanical properties of the final carbon fibre. That is what this thesis is about.
FIGURE 2 MECHANICAL PROPERTIES OF CARBON FIBRES AS A FUNCTION OF HEAT TREATMENT TEMPERATURE.

TENSILE STRENGTH (G N/m²)

TENSILE MODULUS (G N/m²)

HEAT TREATMENT TEMPERATURE
By analysing acryliol fibres and films subjected to equivalent heat treatments in oxidative and inert atmospheres it has been possible to arrive at different chemical formulae for fibres given the two treatments. These fibres have been carbonised (1400°C) and their mechanical properties tested. It has therefore been possible to relate chemical structure of the heat treated precursor to the performance of the final carbon fibres.
CHAPTER 2.

LITERATURE REVIEW.

2.1. Introduction.

The development of PAN as a textile fibre has created much interest in its thermal behaviour. This is because at temperatures greater than the $T_g$, reactions occur which can cause rapid and serious colour changes. Consequently, many papers have been published about the colouration reactions in inert and oxidising atmospheres. Although essentially the same reactions occur during the formation of carbon fibres, inappropriate experimental conditions reduce the usefulness of the early papers. Only since 1965 have papers appeared which are directly relevant to the formation of carbon fibres.

Since this thesis is concerned mainly with elemental and infra-red analysis, only those papers which deal with these topics have been surveyed in detail for the review. The results and conclusions of other papers, which have a direct relevance to carbon fibre formation, will be used in the discussion section.

2.2. Elemental analysis.

2.2.1. Thermal reactions in inert atmosphere.

Houtz (12) in 1950, stated that he carried out elemental analysis, but did not state the chemical composition of the polymer, neither did he distinguish between the thermal treatments in inert and oxidative atmospheres.

Burland and Parsons (13) (1956) carried out elemental analyses on homopolymer powder heated in nitrogen at between 200 and 320°C for various periods. Their total C, H and N contents were incomplete, ranging from 89.6% to 97.0%. This may have been due to absorbed water as the heat treated fibres were found to be hygroscopic. They do, however, consider their results sufficiently reliable to state that because the nitrogen content remains high (> 15%) through the heat treatments, the involvement of nitrogen in the cyclic structures proposed by Houtz (12) (1) is substantiated.
But because the C/H ratio increases significantly only at higher temperatures Burlant and Parsons infer that an unaromatised cyclic structure (II) is formed initially.

![Chemical structures](image)

Kennedy and Fontana (14) (1959) produced similar results on homopolymer powder heated under vacuum at 230°C - 265°C. At 265°C they reported what was described as a minor explosion. They realised their total C, H and N contents were incomplete (86.7% - 95.8%) and stated that they could not explain this.

Monohan (15) (1966) heated homopolymer powder to 450°C (rate not stated) and found lower H contents and higher C contents than any previous author, while the total H, C and N content was 100.0%. If incomplete analyses are due to absorbed water it would appear that the species responsible for the hygroscopic nature of the heat treated material are not present after heating to 450°C.

Miyamichi, et.al. (16) (1966) found that elemental analyses on PAN fibres heated (200-230°C) under nitrogen were complete. Hence previous incomplete analyses were apparently caused either by oxidation due to the inadvertent admission of air or Miyamichi took more care in preventing the fibres from contact with atmosphere between heating and the analysis. The results are published in graph form showing H/C and N/C ratios. At 230°C, the number of hydrogen atoms in the repeat unit reduced to 2.7 after 5 hours, and 2.4 after 16 hours. The N/C ratio was invariant.

Turner and Johnson (17) (1969) heated Courtelle fibres in argon at 1°C/min. The H/C ratio was virtually constant to 220°C and then decreased. The N/C ratio decreased slowly. At 300°C there were 0.9 nitrogen atoms and 2.7 hydrogen atoms per repeat unit.
In a less rigorous paper Shindo (18) (1971) omitted to describe the acrylic fibre, or the rate of temperature rise, but found that at 300°C, 2.4. hydrogen atoms per repeat unit remained. Figures for nitrogen were absent.

2.2. 2. Thermal reactions in oxidative atmospheres.

Burlant and Parsons (13) (1956) published the results of elemental analysis of homopolymer heated in air. The total C, H, N contents were incomplete, but very similar to those of polymer heated in nitrogen. No comment was made about how oxygen was absorbed.

Vosburgh (19) (1960) was the first to take account of the hygroscopic nature of the thermally treated material. He worked with Orlon fibres but does not state their composition. Elemental analyses were carried out on the fibres as received and the results corrected on the basis of water content determination by the Karl Fischer method. Vosburgh concludes that his results would be explained if oxidation, with the formation of hydroxyl groups occurred in 85% of monomer units while dehydrocyanation occurred in the remaining 15%.

Then half of the oxidised units would be dehydrated with the formation of C = C bonds (III).

\[
\begin{align*}
\left[ \begin{array}{c}
H \\
C \\
C \ N \\
\end{array} \right]_N & \rightarrow \\
\left[ \begin{array}{c}
H \\
O \\
H \\
\end{array} \right] & + \\
\left[ \begin{array}{c}
H \\
C \equiv C \\
\end{array} \right]_{0.15N} \\
\left[ \begin{array}{c}
H \\
C \equiv C \\
\end{array} \right]_{0.85N} & \rightarrow \\
\left[ \begin{array}{c}
H \\
C \equiv C \\
C \ N \\
\end{array} \right]_{0.425N} (III)
\end{align*}
\]
The value of Vosburgh's calculations are now doubtful since his proposed reaction omits ladder structures for which strong evidence has since been found.

Miyamichi (16, 20) (1966) carried out a comprehensive elemental analysis on thermally oxidised PAN fibres. He found that at 230°C there was significant loss of hydrogen and uptake of oxygen. After 5 hours 1 H atom was lost and 0.4 0 atoms absorbed, per repeat unit. After 16 hours the repeat unit contained 1.6 H atoms and 0.5 0 atoms. There was no change in the number of N atoms/repeat unit. The main effect of oxygen appears to be the removal of H atoms by reactions which leave oxygen bonded to the molecule.

Standage and Prestcott (21) (1969) oxidised fibres containing 99.6% acrylonitrile. They calculated theoretical C, H, N, 0 contents of two possible repeat units (IV and V) in the oxidised fibres and found that their experimental results lay between the two (Table 2.1).

Their only evidence for the cyclo-ether structures lies in questionable conclusions from infra-red analysis. However, from this and their elemental analysis, they conclude that the structure of the oxidised fibre must lie somewhere between structures IV and V.
TABLE 2.1. Elemental analysis results (21).
(Figures calculated from the results).

<table>
<thead>
<tr>
<th>No. OF ATOMS PER REPEAT UNIT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>ORIGINAL</td>
</tr>
<tr>
<td>STRUCTURE IV</td>
</tr>
<tr>
<td>STRUCTURE V</td>
</tr>
<tr>
<td>FOUND</td>
</tr>
</tbody>
</table>

In 1971 Standage published a more comprehensive paper (22). He used Dralon T fibre which was stated to be a copolymer of acrylonitrile (99.6%) and methyl acrylate (0.4%). N.M.R. and I.R. analyses were consistent with this composition. After removal of surface finishes the fibres were heated in air at 225 - 375°C for various periods. It was found that after either high temperatures or long periods the fibres had oxidised to 95% of their theoretical maximum according to the empirical equation:

\[
(C_3H_3N)_n + \frac{1}{2} n O_2 \xrightarrow{ht} (C_3H_3NO)_n + 2 n H.
\]

This means that in Standage's nearly fully oxidised material the repeat unit had lost 2 H atoms and gained 1 O atom, while the nitrogen content was constant.

The structure previously described by Standage, (V), is consistent with these results.

However, the doubtful I.R. and elemental analysis evidence is insufficient to propose an empirical formula involving cyclic ether groups. For instance, the oxygen could be present in carbonyl groups (VI) while still conforming with Standage's results. Definite evidence for the existence of carbonyl groups will be presented later in this thesis.
Although Potter (1972) heated Courtelle fibres in both air and nitrogen he publishes elemental analysis results for oxidation only (23). He found that after heating in air at 220°C for 7 hours only 1.3 H atoms per repeat unit remained while the nitrogen content was invariant and 0.5 O atoms/repeat unit were introduced. This evidence is used with infra-red analysis to yield the following formula for the oxidised polymer (VII).

\[
\text{(VI)}
\]

\[
\text{(VII)}
\]

2.3 Infra-red spectroscopy.

2.3.1. Introduction.

Because thermally treated PAN is soluble in only strong oxidising acids, analytical techniques which may be applied directly to the solid material, are very important. Papers describing the I.R. spectra of thermally treated PAN fall roughly into two groups: those which make tentative peak assignments only, and those which additionally draw conclusions about their relevance to carbon fibres. The presentation of this part of the thesis is in the form of tables of peak assignments. Where appropriate, their relevance to carbon fibre formation will be discussed in Chapter 5.

I.R. spectroscopy may be applied to PAN in the form of powder, film or fibres. There is no evidence to suggest that the qualitative reactions are a function of the form of the specimen so that all three forms will be considered. (The form of the specimen is important when describing the rate of the reactions).
2.3. The spectrum of polyacrylonitrile.

The I.R. spectrum of PAN is relatively simple for a polymeric material and peak assignments have been made based on theoretical calculations and other standard methods such as polarisation shifts and deuteration (24) (25). Papers differ on some assignments of the weak peaks and shoulders, but there is good agreement on the main fundamental peaks which will be used in this thesis. Table 2.2. is a summary of the peak assignments pertinent to this thesis.

<table>
<thead>
<tr>
<th>Wave number observed.</th>
<th>Intensity.</th>
<th>Assignment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2940-50</td>
<td>vs</td>
<td>( \nu_a (\text{CH}_2) ) stretch</td>
</tr>
<tr>
<td>2870</td>
<td>m</td>
<td>( \nu_b (\text{CH}_2) ) stretch</td>
</tr>
<tr>
<td>2237</td>
<td>vs</td>
<td>( \nu (\text{C} \equiv \text{N}) ) stretch</td>
</tr>
<tr>
<td>1447</td>
<td>vs</td>
<td>( \delta (\text{CH}_2) ) bend</td>
</tr>
<tr>
<td>1355-60</td>
<td>m</td>
<td>( \omega (\text{CH}_2) ) wag</td>
</tr>
</tbody>
</table>

The tertiary CH group should absorb between 3000 and 2800 cm\(^{-1}\) but its intensity is very weak and there is disagreement about its exact position. It is interesting to note that Liang and Krim found a broad absorption at around 1600 cm\(^{-1}\) which they assigned to impurities (24). This is now known to be due to species containing double bonds which are formed as a result of the thermal reactions. Liang's polymer must have been heated too strongly during its preparation and was most probably coloured yellow. It is surprising that he used such a sample in his fundamental study.
2.3.3. The spectrum of polyacrylonitrile after thermal treatment.

Figure 2.1. shows typical spectra of PAN film after thermal oxidation and inert pyrolysis. These two spectra are included for reference. In the following tables, where a particular assignment warrants special comment, a reference is made to a note, eg. (B), which will be found at the end of the tables.

### TABLE 2.3. Spectrum range 4000 - 2500 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Peak (cm(^{-1}))</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidative</td>
<td>3600 - 3200</td>
<td>N - H</td>
<td>26(A)</td>
</tr>
<tr>
<td>Oxidative</td>
<td>3380 - 3330</td>
<td>N - H</td>
<td>22(B), 27.</td>
</tr>
<tr>
<td>Oxidative</td>
<td>3380 - 3330</td>
<td>O - H</td>
<td>16.</td>
</tr>
<tr>
<td>Oxidative</td>
<td>3330 - 3100</td>
<td>O - H</td>
<td>27</td>
</tr>
<tr>
<td>Oxidative</td>
<td>2920</td>
<td>C - H</td>
<td>28(C)</td>
</tr>
<tr>
<td>Inert</td>
<td>3400 - 3350</td>
<td>N - H</td>
<td>13(D), 15, 16, 29.</td>
</tr>
<tr>
<td>Inert</td>
<td>3230 - 3200</td>
<td>N - H</td>
<td>13(D), 15, 16, 29, 30.</td>
</tr>
</tbody>
</table>

### TABLE 2.4. Spectrum range 2500 - 1800 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Peak (cm(^{-1}))</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidative</td>
<td>2215 - 2140</td>
<td>conjugated C = N</td>
<td>16, 23, 26(A), 27, 30, 31, 32(E).</td>
</tr>
<tr>
<td>Oxidative</td>
<td>2170</td>
<td>R N H(^+) (\times)</td>
<td>33(F)</td>
</tr>
<tr>
<td>Inert</td>
<td>2200 - 2185</td>
<td>conjugated C = N</td>
<td>13, 17, 29, 34.</td>
</tr>
<tr>
<td>Inert</td>
<td>2170</td>
<td>R N H(^+) (\times)</td>
<td>33(F)</td>
</tr>
<tr>
<td>Inert</td>
<td>2150</td>
<td>(= C - C \equiv N) or (N = C - C \equiv N)</td>
<td>29(G)</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Peak (cm⁻¹)</td>
<td>Assignment</td>
<td>Reference</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Oxidative</td>
<td>1720</td>
<td>C - O</td>
<td>13, 27, 30(H), 33, 34, 35, 36.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1720</td>
<td>C - N</td>
<td>21, 35.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1680 - 1630</td>
<td>C - O</td>
<td>16, 27, 30, 32, 36, 37(J).</td>
</tr>
<tr>
<td>&quot;</td>
<td>1680 - 1630</td>
<td>C - C</td>
<td>33(K).</td>
</tr>
<tr>
<td>&quot;</td>
<td>1620 - 1585</td>
<td>C - C</td>
<td>16, 21, 27(L), 31, 32, 36, 37, 38, 39.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1620 - 1585</td>
<td>N - H</td>
<td>33(M), 35.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1620 - 1585</td>
<td>C - N</td>
<td>21, 27(L), 31, 32, 36, 37.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1550 - 1540</td>
<td>C - N - H</td>
<td>21.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1550 - 1540</td>
<td>CO₂</td>
<td>33(M)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1380 - 1370</td>
<td>C - H</td>
<td>27, 28(C).</td>
</tr>
<tr>
<td>&quot;</td>
<td>1380 - 1370</td>
<td>R₃C - OH</td>
<td>33(N)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1340</td>
<td>CO₂</td>
<td>33(N)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1290 - 1170</td>
<td>N → O</td>
<td>40 (Direct evidence against this assignment, 36(P), 28(q),).</td>
</tr>
<tr>
<td>&quot;</td>
<td>1165 - 1135</td>
<td>R₂C - OH</td>
<td>33</td>
</tr>
<tr>
<td>&quot;</td>
<td>1165 - 1135</td>
<td>CH - CH₂ - CH - O</td>
<td>21(R)</td>
</tr>
<tr>
<td>Inert</td>
<td>1670 - 1620</td>
<td>C - N</td>
<td>41</td>
</tr>
<tr>
<td>&quot;</td>
<td>1670 - 1620</td>
<td>C - N</td>
<td>34, 42.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1670 - 1620</td>
<td>NH₂</td>
<td>13, 15, 16.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1615 - 1580</td>
<td>C - N</td>
<td>16, 34, 42, 43.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1615 - 1580</td>
<td>C - N</td>
<td>17, 30, 40, 41.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1615 - 1580</td>
<td>NHₓ</td>
<td>33(M).</td>
</tr>
<tr>
<td>&quot;</td>
<td>1550 - 1540</td>
<td>N - H</td>
<td>44</td>
</tr>
<tr>
<td>&quot;</td>
<td>1550 - 1540</td>
<td>CO₂</td>
<td>33(M).</td>
</tr>
</tbody>
</table>

Table 2.5/over
### TABLE 2.5. Spectrum range 1800 - 1000 cm\(^{-1}\) (continued)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Peak (cm(^{-1}))</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert</td>
<td>1420</td>
<td>C - C</td>
<td>34, 42.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aromatic</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>1370</td>
<td>R(_2)C - OH</td>
<td>33((N)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1340</td>
<td>CO(_2)</td>
<td>33((N)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1160 - 1150</td>
<td>C - N</td>
<td>16.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1160 - 1150</td>
<td>R(_2)C - OH</td>
<td>33.</td>
</tr>
<tr>
<td>&quot;</td>
<td>1160 - 1150</td>
<td>C - C</td>
<td>15.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aromatic</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2.6. Spectrum range 1000 - 250 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Peak (cm(^{-1}))</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidative</td>
<td>980</td>
<td>N (\rightarrow) O</td>
<td>28 (Q, evidence against this assignment)</td>
</tr>
<tr>
<td>&quot;</td>
<td>810 - 800</td>
<td>C - C - H</td>
<td>16, 27, 33((U), 36, 38, 39.</td>
</tr>
<tr>
<td>&quot;</td>
<td>810 - 800</td>
<td>N - H</td>
<td>35.</td>
</tr>
<tr>
<td>Inert</td>
<td>965 - 960</td>
<td>aromatic</td>
<td>13, 15.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C - C - H</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>810 - 800</td>
<td>- do -</td>
<td>13, 15, 33((U), 43.</td>
</tr>
<tr>
<td>&quot;</td>
<td>650</td>
<td>1 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C - C - H</td>
<td>38.</td>
</tr>
</tbody>
</table>
FIGURE 2.7  COMPARISON OF PAN FILM
AFTER HEAT TREATMENT AT 225°C FOR
9 HOURS IN (a) AIR  (b) NITROGEN
NOTES.

A. Potter and Scott do not actually make an assignment for this extremely broad absorption, but amines figure in their suggested mechanisms. Their formula for oxidised PAN is unique in that hydrogen atoms can be bonded to the nitrogen atoms causing a break in the C-N conjugated sequences. They assume the presence of oxygen in the form of carbonyl groups only. Although they heated PAN in air and nitrogen, the latter case was very briefly mentioned, and it appears that they were not able to detect a difference in the spectra in the 3600 - 3200 cm⁻¹ region. This very broad absorption insinuates they obtained their spectra by the KBr disc method using damp KBr; the actual method is unstated.

Additionally they degraded PAN in DMF solution containing cyanide ions. They state that these conditions correspond to thermal oxidation as there was enough oxygen dissolved in the system to give values of oxygen uptake similar to those from air oxidation. They found that the intensity of the nitrile peak at 2180 cm⁻¹ was proportional to the cyanide concentration. This peak was assigned to the cyanide which had initiated a cyclised sequence and was thereby conjugated. This provides a potential method for determining the length of the cyclised sequences, for if the number of sequences initiated and the total amount of cyclisation is known the average length can be readily calculated. The main assumption would be that the absorption at 2180 cm⁻¹ was caused solely by cyanide groups used in the initiation of a cyclised sequence. This could be proved by isotope labelling the cyanide.

B. There are two interesting anomalies in this work by Standage and Matkowsky, who publish the transmission spectra of films oxidised for various periods. Much absorption appears in the region 3330-3210 cm⁻¹ while the nitrile peak intensity is not greatly affected. For reasons not stated, the spectra of highly oxidised films are absent; instead, the reflectance spectrum of fibres is published. This is completely different from all the other spectra. There is no absorption in the region 3330-3210 cm⁻¹ and no nitrile peak! The only comment offered, "Fibre reflectance spectra are not considered quantitatively meaningful".
Notes: B (cont)

It seems most probable that the spectrum they obtained by reflectance was from organic contaminants on the surface of either the fibres or the ATR crystal in the reflectance cell.

Additionally, although the conclusion of this work is that oxygen incorporation is probably in the form of epoxide bonding at \( \beta \) carbon atoms, none of the spectra published show significant reductions in the corresponding \( \beta \) hydrogen atoms.

These serious anomalies cast considerable doubt on the value of the conclusions.

C. Rose says that the bands at \( 2920\text{ cm}^{-1} \) and \( 1375\text{ cm}^{-1} \), which are due to tertiary C - H groups, grow during the initial stages of oxidation, and this is evidence that oxygen first attacks secondary hydrogen atoms, i.e. methylene hydrogen. The stated growth is certainly not evident from the published spectra. Additionally there is doubt over the assignment of these peaks: Rose uses Yamadera's assignment (25), but Krimm does not find an absorption at \( 2920\text{ cm}^{-1} \), and at \( 1375\text{ cm}^{-1} \), the shoulder is assigned questionably to \( \text{CH}_2 \) groups. From my results of film also there is no peak at \( 2920\text{ cm}^{-1} \) and while the \( \text{CH}_2 \) absorption at \( 1355\text{ cm}^{-1} \) broadens during the initial stages of oxidation, it later sharpens at \( 1350\text{ cm}^{-1} \). There seems to be significant evidence against Rose's results.

D. All the spectra obtained by Burlant and Parsons were by the KBr disc method. The spectra of pure PAN show an OH peak in the region \( 3350 - 3200\text{ cm}^{-1} \), indicating that the KBr was wet. Consequently the formation of OH in their air oxidation experiments could not be detected, and this important conclusion was missed.

E. Absorption at \( 2210\text{ cm}^{-1} \) is attributed to the system \( N \equiv C - \overset{1}{\overset{\circ}{C}} - \overset{1}{\overset{\circ}{C}} - \overset{\circ}{H} \) only where the \(- C = C -\) group is conjugated. Danner & Meybeck say they did not find this peak in PAN film oxidised in air (\( \frac{3}{4} \) hour, \( 235^\circ\text{C} \)). This is contrary to the results of others, including myself. I found the peak was first significant after 2 hours heating at \( 225^\circ\text{C} \) and in fact there is a small peak at \( 2210\text{ cm}^{-1} \) in the spectrum published by Danner and Meybeck.
F. Deane cites three pieces of evidence for the assignment of this peak to $\text{RNH}_x^+$.

1. The formation of $-\text{CO}_2^-$ indicated by peaks at 1550 and 1340 cm$^{-1}$ dictates that a cation must be present and the most likely one is $\text{RNH}_x^+$. (The assumption that the correct assignment has been made in the 1550 and 1340 cm$^{-1}$ peaks seems somewhat naive).

2. This peak cannot be due to $\text{C} = \text{N}$ in conjugation because the total area of peaks at 2240 and 2170 cm$^{-1}$ remains constant while it is known that the nitrile groups are reacting.

3. The peak shifts to 2050 cm$^{-1}$ on deuteration. This appears the most important piece of evidence. However, Deane points out that quaternary ammonium compounds should also absorb at 2500 cm$^{-1}$, but there is no absorption in that region, so the assignment of the 2170 cm$^{-1}$ peak to $\text{RNH}_x^+$ is left in some doubt.

G. Absorption as low as 2150 cm$^{-1}$ is found by Grassie only when anionic cyclisation initiators are added in the pyrolysis (29). Association of this absorption with the initiation step has been suggested in another paper (26).

H. The IR spectrum of a copolymer containing a $\text{C} = \text{O}$ group (methyl acrylate) absorbed at 1740 cm$^{-1}$. On heating in nitrogen, the peak shifted to 1700 cm$^{-1}$ showing that this group was taking part in the conjugation caused by the cyclisation reaction.

I. In the spectra shown Courtelle and PAN have intense absorptions at 1680 cm$^{-1}$, which disappear after the first heat treatments which are quite mild (Courtelle - 40 min. at 180°C, PAN - 4 hours at 180°C). Bell and Mulchandani attempt to explain this absorption in terms of substituted amides formed during the hydrolysis of ketene-imine structures. However these are produced as impurities during polymerisation (45, 46) and would not be able to produce sufficient amide to give the intense absorptions. The spectra were obtained from films which were solvent cast from N-dimethylformamide (DMF) solution (1.25%). The films were dried, "under an infra-red lamp", and then washed in water. Clearly, the absorption at 1680 cm$^{-1}$ is from the carbonyl group in residual DMF (B.Pt. 150°C) which comes out only after heating to 180°C.
Grassie has recorded difficulty in removing DMF from PAN (47). Additionally, medium intensity absorptions are shown at 2400 - 2300 cm\(^{-1}\) in Courtelle. I have not seen any other spectrum of acrylonitrile polymer with absorption in this region.

K. The peak at 1655 cm\(^{-1}\) was intensified on \(\beta\) irradiation which is the evidence for the assignment to C = C rather than C = O.

L. Conley and Bieron carried out the first comprehensive infra-red analysis of oxidised PAN homopolymer. They confined their analysis to the initial stages of oxidation by employing low temperatures (100-200\(^{\circ}\)C). A strong absorption due to C = C (1600 cm\(^{-1}\)) developed while there was no apparent change in the intensity of the nitrile peak (2240 cm\(^{-1}\)). They concluded that cyclisation was not occurring. However, it must be realized that because of the logarithmic relation between peak intensity and quantity of material absorbing, small changes in an intense peak, such as the C = N at 2240 cm\(^{-1}\), are difficult to measure accurately. Conversely, the C = C peak is initially weak so that small quantities of these groups are relatively easily detected.

M. There are several anomalies here. Using the Du Pont curve resolver, the peak at 1600 cm\(^{-1}\) was found to consist of 3 peaks, at 1550, 1590 and 1610 cm\(^{-1}\). The peak at 1550 cm\(^{-1}\) was assigned to CO\(_2\) even when heating was carried out in an inert atmosphere. We are left to assume it came from oxygen in the comonomer, but it is inferred that the peak is also produced in the spectrum of inert heat treated PAN homopolymer.

Deane does not assign the peak at 1590 cm\(^{-1}\) even though it is the most intense of the 3 in the oxidised copolymer spectrum, and was found to shift on deuteration. (Deuteration was carried out by heating the material in the oxidative or inert atmosphere to which D\(_2\)O had been introduced. Therefore the presence of some kind of interchange reaction is necessary. No comment was made on this).

The peak at 1610 cm\(^{-1}\) was assigned to NH\(_2\). But this did not shift on deuteration !.
Again, the same confusion occurs about the formation of these peaks after heat treatment of PAN in inert atmosphere.

Uchida, et al. heated PAN film in a stream of nitrogen and monitored the spectral changes. While maintaining the temperature (230°C) they then replaced nitrogen with air. Because there was no change in absorption at 1250 cm⁻¹ when air was introduced, they conclude that oxygen does not form N → O bonds. This had been suggested previously by Friedlander (45). However, the assignment of the 1250 cm⁻¹ peak to N → O bonds is controversial.

This is further evidence against nitrone formation: Rose also does not find an absorption at 1290 cm⁻¹ or 980 cm⁻¹.

Standage and Prestcott do not show the spectra they obtained by ATR on 99.6% acrylonitrile fibre. As evidence for the formation of bridging ether groups they say that 1,3 epoxypropane CH₂ - CH₂ - CH₂ - O has three absorption peaks corresponding to those at 1135, 1100 and 1020 cm⁻¹ in the oxidised fibres. This is doubtful evidence because these absorptions in 1, 3 epoxypropane are likely to be ring vibrations which would be suppressed in the cyclised ladder structure of oxidised PAN.

Grassle degraded PAN in a nitrogen atmosphere and assigned the absorptions at 1640 – 1610 to C = N. He claims C = C bonds are definitely not present because there is no definic C – H stretching band at 3100 – 3000 cm⁻¹.

Grassie has altered his opinion in this paper and suggests C = C may be present in an inert, heat treated polymer.

Deane finds the absorption at 800 cm⁻¹ "variable and vanishingly weak in most samples". The samples refer to homopolymer and copolymer heated in air or nitrogen or subjected to β irradiation. The one spectrum in the paper of oxidised copolymer shows a medium intensity absorption at 800 cm⁻¹.
Summary and Conclusions.

Some of the earlier papers covering elemental analysis of polymer heated in inert atmospheres are not reliable because the elemental contents did not total 100%. When the hygroscopic nature of the material was discovered more accurate analyses were reported.

The paper by Miyamichi (16) is one of the most comprehensive on elemental analysis. He shows that the empirical formula of PAN fibres heated at 200°C for 24 hours in inert atmosphere is C\textsubscript{2}H\textsubscript{2.7}N\textsubscript{0.3}, i.e. very similar to the original, C\textsubscript{3}H\textsubscript{2}N. The corresponding fibres heated in air have the following empirical formula: C\textsubscript{2}H\textsubscript{1.9}N\textsubscript{0.6}. So considering two repeat units the main effect of oxidation has been to decrease the number of hydrogen atoms by 2 while 1 oxygen atom has been introduced.

No paper on infra-red analysis has made a serious attempt to use the results to describe why oxidation is necessary to produce high performance carbon fibres. Most papers simply record and describe the spectra obtained.

In the range 4000-2500 cm\textsuperscript{-1} it is apparent from Table 2.3 that during oxidation NH and OH groups are formed while during inert pyrolysis absorptions appear corresponding to only NH groups. Although this conclusion is readily seen from the Table, it is not stated in any single paper. This is a classic example of the value of a comprehensive literature survey. All but one paper assign the new nitrile peak which occurs at slightly lower wavenumbers from the original, to a conjugated nitrile group, or at least one which is taking part in some kind of electron delocalisation. It is apparent that C = C and C = N groups can be produced whether or not the heat treatment is oxidative. Oxygen is thought to be present after oxidation, in the following groups: C = O, CO\textsubscript{2}\textsuperscript{-}, C - OH, C - O - C.

This literature survey has covered papers published both before and during the period of my own work. It has shown that some points require further investigation. Two which could be particularly pertinent are the formation of hydroxyl groups and the distinction between C = C and C = N groups under conditions which lead to the production of high performance carbon fibres.
CHAPTER 5

EXPERIMENTAL

3.1. Introduction.

The acrylic fibre, exclusively used in this study, was Courtelle. It was supplied in a carbon fibre precursor grade, and the various analytical procedures were applied to it. The results, in some cases, were over complicated by the presence of comonomers in Courtelle, which are inherited from the textile usage of the fibre. Consequently, it was necessary to prepare pure homopolymer and subject this to similar analytical procedures. Additionally, infra-red analysis of the fibre proved unsatisfactory and films of Courtelle and polyacrylonitrile were prepared.

Details of the techniques used to prepare carbon fibres are fully described. Care was taken to use similar heat treatment methods for both the chemical analysis and the preparation of carbon fibres. This was thought to be essential because the study was limited in its investigation of the relation between heat treatment conditions and the properties of the final carbon fibres. Variance between heat treatment techniques for chemical analysis and for carbon fibre preparation may invalidate their inter-relation.

The special procedures which were necessary for mechanical testing single high modulus filaments are fully described. These results were recorded on paper tape and a computer program was written to do the calculations and provide statistical data.

3.2 Preparation of precursors.

3.2. 1. Polymerisation of acrylonitrile.

Attempts to remove the inhibitor in acrylonitrile (a hydroquinone derivative) were not entirely successful by the standard methods of washing with sodium hydroxide solution or absorption on silica gel. The inhibitor was removed by distillation, after the addition to the acrylonitrile (150 ml) of concentrated orthophosphoric acid (1.0 ml). The fraction with boiling range 76 - 80°C was collected and stored in a refrigerator at 0 - 5°C.
Several experiments were required to find the most satisfactory conditions for the polymerisation. Emulsion polymerisation produced polymer with very high molecular weight which prevented solution in concentrations greater than 5%. Suspension polymerisation proved better and the procedure of Sorenson (48) was used. A 2L, 3 necked flask was equipped with a stirrer, condenser and nitrogen inlet. The temperature of the flask was regulated in a water bath at 50°C ± 0.1°C. Distilled water (1200 ml), which had been deaerated by boiling for 1/2 hour and the distilled acrylonitrile (88 g) were placed in the flask. About 1/2 hour was allowed for a stream of nitrogen to flush out air in the flask, the contents of which had then equilibrated with the temperature of the bath. A redox initiator was used. Potassium persulphate (1.2 g) was dissolved in water (40 ml) and the solution quickly added to the flask. After thorough mixing, a solution of sodium bisulphite (0.6 g) in water (40 ml) was also added. Polymer was precipitated almost immediately, but 3 hours were allowed for completion. After filtration the products from six syntheses were combined.

The polymer was washed and filtered in water, 50% industrial methylated spirits (IMS) in water and finally IMS. It was dried at 50°C under vacuum to constant weight.

Weight of acrylonitrile 528 g  
Weight of polymer 448 g  
Conversion 85%

Elemental analysis:

<table>
<thead>
<tr>
<th></th>
<th>Theoretical</th>
<th>Found</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C - 67.92%, H - 5.66%, N - 26.42%</td>
<td>C - 66.96%, H - 5.62%, N - 27.06%</td>
</tr>
</tbody>
</table>

Total 99.64%

Determination of molecular weight:

<table>
<thead>
<tr>
<th>Method</th>
<th>Viscometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>Ubbelohde viscometer</td>
</tr>
<tr>
<td>Solvent</td>
<td>N - dimethylformamide</td>
</tr>
<tr>
<td>Temperature</td>
<td>25.0 - 25.4°C</td>
</tr>
</tbody>
</table>
The relation between reduced viscosity \( \eta_\text{SP/C} \) and concentration \( C \) is shown in figure (3). The intrinsic viscosity \( [\eta] \) was found to be 2.39 ± 0.03. The weight average molecular weight \( \overline{M_w} \) was then found from the Mark - Houwink equation (49):

\[
[\eta] = K \overline{M_w}^a
\]

where \( K = 2.37 \times 10^{-4} \) and \( a = 0.75 \) (These constants have been adjusted to give \( \overline{M_w} \) (assuming a Gaussian distribution) and not the viscosity average molecular weight \( \overline{M_v} \)).

\[
\overline{M_w} = 220,000.
\]

3.2. 2. Preparation of films.

Films were cast from solutions (10% w/v) of both polyacrylonitrile and Courtelle in N-dimethylformamide. At least 24 hours were allowed for solution of the polymer. This was accomplished at room temperature because it was found that heating, even to 50°C, caused reaction and discoloration. The solutions were filtered under pressure (100 psi) through a Solvinert 1.5 \( \mu \)m filter.

The solutions were cast onto glass using a film spreader. This is a rectangular container 6" long, 2" wide, 2" deep without a top or bottom. It is placed on a sheet of glass and the solution poured into it. One side of the container can be lifted, by means of adjusting screws, off the glass surface so as to leave an accurately measured and adjustable gap of a few thousandths of an inch. The film spreader is pulled slowly across the glass plate with the lifted side trailing so that a film of the solution is left on the plate.

The gap between blade and glass plate was made 0.010" and the plate was prepared by washing in a 50% Teepol solution in water and then wiping dry. This leaves the plate with a thin covering of surfactant which aids removal of the cast film.

Solvent was allowed to evaporate for 24 hours at room temperature. The films were cut into 3" squares, removed and stored in sealed polyethylene bags to prevent further solvent evaporation.

Prior to infra-red analysis, the films were clamped in a frame which fitted the spectrometer and residual solvent was removed as follows:- immersion in water at 60 - 70°C / 3 hours, immersion in acetone at 15°C / 15 hours, heating at 50°C / 5 hours/under vacuum from a rotary backing pump.

"Film Thickness 0.0005"
Determination by viscometry

Reduced viscosity

\[ \eta_s / C \]

Intrinsic viscosity

\[ [\eta] = 2.39 \pm 0.03 \]

Concentration % C
These treatments did not entirely remove the solvent as the infra-red spectrum of PAN showed a very small carbonyl peak: However this disappeared after only 5 minutes of the inert or oxidative heat treatment at 225°C. Also it was found that the films were sufficiently parallel sided to cause a sinusoidal baseline in the infra-red spectrum. This effect was overcome by adjusting the blade of the film spreader (0.002") down on one side, and up on the other side (0.002"), thus producing a wedge shaped film.

3.2.3 Courtelle fibres.

The fibres used in this work were supplied by Morganite Modmor Ltd., in the form of continuous filament tow containing 10,000 filaments each of 1½ denier. The grade of Courtelle supplied was unspecified, except that it was 'of the type used to make carbon fibres'. Courtaulds, the manufacturers of Courtelle, have not released its exact composition or formation parameters such as degree of stretch. However, Courtelle is stated to be wet spun from solution in 50% sodium thiocyanate in water (50). It consists of 93% acrylonitrile, 6% methylacrylate and 1% dye site. (It is unofficially accepted that this dye site is itaconic acid).

The fibres have an approximately circular cross-section and are supplied coated with finishing agents. These were not removed in the work described here as they are present in a concentration of less than 2% on the weight of the fibres (51).

3.3 Heat treatment procedures.

3.3.1 Low Temperature.

To prevent shrinkage the fibres were tied to a frame. This was made from graphite so that it was not necessary to remove the fibres between the low and high temperature treatments. The dimensions of the frame are shown in figure (5). The tow was wrapped one full turn around the frame and the ends taken up to the posts for securing with two half hitches.

For oxidation the frame was simply placed in a forced draft oven at 225°C. The oven took less than 5 minutes to regain the temperature after the frame was inserted. Extraction facilities
Figure 4  Details of Graphite Frame
were necessary to remove the hydrogen cyanide and ammonia produced during the process.

For inert pyrolysis the frame and fibres were placed in a glass tube (350 ml) through which a current of oxygen free nitrogen (500 ml/min.) was passed. After initially flushing the air out of the tube with a rapid flow of nitrogen, 1 hour was allowed for the removal of oxygen which diffused out of the frame and fibres. In order to place the tube in the oven the nitrogen supply was temporarily stopped and the tube sealed. After the tube was placed in the oven the seals which projected through a hole in the oven roof were removed and the nitrogen supply reconnected. Any air which may have been introduced was removed with a short rapid flow of nitrogen. The temperature inside the tube was checked with a thermocouple passed down the nitrogen inlet. It was found that the lag in temperature between the inside and outside of the tube was negligible.

3.3. 2. Carbonisation.

A number of trial experiments showed that it was necessary to carefully control the rate of temperature rise in the furnace, particularly during the initial stages, i.e. up to 500°C. If the rate of temperature rise was too rapid, severe degradation occurred. A temperature programmer was necessary to achieve linearity in the rate of temperature rise. A diagram of the furnace used is shown in figure (5). The temperature inside the alumina tube was measured by two Pt/Pt 10% Rh thermocouples. One was connected directly to a chart recorder or potentiometer. The other operated the furnace controller through a Eurotherm JA - 06 programmer. The thermocouples were protected from the atmosphere in the furnace by a recrystallised alumina sheath. Thus there was a considerable lag in temperature between the environment of the furnace elements and the control thermocouple. This caused large fluctuations in temperature when the equipment was initially switched on. However, at the slow rates of heating employed, by the time the temperature reached 200°C the fluctuations had ceased.

The ends of the furnace tube were cooled to permit the use of synthetic rubber gas tight seals. A flow of oxygen-free nitrogen
was maintained in the tube and monitored before entry and after exit. A difference between these readings indicated a leak. This was important because hydrogen cyanide was present in the evolved gases. The flow rate of nitrogen was set at 500 ml/min, corresponding to 25 cm/s/min in the tube.

During the early experiments it was found that a white powder coated the fibres after carbonisation and bonded them together. The source of this powder was not found, but the problem was overcome by placing the frame between graphite plates.

Once suitable carbonisation conditions were found, they were not varied in any of the preparations. These conditions were:

- Gas flow: 500 ml/min
- Rate of temperature rise: 60°C/hour to 1000°C
  - 135°C/hour to final temperature
- Hold at max. temperature: ½ hour
- Cooling period: 12 hours

3.4. Analytical methods.

3.4.1. Yield.

The graphite frame was washed in hot water and dried at 110°C for 1 hour. It was stored in a dessicator. Immediately prior to heat treatment the frame was weighed. The fibres were wound on and weighed. Immediately after oxidation or inert heat treatment and carbonisation, the frame and fibres were again weighed.

The weight of the fibres was adjusted for the amount of finishing agent applied, which had been determined during the course of other work (51).

3.4.2. Elemental Analysis.

A Perkin Elmer 420 Elemental Analyser was used to determine carbon, hydrogen and nitrogen contents. Oxygen content was found by difference.

Early results showed considerable scatter in the analyses from any one type of fibre. It was found that this was due to absorbed moisture; a result of the heat treatments was that the polymer becomes increasingly hygroscopic. The following procedure
was then adopted: The fibres were cut into short lengths ($< 1 \text{ mm}$) using scissors. They were then placed in an open specimen tube and heated at $150^\circ\text{C}$ for 10 minutes. The tube was sealed before cooling. Although it was realised that the fibres probably still contained absorbed water, more vigorous treatment was not considered worthwhile, because the fibres had to be weighed before elemental analysis during which they could absorb more water. The weighing, (to 6 places) was carried out as quickly as possible. The result used was the mean of at least 3 analyses on each type of fibre.

A measure of the success of the procedure to remove absorbed water may be obtained from the oxygen contents of Courtelle fibres heated under oxygen-free nitrogen. These fibres did show an increase in their oxygen contents, but the mean increase was only $1.3\%$. This seems sufficiently small so as not to effect the conclusions.

3.4. 3. Infra-red analysis.

3.4.3. 1. Equipment.

A Perkin Elmer 457, diffraction grating instrument was used, (scanning range, $4000 - 250 \text{ cm}^{-1}$). All spectra were recorded using the normal slit opening and medium scanning speed, i.e. 10 minutes for a complete scan.

3.4.3. 2. Spectra from film.

The films, which were prepared as previously described, were heated for a period, cooled and the spectra obtained. Further spectra were obtained after additional heating periods. As a result, the time scale was probably artificially lengthened because the film would have been at temperatures less than the maximum (during heating and cooling) for significant periods of time. It was not considered worthwhile investigating this further, but it should be noted when comparing the spectra presented in this thesis, with others at the same apparent period of heating.

3.4.3. 3. Spectra from fibres.

All fibres were heated continuously for a particular period, and the spectra obtained. A difference in the measured rates of
reaction between fibres and film would therefore be expected, even in inert pyrolysis, as a result of the different methods of heating fibre and film.

The spectra of the fibres were obtained by the potassium bromide disc technique, in the following manner: The fibres were cut into short lengths ( < 1 m.m.) and mixed with potassium bromide in a vibratory mill for 10 minutes (0.005g fibre/0.3g potassium bromide. A disc (dia. 8 mm) was formed, at a pressure of 10 tons/sq.in. for 1 minute.

3.5. Mechanical testing methods.

3.5. 1. Preparation of fibres.

For both mechanical testing and diameter measurement the fibres were bonded across holes and slots in a piece of card (figure 6). For diameter measurement the hole was 4 m.m. in diameter, and for mechanical testing the length of the slot was 5 cm. The arrangement meant that fibre diameter was measured a few centimeters from the section which was to be tested, and it was assumed that the diameter did not change significantly over this distance. A preliminary examination of Courtelle and carbon fibres showed that this was a reasonable assumption.

For mechanical testing it was found to be extremely important that the filament was perfectly aligned on the card, especially for carbon fibres which failed prematurely during testing if the filament was even slightly misaligned. A carbon fibre manufacturer recommended the use of 'Durofix' adhesive. This is a simple polymer/solvent adhesive and it was found that distortion of the filament occurred as the solvent evaporated and the adhesive shrank and hardened. Consequently a non-shrinking adhesive was used, a fast curing epoxide. The manner in which it was used will be evident from figure (6). The main points are that the filament is held taught across the gauge length between the 'Sellotape' strips, while the liquid adhesive is applied up to the edge of the card. The adhesive completely surrounds the filament and provides a firm, even anchorage. The grips of the testing machine are applied over the sellotape, not adhesive, so that the card remains vertical.
FIGURE 6  THE TEST CARD FOR MECHANICAL TESTS

- Hole for Diameter Measurement
- Mounting Card
- Sellotape Strip
- Epoxy Adhesive
- Filament

Gauge Length 5 cm
3.5. 2. Fibre diameter.

The equipment used was a Watson Image Shearing Eyepiece (WISE) which was fitted to an ordinary optical microscope with a movable stage. The total magnification was 400X.

The WISE gives an arbitrary number which is a function of the diameter of the fibre. It is therefore necessary to calibrate the WISE using standard wires of similar diameters to the fibres. Four standard wires with diameters from 8 to 20 μm were obtained from the Royal Aircraft Establishment. Ten readings were taken from each standard wire and a graph was drawn of WISE reading vs diameter. The best straight line through all the points was determined by the method of least squares. The diameter of each fibre was calculated from the WISE reading for the fibre and the slope and intercept of the best straight calibration line. This calculation was done by a computer together with other mechanical testing data.

Sometimes, particularly with Courtelle fibres, irregularities and imperfections could be seen in the fibre when making a WISE reading. In these cases care was necessary in finding a representative diameter.

An attempt was made to determine the extent of 'human error' while measuring the diameter. Twenty readings were made at the same place on an approximately 8 μm fibre. The mean was found and used to calculate diameter (8.01 μm). The highest and lowest readings were used also to calculate the diameters. It was thus found that the measured diameter from a single reading could range from 8.11 to 7.83 μm i.e. the measurement could be in error by ± 0.14 μm. This is less than the probable error in the measurement of the standard wire and was considered satisfactory.

The diameter of the standard wires from RAE were measured by weighing a long length. They were not supplied with details of the level of uncertainty in the measurement. We obtained a single standard wire from the National Physical Laboratory. The diameter of this had been measured using a mechanical device where readings were amplified using optical levers. The diameter was found to be 10.5 μm and the uncertainty in the measurement was ± 0.2 μm.
It was later found that when the NPL standard wire was used to calculate fibre diameter, the strengths and moduli of the fibres was less than expected. By measuring the NPL standard wire with the WISE, using RAE standards, it was found that the RAE wires gave figures for fibre diameter about 0.5μm less than the NPL standard wire. This was causing a large apparent difference in the mechanical properties of the fibres. Subsequently it was discovered that industry and Government were aware of this difference and that the Ministry of Technology specifications for testing carbon fibres (53) recommend the use of RAE standard wires. All the mechanical test data in this thesis were calculated using the RAE standard wires.

3.5. 5. Tensile strength, modulus and elongation to failure.

An Instron Tensile Testing Machine, Model TM-N, was used. A card carrying a single filament with 5 cm gauge length was fixed in the grips so that the filament was in exact alignment with the direction of pull. The card was cut leaving the filament free. The results were presented in the form of a curve of load vs extension from which all parameters can be calculated. Additionally a data log recorded the test data on paper tape which was then processed by computer. Sample outputs for Courtelle and carbon fibres are shown in figures (7) and (8). The details of conditions of testing were invariant for all fibres given heat treatments at 225°C and similarly for carbon fibres. These conditions can be obtained from the figures.
**Figure 7**

**Instron Model Twaron / Data System 2415**

**Fibre Tensile Tests**

<table>
<thead>
<tr>
<th>Figure Type</th>
<th>Courtelle Fibres 1/16 (Heated in Nitrogen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Tests</td>
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</tr>
<tr>
<td>Load Cell</td>
<td>A</td>
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<tr>
<td>Full Scale Reflection</td>
<td>0.1 Newtons</td>
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<td>Crosshead Speed</td>
<td>1000 micros/min</td>
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<tr>
<td>Chart Speed</td>
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**Standard Deviation** 0.02 0.21 0.56 35.9

**Range of Universal Mean** 7.30 1.1 2.402 220.2

**Mean** 7.67 1.23 2.723 243.7
CHAPTER 4.

RESULTS.

4.1. Introduction.

In this chapter the results of the work are presented. There are five principal divisions: carbon yield, mechanical properties, chemical analysis, qualitative and quantitative infra-red analysis. It has been necessary to include individual introductions and summaries for some of the divisions due to their diversity.

The carbon yield and mechanical property results clearly illustrate the importance of oxidising Courtelle fibres prior to carbonisation, thus defining the objective for the analytical techniques. Additionally, they exemplify oxidation and carbonisation conditions which are capable of producing high performance carbon fibres. This ensures the pertinence of the following analytical work.

4.2. Carbon yield.

Whether or not Courtelle fibres are oxidised, has a profound effect on the final carbon yield. Figure (9) illustrates the relation between carbon yield, at 1400°C, and the period of low temperature (225°C) heat treatment in both air and oxygen-free nitrogen. Only short periods of oxidation are necessary to greatly improve the carbon yield which is a maximum after 3 hours. The period of inert pyrolysis has little effect on the carbon yield.

One of the functions of oxidation would therefore appear to be stabilisation of the molecular structure so as to inhibit the formation of low molecular weight carbon compounds. It is surprising then that there is a maximum in the yield/time curve for oxidised fibres; once the stability has been introduced, it should not be easy to remove it unless the thermal conditions are changed. Hence it appears that the fall in yield is due to the formation of groups which promote the removal of carbon containing molecules, such as CO, CO₂ or HCN, during either oxidation or carbonisation.
FIGURE 9 - CARBON YIELD (1400°C)
EFFECT OF INITIAL HEATING AT 225°C IN

- ○ AIR  △ NITROGEN

CARBON YIELD %

0  10  20  30  40  50  60  70
0  2  4  6  8  10  12  14

HOURS
The carbon yield after oxidation has been calculated from the weight changes and the elemental analyses. The ordinate in figure (10) represents the weight of carbon remaining relative to 100g of the precursor. Oxidation causes a steady fall in the carbon content and significant quantities are removed. Also shown in the figure is the weight of carbon remaining after carbonisation relative to 100g of precursor.

To determine whether the fall in final carbon yield can be assigned to the removal of carbon during oxidation, the carbon loss specifically during carbonisation has been plotted against oxidation time, figure (11). The carbon loss reaches a minimum at 3-4 hours oxidation time but then increases slightly indicating that carbon is being removed by a process independent of that during oxidation. But because the rate is reduced, the conclusion is that the fall in carbon yield after carbonisation is due to carbon loss during both oxidation and carbonisation.

4.3. Mechanical properties.


Mechanical testing gave results for modulus, elongation to failure and diameter. Because of the changes in chemical structure which occur with the heat treatment, it was considered inappropriate to examine results after more than two hours of treatment. The validity of this will be discussed later.

The stress/strain curve is 'S' shaped and it is possible to define three modulii. Figure (12). The slope of the curve at zero stress gives the initial modulus. The following minimum in modulus is called the second modulus while the modulus immediately before failure is the third modulus.

During heat treatment at 225°C in air, the initial modulus of Courtelle fibres increases marginally over the first 1/3 hour. Figure (13). The modulus then decreases to be very similar after 2 hours to the initial value. The second modulus also increases slightly and then decreases. But the third modulus decreases by more than 50% in the first quarter of an hour of the heat treatment.
OXIDATION AND CARBONISATION RELATIVE TO PRECURSOR

MOLES CARBON/100 g PRECURSOR

OXIDATION

OXIDATION AND CARBONISATION

C = CARBON CONTENT (%) FROM ELEMENTAL ANALYSIS

x = DECREASE IN WEIGHT OF FIBRES ON OXIDATION FOR TIME t

T = TIME (HOURS)
FIGURE 11  CARBON LOSS DURING CARBONISATION RELATIVE TO THE PERIOD OF INITIAL HEAT TREATMENT

CARBON LOSS
MOLE / 100 g PRECURSOR

TIME (HOURS)
FIGURE 12  RELATION BETWEEN STRESS AND STRAIN OF COURTELLE FIBRES, OXIDISED COURTELLE FIBRES AND CARBON FIBRES
In contrast, inert pyrolysis at 225°C causes a small increase in initial modulus which does not tail off, while the second modulus shows a steady and definite increase. Figure (14). The most striking point is that the third modulus decreases very much more slowly than during oxidation.

There is also a marked difference in behaviour between oxidised and inert pyrolysed fibres in their elongation to failure. Figure (15). The oxidised fibres vary little, while inert pyrolised fibres decrease by over 25% of their original value after two hours of heating.

4.5. 2. Carbon fibres.

Carbon fibres behave in an essentially elastic manner when under stress: extensions of about 1% are allowed before brittle fracture.

Preliminary experiments showed that a carbonisation technique which produced high performance carbon fibres was to heat the fibres from room temperature to 1000°C, at a linear rate over 17 hours, then to 1400°C in 3 hours, hold at 1400°C for 1/2 hour and finally cool to room temperature over about 12 hours. With adequately oxidised fibres, this technique produced carbon fibres with mechanical properties marginally better than the minimum specifications required by the Ministry of Technology for type II fibres (53). The above method of carbonisation was not varied during any of the results.

If Courtelle fibres were given no heat treatment at all prior to carbonisation, they shrank and degraded to such an extent that they were virtually unidentifiable. An oxidation time of only 15 minutes at 225°C in air allowed carbon fibres to be produced. However, oxidation times of 1/2 - 1 hour gave fibres with maximum mechanical properties: there was no further improvement even after 20 hours at 225°C. Figures (16, 17). The 20 hour figures are not shown.

With an initial inert pyrolysis, a minimum of 5 hours at 225°C was necessary before the degradation during carbonisation was sufficiently reduced to obtain identifiable fibres, but these had inferior mechanical properties. Although it appears in figures (16, 17) that the tensile strength and modulus of fibres given oxidations and inert pyrolyses may coincide at longer periods of heating, the 20 hour figures showed slightly more separation than the 15 hour figures.
FIGURE 15  COURTELLE FIBRES DURING HEAT TREATMENT AT 225°C

ELONGATION TO FAILURE %

AIR

NITROGEN

HOURS
FIGURE 16  CARBON FIBRES (1400°C)

EFFECT OF PRECURSOR HEAT TREATMENT AT 225°C

TENSILE STRENGTH (GN/m²)

- • AIR
- • NITROGEN

MINIMUM SPECIFICATION

HOURS
FIGURE 17 CARBON FIBRES (1400°C)

EFFECT OF PRECURSOR HEAT TREATMENT AT 225°C

TENSILE MODULUS GPa/m²

○ AIR
□ NITROGEN

SPECIFICATION LIMITS

0 5 10 15
HOURS
4.4. Elemental analysis.

The exact chemical formula of Courtelle has not been cited, but Siclari (50) states that it contains 6% methyl acrylate. The dye site in the fibre should be present in concentration not greater than 1%. If then Courtelle is assumed to contain acrylonitrile (94%) and methyl acrylate (6%), neglecting the dye site, the calculated carbon, hydrogen, nitrogen and oxygen contents agree well with those found, (Table 4.1.).

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This good agreement not only provides support for the assumed formula of Courtelle, but indicates that the analysis technique employed is capable of giving a reasonably accurate figure for oxygen content, at least before the fibres are heat treated.

Figures (18 and 19) show the results of elemental analysis in terms of percentage by weight of element. During heat treatment in air there is a decline in the carbon, hydrogen and nitrogen contents. This could be due, at least partly, to the inclusion of oxygen, which is clear. The fall in carbon, hydrogen and nitrogen contents during inert pyrolysis is much less. Even so, the oxygen content increases slightly. This must be due either to oxygen in the nitrogen supply or to the absorption of water after heat treatment and before the analysis. However, the effect was considered to be sufficiently small so as not to influence the conclusions.

It is probably more meaningful to examine the ratio of elements in the repeat unit during the heat treatments. This ignores the removal of degradation products which will lead to errors in the calculated ratios unless the degradation process is exclusively depolymerisation
FIGURE 18  ELEMENTAL ANALYSIS OF
COURTELLE FIBRES DURING HEAT
TREATMENT AT 225°C IN AIR

PERCENT

C

N

O

H

HOURS
Figure 19: Elemental analysis of Courtaulds fibres during heat treatment at 225°C in nitrogen.
because in this event, the ratios of elements present and lost would be the same.

The empirical formula of acrylonitrile is $\text{C}_2\text{H}_3\text{N}$. It can be seen Figure (20) that the $\text{H}/3\text{C}$ ratio is slightly greater than 3. This is due to the methyl group in the methyl acrylate comonomer of Courtelle. The comonomer is also responsible for the $\text{N}/3\text{C}$ ratio being less than 1.0.

Comparing oxidation Figure (20) and inert pyrolysis Figure (21), there are two important results. The nitrogen to carbon ratio is invariant. The number of hydrogen atoms in the repeat unit falls during oxidation from 3 to 2 over 7 hours while it is constant during inert pyrolysis. This confirms what would be expected: that the oxidation reactions involve the hydrogen atoms. Hence it would be expected that oxygen is introduced on to the carbon backbone of the polymer. For this reason the oxygen to carbon ratio is not the best way of observing the introduction of oxygen: this ratio includes oxygen in the comonomer which is in the ester side group and not on the backbone.

Figure (22) shows how oxygen is introduced to the backbone. This was calculated from oxygen contents after deduction of oxygen present in the comonomer. Obviously, errors could arise from removal of comonomer oxygen in the degradation. However, no such degradation reactions have been reported and they have been neglected.

It can be seen that during the first hour of oxidation the number of oxygen atoms increases rapidly to one per 6 repeat units. A further 9 hours oxidation is then necessary before there is 1 oxygen atom per 3 repeat units. The important point is that the shape of this curve corresponds very well with that of the increase with oxidation time of carbon fibre modulus. Therefore a relation between carbon fibre modulus and oxygen atoms on the backbone seems possible. This point will be discussed later in the thesis.
Figure 26: Elemental ratios in Courvelle fibres during heat treatment at 225°C in air.
FIGURE 21  ELEMENTAL RATIOS IN COURTEILLE FIBRES DURING HEAT TREATMENT AT 225°C IN NITROGEN

RATIO

H/3C

N/3C

O/3C

HOURS
Figure 2.4: The introduction of oxygen to the carbon backbone of Courtelle fibres heated at 225°C in air.

Repeat units/oxygen atom

Hours

Oxidation process over time.
### 4.5. Qualitative Analysis by Infra-Red Spectroscopy

#### 4.5.1. Introduction

Initially attempts were made to obtain infra-red spectra from the fibres using the attenuated total reflectance technique. This relies upon good contact between the material being examined and a thorium bromide crystal through which the radiation is passed. Poor absorption caused unreliable results and the method was not considered further.

Better results were obtained by the KBr disc technique. Courtelle fibres were cut finely with scissors and ground in a vibratory mill before being incorporated in the disc. However, water in the KBr obscured the spectrum at $3500 - 3000 \text{ cm}^{-1}$. This problem was not satisfactorily overcome, either by attempts to remove the water, or by placing another KBr disc in the reference beam.

Courtelle film could be dried thoroughly, and good spectra were obtained. It will be shown that except for the region $3500 - 3000 \text{ cm}^{-1}$ there is no qualitative difference in the spectra from Courtelle fibres and film.

Unfortunately, the comonomer in Courtelle contains carbon/oxygen groups so that the possible formation of these during the oxidation reactions is obscured. Consequently, film of polyacrylonitrile homopolymer was used and it will be shown that the general features of the reactions in PAN and Courtelle, as monitored by infra-red spectroscopy, are the same.

#### 4.5.2. PAN film during oxidation

**The spectrum of the precursor.**

Peaks which are sufficiently prominent for definite identification are as follows (24) figure (23a).

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<tbody>
<tr>
<td>2930</td>
<td>$\text{CH}_2$</td>
<td>antisymmetric stretch (m)</td>
</tr>
<tr>
<td>2860</td>
<td>$\text{CH}_2$</td>
<td>symmetric stretch (w)</td>
</tr>
<tr>
<td>2240</td>
<td>CN</td>
<td>stretch (s)</td>
</tr>
<tr>
<td>1450</td>
<td>$\text{CH}_2$</td>
<td>bend (s)</td>
</tr>
<tr>
<td>1355</td>
<td>$\text{CH}_2$</td>
<td>wag (m)</td>
</tr>
</tbody>
</table>
FIGURE 23  PAN FILM DURING HEAT TREATMENT
IN AIR AT 225°C FOR (a) NIL (b) 4 HOURS (c) 10 HOURS (d) 47 HOURS
Changes in the spectrum during oxidation.

Oxidation was carried out by heating the films in air at 225°C.

Region 4000 - 2500 cm\(^{-1}\):

There is evidence for the formation of hydroxyl groups during the oxidation: a strong, broad absorption develops with a flat topped peak at 3350 - 3230 cm\(^{-1}\), figure (23). Additionally, the shape of this peak is indicative of hydrogen bonded hydroxyl groups in polymers (54, 55). For instance, polyvinyl alcohol, which is known to be strongly hydrogen bonded, produces a very similar absorption with a peak at 3350 cm\(^{-1}\) (56).

Another group which could also be causing the absorption is N - H in amines, for which the stretching frequency occurs over a similar range to the O - H stretching frequency. For this reason it is often not possible to distinguish between hydroxyl and amine groups. However, hydrogen bonding effects are reduced in amines and as there is obviously much hydrogen bonding present, it seems likely that at least hydroxyl groups are formed.

It is also quite clear from the decrease in intensity of the CH\(_2\) peak at 2930 cm\(^{-1}\), that these groups take part in the reactions. After extended oxidation periods, (40 hours at 225°C), virtually all the CH\(_2\) groups react.

Region 2500 - 2000 cm\(^{-1}\).

There are two absorptions of interest in this region. The C = N stretch at 2240 cm\(^{-1}\) in the precursor steadily decreases during the reactions. An absorption at 2180 cm\(^{-1}\), which is sometimes just visible in spectra of the precursor, steadily increases during the reactions. Almost all publications attempting an explanation of this peak, assign it to a C = N group taking part in conjugation. Deane assigns it to a quarternary amine group RNH\(_3\)\(^+\), mainly on the evidence that the peak shifts on deuteration (33).

There are other possible assignments for the 2180 cm\(^{-1}\) peak. It could be a triple bond of the type R\(_1\) - C = C - R\(_2\) or an isocyanide R - N=C=O. It is not easy to conceive how these groups could be formed during the oxidation, and the literature search did not find a paper which described such reactions. It will be seen that there is evidence for the formation of C = C bonds during oxidation and with the present evidence, it seems most probable that the 2180 cm\(^{-1}\) peak is due to \(\text{C}=\text{C}\) groups such as \(-\text{C} \equiv \text{C} \equiv \text{N}\), in which conjugation can occur.
Region 1800 - 1400 cm$^{-1}$.

There is clear evidence for the formation of carbonyl groups. A small peak at 1710 cm$^{-1}$ develops during the oxidation. It is of low intensity and unsuitable for quantitative measurements because it is rapidly engulfed by broadening of the peak at 1580 cm$^{-1}$.

Assignments of the other two absorptions which develop in this region are more difficult. A low intensity absorption occurs at 1650 cm$^{-1}$. Several authors have assigned this to another carbonyl group (16, 27, 30, 32, 36, 37), although this is generally considered an absolute minimum for a carbonyl absorption, which usually occurs in the range 1870 - 1680 cm$^{-1}$ (57). However, the unconjugated C = C bond absorbs in the region 1670 - 1615 cm$^{-1}$ whereas the conjugated C = C bond absorbs outside this region, i.e. 1600 - 1590 cm$^{-1}$. (57). A C = C bond would also be expected to produce an intense absorption at 1000 - 800 cm$^{-1}$ and this does occur. Unfortunately both conjugated and unconjugated C = N groups absorb in similar regions to the C = C bonds (1690 - 1640 cm$^{-1}$ and 1660 - 1480 cm$^{-1}$ respectively). It is curious that no author has assigned this 1650 cm$^{-1}$ peak to C = N although one has assigned it C = C (33). It would appear that the peak could be due to either or both unconjugated C = C or C = N, but the possibility of C = O cannot be excluded.

In contrast to the two previous low intensity peaks, a very intense peak develops at 1580 cm$^{-1}$. It seems very probable that this peak is due to C = C and/or C = N groups, and most authors make this assignment.

This region provides clear evidence for the formation of double bonds, C = O, C = C and/or C = N. It seems likely that C = C groups are present in both conjugated and unconjugated states.

Region 1400 - 1000 cm$^{-1}$.

Little new information can be obtained from this region. The original polymer has an absorption at 1355 cm$^{-1}$, assigned to the CH$_2$ wagging vibration. This CH$_2$ peak behaves differently during the oxidation reactions from the other CH$_2$ peaks. Those at 1450 cm$^{-1}$ (bend) and 2930 cm$^{-1}$ (antisymmetric stretch) decrease markedly. The 1355 cm$^{-1}$ peak does not, it merely shifts to 1370 cm$^{-1}$ while a very large background absorption grows. It seems likely that a new group is formed during the reactions which absorbs at 1370 cm$^{-1}$. The OH
deformation vibration usually occurs in this region (1400 - 1300 cm\(^{-1}\)) while other possibilities (C - O and C - N stretch) usually occur below 1360 cm\(^{-1}\). This then provides some supporting evidence, tenuous though it is, to the formation of OH groups.

Region 1000 - 400 cm\(^{-1}\).

This is characterised by the formation of a sharp, medium intensity absorption at 800 cm\(^{-1}\). Unconjugated C = C groups carrying H atoms produce such absorptions between 1000 - 800 cm\(^{-1}\) due to the C - H rocking vibration. The actual wavelength of the absorption is specific to the atomic configuration around the group. If the absorption at 800 cm\(^{-1}\) can be assigned to HC = C then it must be due to \(R_1\) HC = C \(R_2\) \(R_3\) as all other configurations absorb between 1000 and 830 cm\(^{-1}\) (58). This configuration could be formed if double bonds were produced on the main chain.

There are other possibilities for the assignment of the absorption at 800 cm\(^{-1}\). Pyrimidines produce an absorption between 825 - 775 cm\(^{-1}\) due to a ring vibration (59).
However, this vibration is likely to be restrained in a polymeric system. The epoxide bond can also absorb in this region but its absorptions tend to be very variable in both frequency and intensity. It has been suggested that a peak at 1250 cm\(^{-1}\) is the only reliable characteristic of the epoxide bond (60).

The assignment due to HC = C seems therefore, to be most probably correct.

**Summary of results.**

1. There is strong evidence for the formation of OH and/or NH groups during the thermal oxidation reactions.
2. The CH\(_2\) groups react and eventually disappear.
3. Nitrile groups react but some remain even after extensive oxidation periods.
4. A new type of nitrile group is formed. This is likely to be conjugated with an unsaturated group such as C = C, C = N or C = O. The evidence for this is fairly strong, but one author, Deane, has strong evidence against the formation of a conjugated nitrile group (33). (Deane's paper has not been published, even though it was written several years ago).
5. Carbonyl groups are formed.
6. Either conjugated or unconjugated C = C groups are formed. There is fairly strong evidence for this.
7. It is not possible to be definite about the formation of C = N groups because they absorb in the same region as C = C groups, for which there is fairly strong evidence.

**4.5. 3. Courtelle film during oxidation.**

Courtelle films were oxidised under exactly the same conditions as PAN films.

The spectra produced, figure (24), show very similar features to those of PAN film. There are two exceptions. The large C = O absorption in Courtelle obscures the possible formation of these groups during the oxidation. However, in PAN, the carbonyl groups are almost certainly produced on the carbon backbone as a result of the oxidation of C - H\(_2\) groups. Because the carbon backbone of
FIGURE 24  COURTELLE FILM DURING HEAT TREATMENT IN AIR AT 225°C FOR (a) NIL (b) 1 HOUR  (c) 4 HOURS  (d) 16 HOURS
both Courtelle and PAN are the same, the formation of C = O groups on Courtelle is very likely. The second difference between the spectra of PAN and Courtelle is that the reactions appear to occur faster in Courtelle than PAN. Possible reasons for this will be discussed in the section on quantitative analysis.

These results show that it is reasonable to assume that the comonomers in Courtelle do not affect the main features of the reaction products when the polymer is in film form.

4.5. 4. Courtelle fibres during Oxidation.

The spectra obtained by the KBr disc technique from fibres, figure (25), show very similar characteristics to the spectra from film. The exception is the region 3500 - 3000 cm^-1 which contains an absorption due to water in the KBr. Nevertheless after several hours heating in air at 225°C the spectra obtained from the fibres are very similar to that from film.

There appears to be a difference in the rate of the reactions: the fibres react faster than film. This could be expected since the fibres will have a greater surface area allowing easier access of oxygen.

These results, and those of the previous section, show that the use of spectra from PAN film to describe the reaction products after thermal oxidation of Courtelle fibres, is valid. The difference found in the rates of the reactions show that the mechanisms are probably different.

4.5. 5. Inert pyrolysis of PAN film.

When the spectra are compared from PAN films heated at 225°C in air and nitrogen some differences are obvious, figure (26).

Firstly there is a relatively sharp absorption at 3200 cm^-1 in the inert pyrolysed film. This can be due to NH only. This confirms that the absorption at 3200 - 3330 cm^-1 in the oxidised film contains contributions from both NH and OH groups, the latter absorbing at the greater wavenumber. The absorption at 1350 cm^-1 in the oxidised film was tentatively assigned to the hydroxyl group, section 4.5.2. However, this absorption is present in the inert pyrolysed film and hence it cannot be due to hydroxyl groups.

Absorption at 1710 cm^-1 is absent in the inert pyrolysed film which confirms its assignment to carbonyl groups.
FIGURE 25  COURTELLÉ FIBRES DURING HEAT TREATMENT IN AIR AT 225°C FOR
(a) NIL  (b) ¼ HOUR  (c) 1 HOUR  (d) 5 HOURS
FIGURE 26 COMPARISON OF PAN FILM AFTER HEAT TREATMENT AT 225°C FOR 9 HOURS IN (a) AIR (b) NITROGEN
In inert pyrolysis, two absorptions occur (1610 and 1570 cm\(^{-1}\)) in contrast to the single absorption at 1590 cm\(^{-1}\) after oxidation. Absorptions in this area could be due to C = C, C = N or N - H. The absorption at 800 cm\(^{-1}\) during oxidation, does not occur during inert pyrolysis except after long periods. This is direct evidence that C = C bonds do not figure in the principle reactions when oxidation is omitted. Additional evidence is that absorption at 1655 cm\(^{-1}\) is absent after inert pyrolysis.

It is not possible to distinguish between absorptions due to C = N and N - H. Consequently, there is no clear evidence for the formation of C = N bonds, which are essential for ladder polymer formation. There is other, albeit circumstantial, evidence and this will be discussed in the next chapter.

An interesting phenomenon is that the CH\(_2\) peak at 2930 cm\(^{-1}\) actually increases in area during inert pyrolysis. Deane has also found this (33). It is not conceivable that CH\(_2\) groups are being produced, or that the film is becoming thicker. Perhaps the effect is associated with a change in physical shape of the film, which initially appears opaque but becomes quite clear (and coloured), during the reactions. Causes of this effect have not been investigated.

4.5. 6. Reactions of PAN with nitrogen.

It was confirmed that nitrogen was indeed an inert atmosphere by comparing the spectra of film heated in nitrogen and argon. No differences were found.

4.5. 7. Conclusions.

It has been shown that the principal reactions occurring during the thermal treatment are qualitatively similar in both PAN and Courtelle. There probably are differences in the rates of particular reactions. Some reactions occur in both oxidative and inert atmospheres. These are:

(a) the removal of C = N groups,
(b) the introduction of conjugation to some remaining C = N groups,
(c) the formation of hydrogen bonded N - H groups,
(d) the possible formation of C = N groups.

The following observations are specific to the case of inert pyrolysis:

(a) The CH\(_2\) groups do not react.
(b) C = C groups are formed only after extended heating periods.
FIGURE 27 SUMMARY OF REACTIONS DURING THERMAL TREATMENT OF COURTELLE FIBRES

HEAT TREATMENT

C = N REACT
N-H FORMED
CONJUGATED C = N FORMED
POSSIBLY C = N FORMED

OXIDATIVE INERT

O-H FORMED
C=O FORMED
C=C FORMED
CH$_2$ REACT
AROMATICS FORMED

CH$_2$ NO REACTION
C=C FORMED AFTER LONG PERIODS
The following observations are specific to the case of thermal oxidation:

(a) OH groups are formed
(b) C = O groups are formed
(c) C = C groups are formed
(d) The CH₂ groups react, eventually to completion.

These conclusions are shown diagramatically in figure (27).


4.6. 1. Introduction.

While infra-red spectroscopy is generally used qualitatively, it is possible under certain conditions to make quantitative measurements. It is reasonable to expect that the amount of energy absorption will depend on the amount of material responsible for the absorption. This latter quantity can be expressed as the product of concentration and the path length of the radiation in the sample. This assumes that all radiation incident on the sample material, either passes through, or is absorbed. The alternative is that it is reflected and therefore does not reach the detector, and this causes false 'absorptions'. In practice, the energy absorbed is recorded as a peak on graph paper. The area of the peak represents the quantity of absorbed energy. To find the area it is necessary to draw the base-line, i.e. the trace which would have been drawn if no energy absorption had occurred. This is possible only when the peak is not close to any other peak and is narrow. However, if these conditions are met there is an approximately constant relation between peak area and height so that the latter may be used to measure the energy absorbed. Although the polyacrylonitrile spectrum contains several clear, sharp peaks, after the initial stages of the heat treatment most peaks broaden and some overlap. The only peaks suitable for quantitative measurements are due to nitrile groups, (2180 - 2240 cm⁻¹).

The relation between energy absorbed and the amount of absorbing material is expressed by the Beer-Lambert Law, which can be written

\[ A = E C d \]

where:
- \( A \) = energy absorbed, measured as optical density.
- \( C \) = concentration of absorbing species.
- \( d \) = path length through sample.
- \( E \) = proportionality constant, called absorptivity or extinction coefficient.
It is usually unwise to use this equation directly to measure the concentration of an absorbing species because the path length can be very difficult to measure with sufficient accuracy and $E$ can vary depending on the chemical environment. Concentrations are often measured by comparing the absorption ($A_2$) at the unknown concentration ($C_2$) with the absorption ($A_1$) at a known concentration ($C_1$) and assuming the path length and extinction coefficient are invariant.

\[ A_1 = E \frac{C_1}{d} \]

and

\[ A_2 = E \frac{C_2}{d} \]

\[ C_2 = \frac{A_2}{A_1} C_1 \]

4.6.2. Correlation between fibres and film.

It is generally not possible to make quantitative measurements from the spectrum of fibres. This is due to false absorptions caused by reflection of radiation from the curved surface of the fibres. This problem is overcome if spectra are obtained from film. In order to make quantitative measurements on the fibres, it is therefore necessary to find a method of correlating the spectra from fibres and film. This can be done only under the assumption that the specific thermal reactions are not a function of the physical form of the polymer. The qualitative analysis results in the previous section substantiate this assumption. Also, the correlation can only be made using a reference parameter independent of the concentration or absorption to be measured. In this case such a parameter is the ratio of peaks at $2180 \text{ cm}^{-1}$ and $2240 \text{ cm}^{-1}$. This ratio, $R$, starts infinitely small and becomes larger during the reactions. The value of $R$ at a particular time is used to identify the overall extent of reaction. Thus if the spectra from fibres and film after different periods of heat treatment have the same $R$ value, the extent of the nitrile reactions in the two materials is taken to be the same. Then, the spectrum from the film can be used for quantitative measurements which can be applied directly to the fibres.
Justification for this method of correlation can be expressed mathematically, using the same assumptions. Suppose, in the spectrum of fibres which had been heated for $t$ hours, the CN (2180) peak had absorbance $A_1$ and the CN (2240) peak $A_2$.

Then $A_1 = E_1 C_1 d_1$ and $A_2 = E_2 C_2 d_1$

$\therefore$ the ratio $\frac{R_1}{R_2} = \frac{A_1}{A_2} = \frac{E_1 C_1}{E_2 C_2}$

For film after heating for $T$ hours at the same temperature, let the respective absorbancies be $A_3$ and $A_4$.

$A_3 = E_1 C_3 d_2$ and $A_4 = E_2 C_4 d_2$

Then $R_2 = \frac{A_3}{A_4} = \frac{E_1 C_3}{E_2 C_4}$

If $R_1$ and $R_2$ are equal, then

$$\frac{E_1 C_3}{E_2 C_4} = \frac{E_1 C_1}{E_2 C_2} \quad \text{i.e.} \quad \frac{C_3}{C_4} = \frac{C_1}{C_2}$$

This shows that the reactions involving the nitrile groups had proceeded to the same extent in fibres after $t$ hours as in film after $T$ hours.

4.6.3 Results and discussion.

The results of the correlation between Courtelle fibres and film are shown in figure (28). During oxidation the reactions, as measured by $R$, occur faster in the fibres than film. In contrast, the rates of reaction during inert pyrolysis are very similar.

These correlation curves have been used to find the rate of the nitrile group reaction in Courtelle fibres. From the spectra of fibres, the value of $R$ is found after specific heating periods. For the same value of $R$, the corresponding heating period for film is found from the correlation graph. At this particular heating period, the nitrile concentration in the film can be found relatively accurately, figure (29). This value is taken to be the nitrile concentration in the fibres because of the identical $R$ values. In this way a graph can be constructed of nitrile concentration versus time in Courtelle fibres, figure (30).
FIGURE 28

CORRELATION BETWEEN COURTELLE FIBRES AND FILM DURING HEAT TREATMENT AT 225°C

RATIO OF I.R. ABSORPTIONS
CN (2180)/CN (2240)

O FIBRES
□ FILM

OXIDATION

INERT PYROLYSIS

HOURS

HOURS
Fibres, film and pan film during thermal oxidation at 225°C

Nitrile concentration %

Hours
There are four features to the nitrile reactions in Courtelle fibres, film and polyacrylonitrile film.

Firstly, the reactions never go to completion under the conditions investigated. Most reaction occurs in Courtelle fibres under thermal oxidation conditions when 85% of the nitrile groups react in a period of 10 hours, figure (30).

Secondly, the nitrile reaction and oxidation reactions are clearly related: under inert conditions the rates of the nitrile reactions are similar for Courtelle fibres, film and PAN film, whereas the rates differ greatly under oxidising conditions, figures (30, 31). Additionally, the nitrile reaction during oxidation occurs faster in Courtelle fibres than film: a difference here is in accordance with a relation between oxidation and the nitrile reaction due to the greater surface area of the fibres.

Thirdly, there is an interesting anomaly. In Courtelle film, the nitrile reaction is faster and goes further during oxidation than in inert heat treatments. This situation is reversed for PAN film, i.e. the nitrile reactions favour inert conditions.

Finally, the nitrile reaction sometimes appears to have two stages. The initial rate of decrease is linear to about 20% reaction, when the rate increases to about 50% reaction. This behaviour is shown in Courtelle film and fibres under inert conditions and Courtelle film and PAN film under oxidising conditions. The difference in rates of the nitrile reaction between oxidation and inert pyrolysis for Courtelle fibres is shown in figure (32).

The nitrile reaction in oxidation of both Courtelle fibres and film exhibits 2nd order kinetics, figures (33, 34). During inert pyrolysis, the reaction is 2nd order during the second stage, but the order during the first stage varies.

The nitrile reaction in PAN film does not have a constant order during either oxidation or inert pyrolysis. The following equation was used to calculate the order of reaction after various time intervals.(61).

\[
\begin{align*}
n & = \log \left( \frac{d C_1}{d t_1} \right) - \log \left( \frac{d C_2}{d t_2} \right) \\
& = \log C_1 - \log C_2
\end{align*}
\]

\[
n = \text{order of reaction} \\
C_1 = \text{concentration at time } t_1 \\
C_2 = \text{"""" } t_2
\]
FIBRES, FILM AND PAN FILM DURING INERT PYROLYSIS AT 225°C

NITRILE CONCENTRATION %

PAN FILM

COURTELL FILM

COURTELL FIBRES

HOURS
Figure 32: Comparison of Courvelle fibres during heat treatment at 225°C.

- O Oxidation
- □ Inert Pyrolysis

Rate of loss of nitrile groups (%/hour)

HOURS

0 2 4 6 8 10
Fibres during heat treatment at 225°C

1. Oxidation
2. Inert pyrolysis

α: Initial concentration
κ: Decrease in concn. after time interval

\[ \frac{1}{(a-x)} (\text{PERCENT}^{-1}) \]

Hours: 0 2 4 6 8 10
FILM DURING HEAT TREATMENT AT 225 °C

- OXIDATION
- INERT PYROLYSIS
- INITIAL CONCENTRATION
- X DECREASE IN CONCENTRATION AFTER TIME INTERVAL

\[
\frac{1}{(a-x)} \text{ PERCENT}^{-1}
\]

HOURS
For both oxidation and inert pyrolysis, values of n ranged between -10.0 and 3.5, over 20 hours of heating. This is further evidence that the reactions mechanisms in PAN and Courvelle are very different.
4.7. Summary.

4.7.1. Carbon yield.

1. Oxidation of the precursor increases the carbon yield, (14% maximum).
2. A maximum carbon yield is obtained after an oxidation period of 3 hours at 225°C. At longer periods of oxidation the carbon yield is reduced. This is due to removal of carbon during both oxidation and carbonisation.

4.7.2. Mechanical properties.

1. It is unlikely that cross-linking occurs during the initial stages of thermal oxidation in Courtelle fibres.
2. Cross-linking probably does occur during the initial stages of inert pyrolysis. However, the extent of the cross-linking appears to be small.
3. Whatever is responsible for the final modulus in Courtelle fibres, it is rapidly reduced during oxidation, but not during pyrolysis.
4. Under the carbonisation conditions used, only very short oxidation periods are necessary to produce high performance carbon fibres.
5. It is possible to produce high performance carbon fibres omitting the oxidation stage, but only after long periods of isothermal heating, in inert atmosphere, at 225°C and with a lower carbon yield.
6. For lightly oxidised fibres, the stabilisation reactions continue through the early stages of carbonisation.

4.7.3. Elemental analysis.

1. Oxidation causes the removal of hydrogen. Its concentration falls from 3 to 2 atoms per repeat unit over a 7 hour oxidation period.
2. Hydrogen is not removed from the repeat unit during inert pyrolysis.
3. Nitrogen is not removed from the repeat unit during any of the heat treatments used.
4.7. 4. Qualitative infra-red analysis.

1. Whether or not the thermal reactions are in oxidative or inert atmospheres, the C=N groups react and conjugated C=N and N-H groups are formed. Possibly C=N groups are also formed.
2. During inert pyrolysis, CH₂ groups do not react and C=C groups are formed only after long periods at 225°C.
3. During oxidation OH, C=O and probably both conjugated and unconjugated C=C groups are formed, and CH₂ groups react to completion. The new chemical structures probably involve aromatic heterocycles.

4.7. 5. Quantitative infra-red analysis.

1. Oxygen appears to have an initiating or catalysing effect in Courtelle, but not Polyacrylonitrile.
2. The reactions during oxidation are diffusion controlled.
3. The comonomers in Courtelle are also capable of initiating or catalysing the nitrile reactions.
4. Not all the nitrile groups react.
5. The oxidation of Courtelle and PAN film, and the inert pyrolysis of Courtelle fibres and film have two distinct stages.
6. During the inert pyrolysis of Courtelle fibres, there is an induction period before the nitrile groups react.
7. During oxidation, the removal of C=N groups in Courtelle follows 2nd order kinetics.
8. The equivalent reaction during inert pyrolysis is 2nd order only during the second stage.
CHAPTER 5.

DISCUSSION.

5.1. Introduction.

The aim of this thesis is to provide scientific reasons for the necessity of the oxidation stage, in the production of carbon fibres. The results of this work have clearly demonstrated the necessity of oxidation in terms of increased carbon yield and improved mechanical properties. Elemental and infra-red analyses then provided data on the chemical differences between oxidised fibres and inert pyrolysed fibres. This chapter of the thesis coagulates the individual results in an attempt to complete a picture.

The analytical techniques which have been employed can be described as essentially static, that is they provide information about the product of a particular treatment rather than what was happening during the treatment. The result is that two different formulae have been derived corresponding to oxidised fibres and inert pyrolysed fibres. These have been discussed firstly in terms of whether or not cyclisation reactions occur, which is currently a controversial topic, and then in terms of general chemical structure. The relationships between these structures and the mechanical properties of the carbon fibres produced from them, are discussed. Additionally, current theories of the mechanisms of the reactions have been reviewed and are discussed in this chapter.

However, organic chemistry alone is incapable of completely describing the process of oxidation and carbonisation of PAN fibres. This is because the most important parameter controlling the high performance properties of carbon fibres, is their physical structure. This can be shown to be a function of the structure of the original PAN fibres. (62). This chapter explores the structural changes in so far as they can be directly related to the organic chemistry. This amounts to a discussion of the mechanical properties of the PAN fibres before and after various heat treatments. However, in order to relate mechanical properties with the organic chemistry, it is necessary to describe the stress/strain curve of PAN fibres in terms of the chemical chemical structure of the fibres. Current theories, as described by
Morton and Hearle (52), are presented. The discussion continues by showing that there is a correlation between the mechanical properties of heat treated fibres and their elemental analyses. Apparent anomalies in either the interpretation of the mechanical properties or the chemical analysis results, become evident. Additionally, the arguments for and against the occurrence of crosslinking reactions during the low temperature heat treatments are discussed.

Finally, a calculation is described to provide data on the length of the cyclised sequences. This has been included because the cyclised length is thought to be important in determining the crystallite size in the final carbon fibre.

5.2. Chemical structure of heat treated Courtelle fibres.

5.2.1. Cyclisation or no cyclisation?

This is probably best tackled in an objective manner. The fact is that acrylic fibres are thermally unstable: they shrink and discolor at temperatures greater than 110°C. However, after a simple heat treatment under specific conditions, the same fibres are converted to a thermally stable material, without losing their fibre characteristics. That means they must still consist of linearly oriented macromolecules in a fibrillar structure.

Now consider the chemical principles of thermal stability in polymers, e.g. the use of bonds with high dissociation energy. Thus C - H (87 kcales/mole) and C - C (59 kcales/mole) should be avoided in favour of C = C (100 kcales/mole), C ð C (194 kcales/mole), C = N (147 kcales/mole) or C = O (170 kcales/mole). Another principle is that ladder and cross-linked structures are necessarily more thermally stable. One reason is that a break in a single main chain bond does not immediately result in molecular breakdown.

Houtz (12) was the first to apply these considerations to heat treated acrylic fibres and realise that it was quite feasible for polyacrylonitrile to react to produce ladder (cyclised) structures. However, Houtz did not describe in detail their chemical nature, nor did he differentiate between oxidation and inert pyrolysis.

Possibly the most direct evidence for cyclisation is that the nitrile groups react but nitrogen compounds are not evolved (except
in small quantities from side reactions and the nitrogen content of the fibres remains constant). The following system is envisaged.

Infra-red spectroscopy neither proves nor disproves the formation of C = N groups.

There are other ways in which the nitrile groups could react without cyclisation. Deane suggests one way (33) but his reactions lead to cross-linking which is his explanation of the thermal stability. But the fact that the fibres maintain their original extension to failure under load is proof that no cross-linking occurs during thermal oxidation. That means that the thermal stability has to be explained by higher bond energies or ladder structures or both.

Additional support for ladder structures comes from the colour of the heat treated fibres - black after oxidation, red after inert pyrolysis. Only if electron delocalisation occurs extensively can such deep colourations be produced. Lengths of cyclised structures, particularly if aromatic, would produce such colours. The fact that the fibres are semiconducting also supports electron delocalisation (64).
Furthermore, infra-red spectroscopy has shown clearly that during thermal oxidation, low energy C - H bonds are removed, figure (25) and that C - C bonds are replaced with C = C bonds.

These facts add up to a very strong case for cyclisation. (The extent of cyclisation, necessary to produce high performance carbon fibres, is arguable however). There is no other suggested structure capable of satisfying these facts.

5.2.2. Chemical structure of heat treated fibres.

In order to determine the difference between oxidation and inert pyrolysis, it is necessary to choose a particular period of heat treatment. Industrial processes for the production of carbon fibres can employ a 5 hour oxidation period at 225°C, and so it seems relevant to compare fibres heat treated for this period.

The mechanical test results on the final carbon fibres, figure (17) show that this period of oxidation is perfectly satisfactory for the production of high performance carbon fibres, while the corresponding inert pyrolysed fibres produce unacceptable carbon fibres.

The elemental and infra-red analyses, (figures (20, 21, 30, 31) have been used to formulate the chemical structures of 5 hour oxidised and inert pyrolysed fibres, figure (35). These structures were derived by a stepwise process. Firstly the carbon backbone was laid down.

Ideally, the structure should consist of 261 monomer units containing 250 acrylonitrile molecules, 10 methyl acrylate molecules and 1 itaconic acid molecule. This would then contain every species present. It is, however, unpractical and 14 monomer units have been illustrated, omitting methyl acrylate but containing one itaconic acid structure which is assumed to initiate the cyclisation.

Having decided on the carbon backbone, the cyclised section was entered. The ratio of reacted to unreacted nitrile groups was found from the infra-red spectra (figures 30, 31).

Elemental analysis (figures 20, 21) was then used to fix the numbers of hydrogen and oxygen atoms present.
Figure 35 Chemical Structures of Courtelle Fibres after Oxidation and Inert Pyrolysis for 5 Hours at 225°C.
There is insufficient information to place the hydrogen and oxygen atoms accurately in the formulae, but the following infra-red results, figures (23, 24, 25, 26) were used as a guide:

1. The methylene groups have almost completely reacted during oxidation, but are largely unaffected during inert pyrolysis.
2. Oxygen is present mainly in hydroxyl groups, but also in carbonyl groups.
3. Amine groups are produced during both inert pyrolysis and oxidation.

The presence of hydrogen in hydroxyl and amine groups reconciles the anomaly in oxidised fibres, that infra-red spectra indicates almost complete removal of methylene (CH₂) groups, while elemental analysis shows a drop of only 1 in 3 hydrogen atoms.

Having then arrived at a formula in which the cyclised/linear ratio and elemental ratios were correct, the final step was to adjust the carbon carbon-bonding to satisfy the elemental valence states.

There are three major differences between the formulae of oxidised and inert pyrolysed fibres:

1. Oxidised fibres contain more cyclised structures and less linear structure.
2. Oxidised fibres contain more unsaturated groups, particularly C = C groups, which are almost absent in inert pyrolysed fibres. Some of these C = C groups will be present in cyclised sequences allowing the possibility of aromaticity.
3. The oxidised fibres carry oxygen in the form of hydroxyl and carbonyl groups on the backbone of the polymer.

These three differences can be used to explain some of the phenomena observed during the preparation of carbon fibres. For instance, oxidation of the precursor increases the carbon yield because (a) more ladder polymer is produced, (b) more high energy bonding is introduced with the possibility of further stabilisation by means of aromaticity. The oxidised fibre is therefore comparatively thermally stable, and able to
withstand the high temperatures encountered in carbonisation, with less molecular breakdown. These two reasons also account for the improved mechanical properties of the carbon fibres from oxidised precursor. With higher bond energies, more ladder structure and less molecular breakdown, the macromolecular structure will suffer less disorientation. The direct relationship between orientation and high performance properties has been stated (Chapter 4). Additionally, oxygen bonded to the backbone of the polymer can also help to prevent molecular disorientation.

Watt, (65), Uchida (36) and Fiedler et.al. (66) have detected water evolved in the early stages of carbonisation (\(<\ 350^\circ C\)) from oxidised fibres. Watt also found that an increase in modulus accompanied the loss of water and reasoned that water was evolved during cross-linking reactions involving oxygen bonded to the backbone of the polymer (67). In contrast, the modulus of inert pyrolysed fibres did not increase during carbonisation until after \(450^\circ C\) allowing more opportunity for molecular disorientation. The work reported here supports Watt's conclusions in that coincidence was found between the oxygen uptake of the fibres and the improvement in the mechanical properties of the corresponding carbon fibres.

While many published papers describe the chemical structure of inert pyrolysed polyacrylonitrile, only three papers have attempted the chemical structure of oxidised fibres. Standage and Matkowski used elemental and infra-red analysis to arrive at the conclusion that oxygen formed only bridging ether groups (22) figure (36a). As I have also used these techniques, it is surprising that our conclusions are so different. Standage and Matkowski publish the spectrum of PAN film oxidised to 8\% of maximum (22). The spectrum is virtually identical to the spectrum which I obtained from PAN film oxidised for 9 hours at 225^\circ C. My interpretation of the absorbances at 3330 cm\(^{-1}\) and 3200 cm\(^{-1}\) were hydroxyl and amine groups (see Chapter 4). Standage and Matkowski attributed both peaks to amine groups on the basis that Burland and Parsons made this assignment (13). However, these authors used wet KBr pellets to obtain their spectrum and so the range 3500 - 3000 cm\(^{-1}\) was flooded with hydroxyl absorption from the water. Therefore, the development of hydroxyl absorption during the heat treatment, was missed. Another disturbing feature in the paper by Standage and Matkowski is their spectrum of highly oxidised (84\%) PAN fibre, obtained by reflectance. This shows no absorption in the range 3330 - 3200 cm\(^{-1}\), the methylene
FIGURE 36 PREVIOUSLY PROPOSED CHEMICAL STRUCTURES OF OXIDISED POLYACRYLONITRILE.
absorption is very strong and there is a massive carbonyl absorption at 1750 cm\(^{-1}\). In spite of this, their formula for oxidised fibres shows no methylene groups or carbonyl groups. It seems probable that their reflectance spectrum is from impurities on the surface of the fibre.

Watt has used evidence from model compounds, elemental analysis, infra-red spectroscopy, mechanical properties and gas evolution analysis to arrive at a formula for the oxidised fibres where oxygen is present in the form of carbonyl groups (68), figure (36b). Whilst there is considerable evidence for the presence of carbonyl groups (Chapter 4) it seems highly unlikely that oxygen is not present in any other form. Additionally, Watt's formula does not show the presence of C = C groups for which there is fairly strong I.R. evidence and which can help to explain some of the features of the oxidised fibres, e.g. their colour and thermal stability.

A study of model compounds was used by Friedlander et.al. to arrive at a formula involving oxygen in nitrone groups (45) figure (36c). The possibility of nitrone group formation cannot be denied. However, there is no doubt at all that the methylene groups are mostly consumed during the oxidation. Friedlander's formula can represent only a minor proportion, if any, of the molecule. This clearly illustrates the great danger of using model compounds, particularly when out of context, for Friedlander et.al. did not consider the importance of oxidation to the bulk chemical and physical properties of the materials.

There are three important differences between the formula I am proposing and those described above. Firstly, my interpretation of the evidence is such that oxygen is predominantly in the form of hydroxyl groups. Carbonyl groups are present to a relatively small extent while both groups may on occasion be combined in carboxyl groups. Secondly, my formula uses principally carbon carbon-unsaturated groups to explain the increased thermal stability on oxidation. The evidence for this is the increased carbon yield. These two features have been suggested by other authors. Danner and Meybeck (69) (1971) have suggested a mechanism of oxidation whereby aromatic heterocycles carrying hydroxyl groups are produced. The third difference is that none of these authors, with the exception of Watt, has put their conclusions into context. That is, they have not attempted to describe why oxidation is a necessary preliminary step in the production of carbon fibres. An advantage of illustrating a relatively large part of the polymer molecule is that the fundamental concepts can be more clearly understood.
5.2.3 Stadtler Reference Spectra (70).

These spectra were consulted in order to obtain supporting evidence for the proposed chemical structures after heat treatment. Firstly, the infra-red peak at 2180 cm$^{-1}$ was considered. All spectra were examined which absorbed in the range 2210 - 2180 cm$^{-1}$ - there were only 34. All but 9 of these were either deuterated hydrocarbons or members of an homologous series in which the functional group did not change. Of these 9, 4 contained conjugated nitrile groups, eg. $\text{CH}_2 - \text{CH} = \text{CH} - \text{C} \equiv \text{N}$, 3 contained nitrile groups adjacent to very strong electronegative centres, eg. $\text{CF}_2 - \text{C} \equiv \text{N}$, 1 was an isocyanate and 1 was an isothiocyanate. This supports the theory that the 2180cm$^{-1}$ peak is due to a nitrile group attached to an electronegative centre, perhaps even conjugated to it. No paper reviewed has assigned the peak to an isocyanate.

All spectra were examined which had principle peaks at the following wavenumbers, 3220, 1590, 1370, 1250, 800 cm$^{-1}$. Excluding nitrile absorptions, this covers the main features of the spectra produced from PAN. The spectra examined contained additional peaks to those listed. There were 5 spectra, produced from aromatic and heterocyclic compounds, figure (37).

In a complicated system such as heat treated PAN, it would be naive to hope that its spectrum would be exemplified by a well characterised compound in the Stadtler reference system. In these circumstances the reference spectra can have only a supporting role. It is pertinent that all but two of the spectra with absorptions at 2210 - 2180 cm$^{-1}$ contained 'modified' nitrile groups and that the remaining two spectra were due to isocyanates and isothiocyanates, the formation of which is highly unlikely.

It is also significant that the spectra which compared most closely to that of thermally oxidised PAN were due to compounds which had very similar chemical structures to those proposed in this thesis. The main features of these compounds were their cyclic, aromatic character; some were heterocycles.

The role of the reference spectra in this context has been to provide support for the proposed chemical structure of oxidised PAN.
FIGURE 37 CHEMICAL STRUCTURES

RESULTING FROM SEARCH IN

STADTLER REFERENCE SPECTRA
5.3. Mechanisms of reactions.

5.3.1. Introduction.

It could be considered that a knowledge of the mechanisms of the chemical reactions occurring during the thermal treatments is of academic interest only. The technology of carbon fibre formation is well known and any changes in current methods will almost certainly cause an increase in cost which may not be tolerated by the industry. Perhaps the greatest advantage of knowing the mechanisms is that they may indicate chemical species which would have catalytic effects. The oxidation stage in the production of carbon fibres is comparatively slow and the use of catalysts would be considerably advantageous.

However, many of the published mechanisms have been deduced by determining the starting and final chemical structures and simply guessing the mode of the transformation. Also, most of the literature describes mechanisms for the formation of certain chemical species rather than giving a systematic description of initiation, propagation and termination of the reactions. This is particularly so in the case of thermal oxidation, about which very little has been written.

The main features of the reactions which the mechanisms should explain are:

(a) The nitrile reaction in Courtelle is faster during the oxidation compared with inert pyrolysis,
(b) The situation is reversed for polyacrylonitrile,
(c) The nitrile reaction during oxidation and during initial inert pyrolysis is faster in Courtelle than polyacrylonitrile.

This chapter describes the mechanisms proposed in the literature. Where appropriate new mechanisms have been suggested.

5.3.2. Inert pyrolysis.

5.3.2.1. Initiation.

The first case to consider is pure homopolymer. That the thermal reactions are free radical in nature has been proved by the inhibiting effect of added free radical acceptors (29). Any polymer carrying unsaturated side groups is susceptible to homolytic fission because one of the resulting radicals is resonance stabilised, figure (38A).
RADICAL INITIATION OF CYCLISATION

(A)

(B)

(C)
However, it appears that the tertiary hydrogen atom in polyacrylonitrile plays an important role in either initiation or propagation. This is inferred because the thermal degradation products from polymethacrylonitrile are entirely different; much less nitrile polymerisation occurs and monomer production (unzipping) is an important reaction (71). Consequently, a mechanism is suggested in figure (38B), which is based also on homolytic fission producing resonance stabilised radicals, but no main chain scission.

It seems unlikely that the linear radical $C = C = N^*$ would initiate the cyclisation because the first step in propagation requires the formation of an hexagonal structure. This radical may initiate double bond formation in the main chain via an hydrogen transfer reaction figure (38C). The resulting radical would be sterically capable of initiating the cyclisation. However, an argument against this method of initiation is that the radical would be resonance stabilised with the $C = N$ and $C = C$ double bonds, thus reducing its propagating capacity.

Another mechanism involving the tertiary hydrogen atom has been suggested by Grassie (71) and Madorsky (72), figure (39). The mechanism involves the main chain twisting back onto itself, a process called 'backbiting'. This raises the question of whether it is feasible in a system in which the macromolecules are both highly oriented and cross-linked by the strong dipole forces of the nitrile group. It is worth noting that Grassie and Madorsky were working with unoriented polymers.

It has been shown that some comonomers and additives can initiate the thermal reactions (29) (73). Particularly effective are acidic comonomers, e.g. acrylic acid and a mechanism has been suggested, figure (40A). The polar nature of the acidic OH group induces further polarisation of an adjacent nitrile group. Migration of an electron pair onto the nitrogen atom causes cleavage of the OH bond, resulting in ring closure leaving the nitrogen atom negatively charged. This then causes further cyclisation of the nitrile groups. It would appear that copolymerised acids cause rapid cyclisation because the acidic OH group is more able to induce polarisation of the nitrile group, than another nitrile group. This could be due to the steric arrangement of the carbonyl group causing closer approach between the OH and $C = N$ groups, than is possible between two nitrile groups. The strength of ionic interactions is inversely proportional to the square of the distance between them (74). Another possibility is that the comparatively
FIGURE 3: A MECHANISM FOR THE TERMINATION OF A CYCLISING SEQUENCE WITHOUT INTERRUPTION TO THE KINETIC CHAIN LENGTH.

(71)
FIGURE 40  MECHANISMS OF ACID INITIATION  
AND PROPAGATION OF CYCLISATION
large acidic group causes greater separation of the molecular chains which decreases the dipole forces of the nitrile groups in the immediate vicinity of the acid groups. This would allow at lower temperatures, rotation of the nitrile groups, about the H₂C - CH bond, into the correct geometry for reaction. This mechanism is ionic: further evidence for it could be obtained by determining the effect of added free radical acceptors. There is no record of this in the literature.

However, Grassie has found that some inorganic salts can also cause rapid polymerisation of the nitrile groups (29). These salts include NaOH, Na₂S, NH₄SCN, Zn Cl₂ and KCN. They presumably operate in a similar fashion to copolymerised acid groups, i.e. by promoting greater ionisation of the nitrile groups.

Lewis acids also increase the rate of nitrile polymerisation but it is more difficult to understand how the acid is operating. By analogy with monomeric compounds, the following complex between the acid and the nitrile group should be produced:

\[
\text{- C = N + Sn Cl}_4 \rightarrow \text{- C = N - Sn Cl}_4
\]

It seems unlikely that this species would initiate cyclisation because the nitrogen atom carries a positive charge. There is additional doubt concerning the concentrations of Lewis acids which are effective. It has to be assumed that the added salt is not mobile in the polymer, and therefore one salt molecule is unlikely to initiate more than one cyclisation reaction. A bulk of evidence suggests that the cyclised lengths are short and therefore many are present. Consequently effective concentrations of Lewis acids would be expected to be higher than actually they are. The practice is to add the acid in 1 - 15% concentration. Because Lewis acids are generally metal halides, the number of acid molecules per monomer unit may be very small indeed. For instance, if a fibre contains 10% stannic chloride, there will be one Sn Cl₄ molecule per 45 monomer units. It is very difficult to see how a Lewis acid in this concentration has a significant effect on the rate. However, Lewis acids which have been found to increase the rate of the nitrile polymerisation are stannic chloride (75, 76, 77), titanium tetrachloride, plumbic chloride and stannic bromide (78). The complex formed between ethylene diamine and copper nitrate has also been effective (79).
5.3. 2.2. Propagation.

Relative to initiation free radical propagation appears to be quite a simple process, figure (40B). A similar mechanism is thought to operate in ionic propagation, figure (40C).

The free radical nitrile polymerisation mechanism has been shown to have a slow initiation step and a fast propagation step. Ionic polymerisation is the reverse, a fast initiation and slow propagation due to the necessity of separating the electrostatic charges and migrating the counter ion (29).

The propagation step requires the close approach of two nitrile groups. Because the polymer is atactic, a necessary preliminary to propagation probably is the rotation of molecular segments about the $\sigma$ bond between $\alpha$ and $\beta$ carbon atoms.

Grassie uses the 'backbiting' process to explain why only a small quantity of initiator can cause much nitrile polymerisation when the cyclised lengths are short, figure (39). The process fits into the overall picture of polymerisation by providing chain transfer mechanism. Thereby, the nitrile polymerisation is terminated concurrently with the initiation of a new chain. This has the virtue of utilising the tertiary hydrogen atom but the suspected inapplicability of the 'backbiting' mechanism.

5.3. 2.3. Termination.

The free radical reaction can be terminated by combination of any of the radicals present. The ionic reaction is probably terminated by steric factors or when the environment becomes insufficiently polarising to maintain separation of the charge.

5.3. 3. Oxidation reactions.

5.3. 3. 1. Initiation.

In the published literature there is a general reluctance to describe the mechanisms of the oxidation reactions. But Grassie, et.al. who have probably published more on mechanism than any other single group, assumes that the nitrile polymerisation is essentially the same in oxidative and inert atmospheres and the oxidation reactions
are additional. The evidence presented earlier in this thesis is contrary to Grassie's assumption and an anomaly exists in that for homopolymer the nitrile reaction is slower during oxidation than inert pyrolysis, while for Courtelle the nitrile reaction is faster during oxidation.

In general the oxidation reactions of polymers have been found to proceed via free radical reactions. There seems to be no reason to suspect this is not the case for polyacrylonitrile. Initiation is therefore likely to be similar to the case of inert pyrolysis, i.e. homolytic bond fission. This will be followed by reaction with oxygen to produce peroxy radicals, figure (41A). It is also likely that C - H bonds cleave producing radicals, but there is controversy regarding whether the \( \alpha \) H atoms or the \( \beta \) H atoms are most sensitive. Danner (32) and Conley (27) believe the \( \alpha \) H atoms initially separate figure (41B), while Makschin (80), Friedlander (45) and Grassie (30) believe the \( \beta \) H atoms are most vulnerable, figure (41C).

It appears that oxygen can affect the rate of the nitrile reaction in two ways. When the nitrile reaction is a free radical process oxygen can promote the process by immediately reacting with radicals as they form, producing relatively stable peroxy radicals. These have sufficient lifetime to react with the system rather than spontaneously terminating with the counter radical from the cleavage reaction. Alternatively, the peroxides may react with hydrogen producing stable hydroperoxides which could inhibit the free radical reactions during propagation.

5.3.3.2 Propagation.

Danner has published a mechanism for oxidation which shows the simultaneous propagation of nitrile polymerisation with free radical attack at the \( \alpha \) carbon atom (32). However, no evidence is given for this correlation between the nitrile polymerisation and oxidation figure (42A). Danner suggests that free radical attack initially occurs at the \( \alpha \) carbon atom resulting in the formation of an hydroxyl group via the formation of the hydroperoxide. Condensation between the hydroxyl group and a \( \beta \) hydrogen atom puts a double bond in the chain at the same time cyclisation occurs.
FIGURE 41  THE FORMATION OF PEROXY RADICALS ON A AND B CARBON ATOMS

A

\[ \text{H}_2\text{C} - \text{H} - \text{C} - \text{C} - \text{N} \rightarrow \text{H}_2\text{C} - \cdot \text{H} - \text{C} - \text{C} - \text{N} \overset{\text{O}_2}{\rightarrow} \cdot \text{O} - \text{O} - \text{C} - \text{C} - \text{C} - \text{N} \]

B

\[ \text{H}_2\text{C} - \text{H} - \text{C} - \text{C} - \text{N} \rightarrow \text{H}_2\text{C} - \cdot \text{H} - \text{C} - \text{C} - \text{N} \overset{\text{O}_2}{\rightarrow} \cdot \text{O} - \text{O} - \text{C} - \text{C} - \text{C} - \text{N} \]

C

\[ \text{H}_2\text{C} - \text{H} - \text{C} - \text{C} - \text{N} \rightarrow \text{H}_2\text{C} - \cdot \text{H} - \text{C} - \text{C} - \text{N} \overset{\text{O}_2}{\rightarrow} \cdot \text{O} - \text{O} - \text{C} - \text{C} - \text{C} - \text{N} \]
**Figure 42A**  MECHANISM OF DOUBLE BOND FORMATION AFTER OXIDATION

![Chemical structure diagram showing the mechanism of double bond formation after oxidation.]

**Figure 42B**  THE FORMATION OF HYDROPEROXY GROUPS

![Chemical structure diagram showing the formation of hydroperoxy groups.]

The propagation mechanism must explain why for homopolymer the nitrile polymerisation in the presence of oxygen is slower than that in inert pyrolysis. One explanation could be that the initiating radicals produced by bond fission are immediately stabilised by the formation of hydroperoxides, figure (42B). The hydroperoxides are likely to be formed from peroxides by hydrogen abstraction from methylene groups as these hydrogen atoms are most prominent on the molecule.

It is much more difficult to explain why for a copolymer such as Courtelle the rate of nitrile polymerisation is increased in the presence of oxygen. Perhaps this is associated with ease of removal of the tertiary hydrogen atom at the comonomer site. Alternatively free radical attack may take place in the ester group. Because it seems likely that an ionic polymerisation mechanism occurs in Courtelle, due to the presence of acid comonomers, perhaps a radical/ion initiator is responsible for the increased rate of nitrile polymerisation.

Clearly, there is hardly sufficient experimental data to discuss meaningfully the mechanisms of the oxidation reactions.

5.3. 3. 3. The formation of carbonyl and hydroxyl groups.

Carbonyl groups are assumed to be formed at \( \beta \) carbon atoms. Most of the evidence for this relates to the analysis of oxidised model compounds. \( \beta \) hydrogen atoms are known to be more sensitive to free radical attack than \( \alpha \) hydrogen atoms, when they are adjacent to an unsaturated group (81). Hence it would appear likely that the hydrogen atoms are most probably attacked after double bond formation, see section 5.3.3.4. This would overcome the anomaly clarified by Friedlander (45) that substituted groups appear at the \( \beta \) carbon atoms, when they would be expected at \( \alpha \) carbon atoms due to the labile tertiary hydrogen atom situated there, figure (43).

Conley has suggested that diketones are produced by the oxidation of \( \alpha \beta \) ketonitriles (80), figure (44A). This suggestion was made to explain the infra-red absorption at 1680 cm\(^{-1}\).

Following the formation of carbonyl groups, keto-enol tautomerism has been used to explain the presence of hydroxyl groups (30, 45), figure (44B). Hydroxyl radicals are almost certain to be present in any organic free radical oxidation process. Consequently, hydroxyl
Figure 43. Mechanism of double bond formation after oxidation, without cyclisation (45).
Figure 44A Formation of αβ Diketones

Figure 44B Keto-Enol Tautomerism in Oxidised Polycrylonitrile

Figure 44C Ionisation of Polycrylonitrile Compared with Polystyrene
groups will be formed wherever the corresponding termination reaction occurs.

It is worth considering the oxidation mechanism of polystyrene, because this macromolecule also has a side group with an electron accepting character not unlike that of the nitrile group in polyacrylonitrile, figure (44C).

It has been shown that at 180 - 200°C in air hydroperoxides are formed at the α carbon atom, and these subsequently decompose with chain cleavage. Two methods have been proposed, figure (45A), (82, 83). It is conceivable that these reactions occur also in polyacrylonitrile. Grassie has shown conclusively that no volatile fragments of main chain are driven off during oxidation, (30). But this does not mean that there is no chain cleavage because the strong dipole forces may still hold the fragments. Additionally, the formation of unsaturated groups either in the main chain or substituted at the α carbon atom, would explain the 2180 cm⁻¹ absorption in the infra-red spectrum, by virtue of resonance with the nitrile group, figure (45B).

However, these reactions do not explain the increase in rate of the nitrile reaction with oxidation, as resonance involving the nitrile group is likely to decrease its activity in the polymerisation reaction.

5.3. 3. 4. The formation of C = C bonds.

The formation of C = C bonds during reactions producing carbonyl and hydroxyl groups, have already been described.

Additionally, it has been proposed that keto-enol tautomerism can be catalytic towards the formation of C = C groups (30), figure (46A).

Strictly speaking, this is not catalytic activity as one keto-enol group can produce only another one C = C group.

Another suggestion is that an substituted hydroperoxide can decompose producing 2 hydroxyl radicals and CH₂⁻ C = C group directly (27), figure (46B).

By analogy with the thermal reactions of polyvinyl chloride (84), double bonds could be formed in a condensation reaction, figure (46C). Hydrogen cyanide certainly is evolved during the oxidation reactions (85). However, it seems unlikely that this mechanism is applicable because it would be expected during inert pyrolysis when the formation of C = C groups is believed to be insignificant.
**Figure H5A**  Oxidative Degradation of Polystyrene

\[
\begin{align*}
\text{H}_2 & \quad \text{C} & \quad \text{H}_2 \\
& \quad \text{C} & \quad \text{C} \\
& \quad \text{O} & \quad \text{C} \\
& \quad \text{O} & \quad \text{H}_2 \\
& \quad \phi & \quad \phi \\
& \quad \phi & \quad \phi
\end{align*}
\]

**Figure H5B**  Electron Resonance in Oxidised Polycrylonitrile

\[
\begin{align*}
\text{H}_2 & \quad \text{C} & \quad \text{H}_2 \\
& \quad \text{C} & \quad \text{H}_2 \\
& \quad \text{O} & \quad \text{C} \\
& \quad \text{O} & \quad \text{H}_2 \\
& \quad \phi & \quad \phi \\
& \quad \phi & \quad \phi
\end{align*}
\]
FIGURE 46  DOUBLE BOND FORMATION
IN POLYACRYLONITRILE

A

B

C

\[ \text{H}_2\text{O} \text{C} \text{C} \text{H}_2 \rightarrow \text{H}_2\text{C} \equiv \text{C} + 2 \text{HO}^- \]

\[ \text{H}_2\text{C} \equiv \text{C} + \text{H}_2\text{C} \rightarrow \text{H}_2\text{C} \equiv \text{C} + \text{H}_2\text{C} \equiv \text{C} \]

\[ \text{H}_2\text{C} \equiv \text{C} + \text{H}_2\text{C} \rightarrow \text{H}_2\text{C} \equiv \text{C} + \text{H}_2\text{C} \equiv \text{C} \]
5.3. 3. 5. The formation of epoxide groups.

This has been suggested by Standage to account for the empirical formula of the oxidised fibres (22). However, it is quite possible to write empirical formulae not involving the epoxide group, figure (47A). N.B. The epoxide group is not suitable for analysis by infra-red spectroscopy in this system due to strong absorptions in areas where the epoxide absorption would occur. There are at least two mechanisms for the formation of epoxide groups which are feasible in oxidation of polyacrylonitrile, figure (47B).

5.3. 4. Summary.

An attempt has been made to systematically discuss the thermal reactions of polyacrylonitrile and Courtelle in terms of the mechanisms. The results of quantitative infra-red spectroscopy indicate that different reaction mechanisms operate between polyacrylonitrile and Courtelle during both oxidation and inert pyrolysis.

Grassie has shown that the nitrile polymerisation may proceed via ionic or free radical mechanisms. The free radical mechanism will operate unless ionic initiators or highly ionising environments are present. Courtelle contains ionisable groups, the acidic comonomer. Consequently, in inert pyrolysis the mechanism probably is free radical for polyacrylonitrile and ionic for Courtelle. During the thermal oxidation of polyacrylonitrile, the slower nitrile polymerisation may be caused by the formation of relatively stable hydroperoxides. Whether the thermal oxidation of Courtelle proceeds via ionic or free radical mechanisms is not known and the reason for the nitrile polymerisation being faster than in inert pyrolysis is not clear.

The most satisfactory explanation for the nitrile reaction during oxidation in Courtelle being faster than in polyacrylonitrile seems to be the initiating effect of the acid comonomer. A chain transfer mechanism may explain why only a few acid sites can result in much cyclisation.

This review has shown that there has been no systematic approach to study the mechanisms of the oxidation reactions of Courtelle fibres in particular. However, Grassie's work on ionic initiators has proved interesting as the catalytic activity of some compounds has been demonstrated.
POSITION ON THE CHAIN

CHAIN IN POLYACRYLONITRILE

A

\[
\begin{align*}
H & \quad \text{OR} \\
\text{O} & \quad \text{H} \\
\text{C} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

CONSENSATION

\[
\begin{align*}
\text{H}_2 & \quad \text{H}_2 \\
\text{O} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]

B

ADDITION

\[
\begin{align*}
\text{H} & \quad \text{H}_2 \text{C} \text{O} \text{CH}_2 \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}_2 \text{O} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]
5.4. Mechanical properties and chemical structure.

5.4.1. Courtelle fibres.

The stress/strain curve of the unheated fibres is 'S' shaped, figure (12). There are three distinct regions of the curve to which have been assigned molecular mechanisms of the strain. Before describing these, a description of the molecular structure in the unstrained fibre is necessary.

The fibre is anisotropic. High degrees of stretch (6-20X) were employed during the formation of the fibre, and the resulting molecular structure is thought to consist of approximately parallel molecular chains collected in micro-tows called fibrils. The fibrils also lie approximately parallel to the fibre axis and are branched and interconnected. Electron micrographs of this fibrillar structure have been published.

However, unlike most other synthetic fibres Courtelle does not produce an x-ray fibre diagram consisting of sharp reflections and an amorphous halo. Instead, equatorial arcs are present with no amorphous halo (86). The cause of this has been assigned to the polarity of the nitrile groups. The interchain forces are so strong that order in the lateral direction is more prevalent than that in the longitudinal direction, (87). This then is the background to the unique molecular structure of acrylic fibres.

The molecular interpretation of the stress/strain curve has been described by Morton and Hearle and is representative of current theories, (52). When the fibre is stressed, the initial strain is accommodated by stretching and bending the covalent bonds between atoms. This is a reversible process obeying Hooke's Law and is responsible for the initial modulus. As the stress increases, there comes a time when the forces between molecules are overcome allowing molecules to slide over each other. This corresponds to the centre part of the stress/strain curve where strain is high for small increases in stress. As a result of this increase in strain, molecular orientation is increased and this allows greater opportunity for intermolecular, particularly dipole/dipole forces to operate. This gives rise to the gradually increasing stress levels until the fibre fractures.

Although the theory seems integral and plausible, it does not satisfactorily explain two points. The bonding between atoms in the molecule is the strongest form of bonding present, and so the question
arises as to why this should be the first to show strain when the fibre is stressed. Secondly, the theory seems too simple to be applied to the complicated heterophase structure of the fibre: no account is taken of the fibrillar nature of the fibre structure.

Furthermore, the theory does not seem to be compatible with the mechanical behaviour of the fibres after heat treatment. When Courtelle fibres are heated at 225°C in air for just 15 minutes, the third modulus and the UTS are reduced by approximately half. In the absence of air there is little change. Normally, the reduction in the UTS would be indicative of a molecular weight drop. However, this is not consistent with the fact that the crystallite orientation in the final carbon fibre is a function of the molecular orientation of the precursor, (88). Additionally, the need to restrain the fibres during the initial heat treatments is indicative of a direct relation between the orientations of the precursor and carbon fibre. Molecular weight reductions would be expected to allow disorientation to occur. Additionally, Grassie has concluded that a principal difference between oxidation and inert pyrolysis is that there is no chain breakage during oxidation, (30). Grassie's technique for detecting chain breakage relies upon volatalising chain fragments under high vacuum. However, if chain breakage occurs randomly rather than by depolymerisation, the formation of small fragments would be minimal in the early stages, and Grassie did confine his work to the early stages of heat treatment. He did not detect volatile fragments at all in oxidised fibres.

Turning to the reduction in third modulus, this is compatible with the concept of chain breakage, and the molecular theory of the stress/strain diagram. If limited chain breakage occurs in a random fashion, there would be little change to the initial or secondary modulii because these are functions of the total primary and secondary bonding forces in the molecules. But the third modulus depends upon achieving increasing degrees of molecular orientation which would not be possible were the molecular weight too low.

This is strictly a qualitative argument and it is worth considering other possible causes of the fall in third modulus after only 15 minutes oxidation. Elemental analysis shows that the oxygen content of the oxidised fibres increases by 2%, figure (18), which corresponds to the introduction to the backbone of 3 oxygen atoms per 100 monomer units while I.R. spectroscopy shows that 8 nitrile groups react per 100 monomer...
units, figure (30). There was no detectable oxygen uptake or nitrile reaction in the corresponding inert pyrolysed fibres, figures (19, 31).

It is very difficult to use the introduction of so few oxygen atoms, or the loss of so few nitrile groups to explain the 50% fall in third modulus.

If the molecular theory of the stress/strain curve is correct, then the loss of the third modulus would appear to be due to loss of the dipole/dipole forces between molecules. This means the nitrile groups have reacted, but this has been shown to be incorrect in that only 8% have reacted when the third modulus has decreased by 50%. However, this cannot be considered unequivocal for two reasons: the doubt associated with the quantitative I.R. measurements and the possibility that only a fraction of the nitrile groups present may take part in dipole/dipole attractions so that an 8% loss of nitrile groups may bear little relation to the loss of intermolecular forces.

The loss of the third modulus could also be caused by a plasticization effect, and so it is worth considering whether oxygen could behave as a plasticizer. A plasticizer in this system would have to operate by separating the molecular chains and so reduce the intermolecular dipole/dipole forces. It seems unlikely that oxygen bonded to the backbone could operate in this fashion, even if it was present in sufficient quantity. Because the polymer is atactic and the nitrile groups are larger than the oxygen atom, it is unlikely that oxygen bonded to the backbone would have a significant effect. However, if oxygen did act as a plasticizer, it would be expected to decrease the initial modulus as well, and this does not occur. But it could be argued that some cyclisation is occurring simultaneously and this would increase the initial modulus: the almost zero change in initial modulus is the result of the two opposing effects balancing each other.

Another factor to be considered is that oxidation over the first 15 minutes, may involve only surface layers in the fibre, i.e. the oxidised fibre may have a highly oxidised skin and a virtually unreacted interior. It must be presumed that no disorientation occurs when the fibre is heated due to the mechanical restraint. It is very difficult to use these ideas to postulate a reason for the drop in third modulus. Equally, because the role of the fibrillar structure in the mechanical properties is not known, it is difficult to relate the drop in third modulus to a feature of the fibrillar structure.
5.4. 2. Carbon fibres.

It is clear from figures (16, 17) that oxidation of the precursor plays a major role in the development of the mechanical properties of carbon fibres. Furthermore, only a small amount of oxidation is necessary ($\frac{1}{2}$ hour, $225^\circ C$) to obtain satisfactory carbon fibres and that additional oxidation does not improve the performance of the carbon fibres.

It is pertinent to consider that the industrial process for carbon fibre production uses much faster heat up rates in carbonisation ($1200^\circ C$ in $\frac{1}{2}$ hour). Under these conditions longer periods (5 hours) of oxidation at $225^\circ C$ are required. Thus it would appear that a relation exists between rate of carbonisation and the period of oxidation. A high rate of carbonisation requires a long oxidation, and vice versa. Two conclusions can be drawn from this. During the oxidative heat treatment at $225^\circ C$, the thermal stabilisation reactions are occurring over at least the first 5 hour period. Secondly, if the oxidation period is short, and the rate of carbonisation slow, then the stabilisation reactions continue during the early stages of carbonisation.

If Courtelle fibres are heated in an inert atmosphere instead of air, then a period of 5 hours at $225^\circ C$ is necessary before the degradation during carbonisation is sufficiently reduced to prevent destruction of the fibres, figures (16, 17). This infers that the role of oxygen would be to produce a thermally stabilised skin which provides structural rigidity for the severe conditions of carbonisation. This does correlate with the effects mentioned above: if the oxidation period is short then the skin is frail and the carbonisation reactions must be slow. The longer the period of oxidation, the thicker the skin and less need for slow carbonisation. This does assume that the necessary stabilisation reactions do ultimately occur in inert pyrolysed fibres as the temperature is increased over $225^\circ C$. There is evidence for this (Section 4.4.1).

In conclusion, it is possible to say that two reactions leading to increased thermal stability are cyclisation and dehydrogenation leading to carbon carbon unsaturation. The results detailed earlier show a good correlation between the development of acceptable mechanical properties in inert pyrolysed carbon fibres, figures (16, 17) with the appearance of a $C = C$ absorption ($800 \text{ cm}^{-1}$) in the infra-red spectrum, figure (25).
5.4.3. Correlation between mechanical properties and elemental analysis.

Three effects which have already been mentioned correlate so well that it is worth devoting a section to drawing them together and illustrating the point, figure (48). Relative to the period of oxidation of Courtelle fibres, the development of high performance properties in the corresponding carbon fibres, the fall in the third modulus and the introduction of oxygen to the backbone of the polymer all have similar characteristics. They change rapidly over the first half hour of heating and then relatively little.

Thus it would appear that there is a definite relation between the development of tensile strength and modulus in the carbon fibres with the uptake of oxygen and/or the drop in third modulus of the precursor fibres. The earlier discussion has illustrated the difficulties in finding molecular reasons for the drop in third modulus. Consequently it is equally difficult to correlate this with the mechanical properties of the carbon fibres. Additionally, the role of oxygen uptake has been discussed, but one aspect remains. If oxygen is introduced to the backbone as carbonyl or hydroxyl groups there is opportunity for dehydration reactions during the early stages of carbonisation. This seems very likely because not only has water been analysed in the evolved gases at temperatures less than 300°C (36, 66) but the modulus of the fibres begins to increase simultaneously (65). The modulus of inert pyrolysed fibres does not increase until a temperature of 400°C is reached. This is clear indication that one role of oxygen is to form crosslinks and prevent molecular disorientation before and during the carbonisation process.


The importance of discussing crosslinking is that this is a recognised and well proven method of thermal stabilisation and may play a role in the formation of carbon fibres. Early papers concluded that crosslinking was a major reaction due to the insolubility which develops when PAN polymers are heated (41). However, the cyclisation reaction would also account for the insolubility. Also, with molecular structures so different before and after the heat treatment it is not possible to use the moduli of the fibres to indicate the presence or absence of crosslinking. Nevertheless, tentative correlations may be
Figure 48: Correlation between behavior of precursor fibre on thermal oxidation and the development of modulus in the corresponding carbon fibres.

- Tensile modulus, carbon fibre (1400°C) (Figure 47)
- Third modulus, Courtaulde (Figure 46)
- Monomer groups/oxygen atom, Courtaulde (Figure 45)

Air 225°C, 0 5 10 hours
made during the early stages of the reactions, before much cyclisation has occurred. During the first $\frac{1}{2}$ hour of oxidation, the initial modulus increases slightly, then it decreases over the next 2 hours, figure (13). The second modulus which should be a more acute test of crosslinking, according to the molecular theory of mechanical properties, does not vary significantly. It appears, therefore, that crosslinking is not an important phenomenon in the early stages of the oxidative heat treatment. In contrast, the initial modulus of inert pyrolysed fibres increases slightly over the first hour, and then remains constant while the second modulus increases steadily over the first two hours of heating, figure (14). It would seem quite likely that crosslinking does occur in this case, but its effect in stabilising the structure must be minimal since Grassie has detected molecular fragmentation during low temperature inert pyrolysis but not during the equivalent oxidation (30).

These conclusions are supported by the extensibility of the fibres. Courtelle fibres oxidised at 225°C for up to 2 hours, all fail at about the same extension, figure (15), indicating no crosslinking. In contrast, the inert pyrolysed fibres fail at progressively smaller extensions, indicating the possible occurrence of crosslinking.
5.5. The Length of the Cyclised Sequences.

5.5.1. Introduction.

While describing the thermal stability of heat treated acrylonitrile polymers, the early papers assumed that cyclisation went to completion. Then infra-red spectroscopy showed that at temperatures less than 300°C the nitrile peak never completely disappeared. If only some of the nitrile groups react, then the cyclised sequences must be of finite length and be separated by unreacted repeat units. The lengths of the cyclised sequences could be an important parameter because if short and separated by reasonably long linear sequences, the use of cyclisation to explain the thermal stability becomes less plausible. Additionally the size of the graphite 'crystallite' in high performance carbon fibres is very small compared with that in other forms of graphite and it would be interesting to compare the 'crystallite' size with the length of the cyclised sequences after the low temperature heat treatment.

The literature does not contain an actual calculation, but Grassie, Berlin and Noh draw the conclusion from their work that the cyclised length must be quite short, just several repeat units long.

Grassie's argument applies to inert pyrolysis and is as follows, (47). The nitrile polymerisation should not involve any loss in weight, as no single bond cleavage is necessary. But volatile products such as HCN, NH$_3$ or chain fragments are always produced. Additionally, infra-red analysis clearly shows substantial reaction of the nitrile groups. Grassie says that these facts are not consistent with the concept of a small concentration of initiating centres and long cyclised lengths. The removal of HCN must be from a non-cyclised monomer unit and the resulting structure would prevent the progress of the nitrile polymerisation. To explain the reaction of the nitrile groups and the gas evolution reactions Grassie suggests a mechanism in which a transfer reaction occurs, thereby halting a growing cyclised sequence while simultaneously providing a new initiation site, figure (39).

However, during oxidation rather than inert pyrolysis, much less HCN is produced and there is virtually no detectable chain fragmentation. Also the production of ammonia is most probably associated with cyclisation (16), (30), (89) and is fairly constant whether or not oxidation occurs. Hence it would appear that Grassie's argument is less applicable to the case of oxidation. Grassie does not comment on this.
He does, however, hazard a guess at the length of the cyclised sequences — 1 to 6. (73).

Berlin carried out the reaction in N-dimethylformamide solution, when apparently some oxidation did occur (38). A UV absorption due to C = N developed during the heating. But this absorption did not show a bathochromic shift as the reaction proceeded and Berlin concluded also that the cyclised length must be quite short. However, these experimental conditions make it doubtful whether the conclusions can be meaningfully applied to the case of atmospheric oxidation.

Noh and Yu found from quantitative infra-red spectroscopy that the nitrile group reaction was first order. This led them directly to the conclusion that the cyclisation length was short.

None of these arguments are conclusive. They do little more than back up an idea which seems probable. The concept that in oxidation there would be many initiation sites along the chain seems very reasonable because oxygen itself can act as initiator and this obviously would lead to a comparatively short cyclised length. Additionally, because the polymer is atactic bond rotations will be necessary for cyclisation and steric hinderance can be envisaged, which would hinder the development of long cyclised lengths. The case of inert pyrolysis is different in that there will be a reduced number of initiation sites. The following calculation is therefore interesting, but because of the assumptions made, its practical value is doubtful.

5.5. 2. The Principle.

It is not difficult to find the overall amount of cyclisation that has occurred after a particular heat treatment. For this, measurement of the fall in intensity of the nitrile peak is quite satisfactory. But this alone gives no information about the length of the cyclised sequences. However, if the number of cyclised sequences can be found then the cyclised length is readily calculated. For instance, if 50 nitrile groups react in 100 which contain 10 cyclised sequences, then the average length of the cycles is 50/10 = 5. If a chemical species could be found which was specific to a single cyclised sequence, then quantitative estimation of this species would give the number of cyclised sequences. For the purposes of this calculation such a group is assumed to be the nitrile group which absorbs at 2180 cm\(^{-1}\) in the infra-red spectrum. The pertinence of the calculation rests on the validity of this assumption.
which is described in more detail below.

5.5.3. Assumptions.

The main assumption is that the peak which appears at 2180 cm\(^{-1}\) is due to a nitrile group adjacent to a cyclised sequence. Virtually everyone who has considered this peak has assigned it to a nitrile group taking part in some kind of electron delocalisation (section 4.5.) This is because shifts in frequency of absorption of the kind noticed are typical of the effects of electron delocalisation. Thus the assumption is reduced to: the only electron delocalisation present is that occurring in a cyclised sequence. Evidence has been described (section 5.2.2.) showing that C = C bonds can be produced in the main chain, especially during oxidation. This is why the calculation has very little practical use, but nevertheless it remains an interesting exercise.

Other assumptions have necessarily to be made regarding correlations between both fibres and film, and taking quantitative measurements from infra-red spectra. These are described in the section 4.6.

5.5.4. The Method.

1. For either oxidation or inert pyrolysis of Courtelle fibres after any time \(t\), the ratio \(R\) of CN (2180)/CN (2240) is found from figure (28).

2. The corresponding time \(T\) for film, which also has ratio \(R\) is found from the same figure.

3. At this time \(T\) the decrease in nitrile content for film, \(N\%), is found from figure (29). This is assumed to be the same for fibres after time \(t\).

4. \(R\) gives the number of CN (2180) present per 1 CN (2240) and there is \((100-N)\%\) of CN (2240) remaining, therefore the number of cyclised sequences per 100 monomer units is \(R\) \((100-N)\), \(\frac{2.5}{2.5}\), where 2.5 is the absorptivity factor. This is introduced because absorptivities of the two CN peaks are different. It has been found that the absorptivity of a saturated alkyl nitrile, e.g. methyliminodiacetonitrile \((0.007 \text{ l/gm})\) is 2.5 times less than that of an unsaturated alkyl nitrile, e.g. aminoacrylonitrile \((0.018 \text{ l/gm})\), (90).
5. The total number of nitrile groups which have polymerised per 100 monomer units is given by the decrease in nitrile concentration ($\%$), $N$, less those nitrile groups which have become adjacent to the cyclised sequences (i.e. $2180 \text{ cm}^{-1}$) less those which have reacted to form HCN and $\text{NH}_3$, $X$;

$$i.e. \quad N - \left( \frac{R}{2.5} \frac{(100 - N)}{} \right) - X$$

6. The length of the cyclised sequences is given by the total amount of cyclisation, i.e. the number of cyclised units/100 monomer units, divided by the number of cyclised sequences per 100 monomer units;

$$i.e. \quad \frac{2.5 \left( N - \frac{R}{2.5} \left(100 - N\right) - X \right)}{R (100 - N)}$$

7. The length of polymer between cyclised sequences is given by the difference between the amount of CN originally present, and the CN which has become cyclised, divided by the number of uncyclised lengths. This assumes that the number of cyclised sequences equals the number of linear sequences.

The length between ladder sequences in terms of the number of monomer units

$$= \frac{100 - \left( N - \frac{R}{2.5} \left(100 - N\right) - X \right)}{R/2.5 \left(100 - N\right)}$$

$$= \frac{2.5 X}{R (100 - N) + 2.5/R + 1}.$$  

(In fact the numbers of uncyclised and cyclised lengths are equal only when a molecule is bounded by an uncyclised length at one end and a cyclised length at the other end. If the molecule has a cyclised length at both ends, the numbers of cyclised lengths exceeds the uncyclised lengths by one and vice versa).

5.5. Results and discussion.

Using the above formulae, graphs have been drawn showing the length of the cyclised structures as a function of heat treatment time at $225^\circ \text{C}$ in both oxidative, figure (49) and inert atmospheres, figure (50). The figures show the effect of taking into account the evolution of HCN and $\text{NH}_3$, values for which were taken from the results of Bell and Fiedler (66). Bell heated Courtelle fibres (3 denier) at $180^\circ \text{C}$ and his results caused little difference to the trace during either oxidation.
FIGURE 49

COURTELLE FIBRES: LENGTH OF LADDER SEQUENCES AFTER HEAT TREATMENT AT 245°C

HNC/NH₃ CORRECTION FROM RESULTS BY

@ Bell and Mulchandani

@ Medler, Fitzer, and Müller

@ No correction

OXIDATION

LENGTH OF LADDER SEQUENCES

LENGHT OF LADDER SEQUENCES

0 1 2 3 4 5 6 7 8 9 10
HOURS
FIGURE 50

COURTELLE FIBRES: LENGTH OF LADDER SEQUENCES AFTER HEAT TREATMENT AT 225°C

HCN/NH₃ CORRECTION FROM RESULTS BY

Bell and Mulchandani

Fiedler, Fitzner and Müller

No correction

Inert Pyrolysis

LENGTH OF LADDER SEQUENCES

0 1 2 3 4 5 6 7 8 9 10 HOURS
or inert pyrolysis. But if higher temperatures had been used the effect would have been to reduce the cyclised lengths shown in figure (49).

Bell also used fibres of larger diameter, 3 denier, compared with 1½ denier. Thus the diameter of their fibres was probably 18 - 20 m compared with 13 - 14 m used in my work. (Courtelle fibres of 3 denier also have circular cross-sections). However, the effect of this greater diameter is not clear. The proportions of HCN and NH₃ that are evolved during oxidation and inert pyrolysis are significantly different figure (51). It may be expected that during oxidation in air, the centre of a larger diameter fibre may be reacting in non-oxidising conditions for comparatively longer, because of the greater distance through which the oxygen has to diffuse. With currently available data it is not possible to quantify this effect.

In contrast, the results of Fiedler, Fitzner and Muller, figure (52), have a much greater effect: the maximum cyclised length in oxidation is reduced from 16 to 10 and in inert pyrolysis from 32 to 24. These authors used Dralon fibres (2 denier) containing only 0.4% comonomer, with a kidney shaped cross-section and were heat treated at 250°C. In this case the main errors in using their results of HCN and NH₃ evolution arise from the higher temperature and lack of comonomer. It has been found that some comonomers can increase the rate of the cyclisation reactions (91). Either the comonomer can act as an initiator, or the decrease in density as a result of incorporation of the larger molecule increases the rate of oxygen diffusion, thus providing more initiation sites. As a result of the lack of comonomer in Dralon fibres, less HCN and NH₃ would be expected, but the temperature of heat treatment was higher. Thus these two factors tend to cancel, but again quantifying the effects is not possible.

It can be seen from figures (49, 50) that the maximum average length of the ladder sequences is achieved after less than 1 hour for oxidation and about 6 hours for inert pyrolysis. The maximum length is much less on oxidation than inert pyrolysis: 10 - 16 compared with 24 - 32. Also the rate of increase in the length of ladder sequences is much greater on oxidation. These results are entirely consistent with an addition polymerisation reaction, where it is well known that the greater the quantity of added initiator, the faster the reaction
**Figure 51**

Evolution of HCN and NH$_3$ from Courvelle fibres (2 denier) heated at 180°C.

(From results of Bell and Mulchandani, Ref. 37).

**Mole %**

**Oxidation**

- HCN
- NH$_3$

**Mole %**

**Inert Pyrolysis**

- HCN
- NH$_3$

(Mole % = Mole of gas per 100 mole of acrylonitrile monomer units.)
Figure 52

Evolution of HCN and NH₃ from polyacrylonitrile fibres, heated at 250°C (from results by Fiedler, Fitzer and Müller, Ref. 66).

Oxidation

- HCN
- NH₃

Inert pyrolysis
- HCN
- NH₃

Mole %

Hours
and the less the molecular weight. In this case, if oxygen can be considered the initiator and if molecular weight can be represented by the length of the ladder sequences, the same relation exists. This is good evidence that cyclisation is an addition polymerisation, initiated probably by oxygen when the heat treatment is in air. In inert atmospheres the initiation possibly occurs by bond cleavage reactions producing free radicals.

There could be a number of reasons causing the ladder sequences to stop growing. Steric hinderence seems quite likely. Because the polymer is atactic an essential to the growth of ladder sequences is the rotation of a monomer unit to bring nitrile groups close enough for reaction. This rotation about a carbon-carbon single bond could be inhibited by either the dipole interactions of nitrile groups or the formation of carbon-carbon double bonds. Thus greater inhibition would be expected for oxidised fibres in which it is thought that the formation of carbon double bonds is an important reaction. This is consistent with the shorter ladder sequences in oxidised fibres.

Another important possible reason for the ladder sequences to stop growing is de-activation of the growing end. A radical on the end of a ladder sequence propagates cyclisation by reaction with another nitrile group. But reaction with a free radical would terminate the ladder sequence. It has been suggested that this kind of reaction is a principal method for the production of ammonia (16). Reaction with another part of the molecule would also terminate the ladder sequence. Grassie has suggested such an intramolecular transfer reaction. (71).

Another mechanism for termination of the nitrile polymerisation could be de-activation by electron delocalisation. As the ladder sequence grows, so the extent of possible delocalisation increases. Thus the reactivity of the 'growing end' is steadily decreased. This is in accordance with the result that the ladder sequences are shorter on oxidation when more C = C and C = N bonds are produced and the opportunities for electron delocalisation are thus greater. In inert pyrolysis, the reduced delocalisation maintains the reactivity of the growing end allowing longer sequences to build up. This mechanism of termination is responsible for the inability to produce poly p-phenylene with a degree of polymerisation greater than about 10. This subject has recently been reviewed (92).
In both oxidation and inert pyrolysis, the length of the ladder sequences falls after the maximum. One reason for this could be that the absorptivities of peaks at 2240 cm\(^{-1}\) and 2180 cm\(^{-1}\) change during the heat treatments. However, qualitative infra-red spectroscopy has shown that more unsaturated centres, or even aromatic structures are produced during the heat treatments. The effect of this would be to increase the absorptivity factor which would increase the calculated cyclised length.

If the main assumption became inapplicable, that is nitrile groups were being situated at centres of electron delocalisation other than the cyclised sequences, the effect would be to increase the calculated cyclised length. After longer periods of oxidation, the cyclised length does increase slightly, which could be explained by absorptivity changes and/or failure of the main assumption. The decrease in the cyclised length is very difficult to explain.

The calculation for the length between cycles is also modified by HCN or NH\(_3\) evolved during the cyclisation reaction. After heat treatment in air for 1 hour at 225°C the length between cyclised sequences is 25, reducing to 3 after 10 hours, figure (53). Heat treatment in inert atmospheres leaves very long linear sequences - 60 monomer units after 4 hours at 225°C reducing to 17 after 10 hours, figure (54).

Summary of Results.

1. The calculation for the length of the cyclised sequences is little affected by taking into account HCN and NH\(_3\) evolution according to the results of Bell and Mulchandani, but is significantly affected by the results of Fiedler, Fitzer and Muller.

2. On oxidation the maximum length of the cyclised sequences is 10-16, while on inert pyrolysis it is 24-32.

3. The rate of increase of cyclised length is greater on oxidation.

4. The graphs show a decrease in cyclised length with heat treatment time which is difficult to explain.

5. The length of linear polymer between cyclised sequences is much smaller on oxidation than inert pyrolysis.
Figure 53

Courtelle Fibres: Length between Ladder Sequences after Heat Treatment at 225°C

HCl/NH₃ correction from results by Bell and Mulchandani

Fiedler, Fitzner, and Müller

No correction

Oxidation

Monomer units between ladder sequences

Hours
FIGURE S4

COURTILLE FIBRES: LENGTH BETWEEN LADDER SEQUENCES AFTER HEAT TREATMENT AT 225°C

HCN/NH₃ CORRECTION FROM RESULTS BY

○ BELL AND MULCHANDANI

□ FIEDLER, FITZER, MÜLLER

△ NO CORRECTION

INERT PYROLYSIS

![Graph showing length between ladder sequences for Courtille fibres after heat treatment at 225°C with HCN/NH₃ correction from results by Bell and Mulchandani, Fiedler, Fitz, and Müller. No correction is also shown.](Image)
5.5. 6. Conclusions.

Early papers on the thermal reactions of polyacrylonitrile assumed that cyclisation went to completion (12, 19), and that this was the main reason for the increased thermal stability. Cyclisation alone cannot account for the thermal stability because this work has shown clearly that significant lengths of linear polymer exist in an oxidised fibre from which a high performance carbon fibre can be produced. In fact surprisingly long lengths of linear polymer seem to be permissible. The results of the calculation show that after 1 hour at 225°C in air, the molecules in Courtelle fibres contain ladder sequences of average length 10 - 15 cycles and linear sequences of 25 - 35 monomer units. After 5 hours these figures become 8 - 12 cycles and 6 - 11 monomer units. After oxidation, the linear sequences may be stabilised by double bonding.

After inert pyrolysis for 1 hour, although the cyclised lengths appear similar, the linear lengths between cycles are still very long, i.e. 200 - 260. (These figures were calculated but not entered in figure (54). After 5 hours the cyclised lengths have increased to 20 - 30 while the linear sequences decreased to 45 - 55. In this case there will be very little double bonding and stabilisation in the linear sequences.

It was found that 5 hours of inert pyrolysis at 225°C was necessary before the fibres could be carbonised without disintegration. At this time the lengths of the linear sequences were similar to those in fibres given a minimum oxidation treatment, i.e. ½ hour at 225°C. It would appear that the length between cycles could be a more important parameter in explaining the thermal stability than the length of the cycles.

One of the characteristic features of the graphite structure in the carbon fibre is that its 'crystallite size' is very small compared with that in other forms of graphite. It has been thought that this small crystallite size may be fundamental to high strength and modulus properties in carbon fibres. It is difficult to define practically what a crystallite is in a carbon fibre; this has been discussed in chapter 1. However, the wide angle x-ray diffraction pattern of carbon fibres includes a reflection from the 10 plane.

The breadth of this arc is a function of the length of the crystallites, La.
Watt has measured La during the carbonisation of 1½ denier Courtelle fibres, oxidised for 5 hours at 220°C (93). His results are shown in figure (55). Also shown is the length of the ladder sequences calculated from I.R. spectroscopy on Courtelle fibres oxidised for 5 hours at 225°C. Additionally Kasatochkin has measured La and found it to be 3.6 nm at 500 - 800°C (26). Figure (55) shows that there is good correlation between the length of the ladder sequences and the length of the crystallites; both have similar orders of magnitude.

However, considerable doubt is involved in all these measurements and calculations. The limiting assumptions in the ladder length calculations have been described. The x-ray diffraction pattern tends to be indistinct at the lower temperatures. It has been suggested that because line broadening is not only a function of La but includes a contribution from changes in interatomic spacing, calculations of La have been over-estimates. Nicholas, et. al. has calculated La at 2.0 for a 1100°C fibre, (94). Kasatochkin does not describe in detail his precursor fibres, or the conditions under which the fibres were oxidised.

The situation therefore is that there may well be a relation between ladder length and crystallite size. Unfortunately, on the basis of the work described in this section it is not possible to be more specific.
CORRELATION BETWEEN LADDER LENGTH AND CRYSTALLITE LENGTH

A. RANGE OF MEAN LADDER LENGTH AFTER OXIDATION AT 225°C
B. KASATOCHKIN'S CRYSTALLITE LENGTH (26)
C. WATT'S CRYSTALLITE LENGTH (93)
D. NICHOLAS'S CRYSTALLITE LENGTH (94)

LENGTH (nm)

CARBONISATION TEMP. (°C)
6. Conclusions.

This thesis has been about the process of introducing thermal stability to polyacrylonitrile fibres so that, from them, carbon fibres may be produced. The chemical reactions have to be controlled so that minimum disruption to the molecular structure occurs during both processes—thermal stabilisation and carbonisation. To this end, the great advantage, if not necessity, of thermal oxidation of the precursor, rather than inert pyrolysis, has been clearly demonstrated. The way in which oxidation affects the maintenance of molecular structure has been indicated, in terms of polymer chemistry, by elemental and spectroscopic analysis. More ladder structure is produced, the covalent bonding is stronger and potential cross-link sites are introduced. The pertinence of this work lies in the analytical techniques which were applied, so far as was possible, to the fibres themselves in conditions identical with the carbon fibre production process. Consequently, unlike much published work, the results are directly applicable.

The concepts of thermal stabilisation, used here to provide reasons for the importance of oxidation, are entirely consistent with current theories of stabilisation in polymers. The theories proposed as a result of this work do not contradict the main concepts of the carbon fibre formation process. For instance, cyclisation or polymerisation of the nitrile groups occurs to a large extent, cross-linking does not occur at temperatures below 225°C and much unsaturation is introduced. The reasons for the apparent necessity of oxidation appear to be plausible, clearly defined and complete. However, complacency is averted by several results which undermine the fundamentals of current theories.

Perhaps the most impressive is the fact that only $\frac{1}{8}$ hour of oxidation was necessary to produce satisfactory high performance carbon fibres. This is a unique result, not previously reported and the implications have been fully discussed in the previous sections; but no satisfactory explanation has been proposed. Similarly current theories on polymer structure cannot explain the dramatic fall in the final modulus of the acrylic fibres when they are oxidised. If reasons for this effect could be found, then perhaps the correlation between the fall in final modulus, the oxygen uptake and the development of high performance properties in the final carbon fibre, could be understood.
In view of the invalidity of the assumptions used in the cyclised length calculation, the result that the cyclised length on oxidation is about the same as the measured crystallite length in the carbon fibres, cannot be used to conclude that a definite relation exists. If the technology of adjusting the crystallite length was known then it might be possible to correlate the crystallite length with the ladder length.

The anomalies and unexplained results indicate clearly the need for more research at the low temperature end of the thermal processes. Additionally, the chemical reactions occurring during the higher temperature carbonisation processes have received relatively minor attention, which perhaps reflects the increased difficulty of applying conventional analytical techniques to high temperature reactions. Nevertheless, that the reactions are probably very interesting is indicated by the result that nitrile groups are still present at $500^\circ C$ (95) and that at sometime during the heat treatment, the heterogeneous hexagonal rings must coalesce with the replacement of nitrogen by carbon.

It is interesting to try to use the conclusions of this work to suggest alternative precursors. Necessary characteristics of the precursor would appear to be:

(a) macromolecular structure oriented along the fibre axis
(b) ladder molecular structure
(c) high energy carbon-carbon or carbon-nitrogen bonding
(d) the ability to cross-link at temperatures below $350^\circ C$.

Apart from (d), these are the characteristics of the new generation of fibre forming thermally stable polymers. It may be possible to introduce (d) in these fibres by the same method as for acrylic fibres, i.e. oxidation.

However, a conflict exists between (a) and, (b) and (c). An additional property of ladder structure and high energy bonding, apart from thermal stability, is molecular stiffening. As a result, thermally stable polymers often do not have a practically significant glass transition temperature. Consequently, the degree of molecular alignment which can be introduced by a stretching process is limited. So thermally stable polymers may not be suitable as carbon fibre precursors. Although there are references in the literature to the
use of thermally stable polymers for carbon fibre production (96, 97, 98, 99), it appears that high performance properties are not readily attained. This substantiates the conclusion above.

The final conclusion, therefore, is that a precursor must be a linear polymer in which molecular alignment can be achieved before ladder structure and high energy bonding is introduced. It is exceptionally fortunate that these qualities were found in a polymer which was already established as a textile fibre, and therefore freely available in a suitable form.
Suggestions for further work come mainly from three areas, infra-red spectroscopy, the mechanisms of the reactions and the anomalies in relating chemical changes to mechanical properties.

The absorption peaks in the infra-red spectrum corresponding to hydroxyl and amine groups (3200 - 3340 cm\(^{-1}\)) are broad, due at least partly, to hydrogen bonding effects. The evidence for the formation of hydroxyl groups, during oxidation, is not as definitive as it might be. Supporting evidence for the presence of hydroxyl groups and/or amine groups could be gained by synthesising model compounds consisting of polyacrylonitrile carrying hydroxyl and amine groups, and comparing their spectra with those obtained from this work. A similar approach may lead to better differentiation between \(C = C\) and \(C = N\) in the spectra.

Another feature of the spectra which warrants further work by virtue of its academic interest only, is the increase in area of the \(C - H\) peak during inert pyrolysis of polyacrylonitrile. It is possible that some kind of change in state occurs as the polymer is heated through the second order transition temperature and this somehow adjusts either the quantity of \(C - H\) groups absorbing or the absorptivity of these groups.

The discussion on reaction mechanisms leads to the conclusion that the reactions may have either free radical or ionic mechanisms. This difference could be the underlying cause for the anomaly that the reaction of nitrile groups in Courtelle film is faster during oxidation than inert pyrolysis, but in polyacrylonitrile film is faster during inert pyrolysis than oxidation. Present knowledge cannot explain these effects and this is one area where further research would be beneficial. The precise mechanism of the nitrile reaction of homopolymer in an inert atmosphere requires detailed explanation. This should be followed by examining the effect on the mechanism of oxidation and the presence of comonomers.

There are two aspects of the mechanical property results which warrant further investigation. If the main reasons for the necessity of oxidation are (a) to introduce thermal stability by means of ladder structure and high energy bonding and (b) to introduce potential crosslink
sites, then the adequacy of the $\frac{1}{4}$ hour oxidation is not explained. After this period of time, the predominant molecular structure is still that of the precursor. The relative roles of cyclisation, high energy bonding, potential crosslink sites and unreacted polymer need to be quantified, although it is realised this may be an idealistic viewpoint.

Finally, it seems improbable that the microstructure does not have a role in determining the stress/strain characteristics of the fibres. Current theories for the stress/strain curve involve the deformation or breaking of only primary and secondary bonds.
REFERENCES.

4. P.J. Goodhew (University of Surrey), unpublished work.
8. R. Morton, (Royal Aircraft Establishment), private communication.
9. A.J. Clarke, (University of Surrey), unpublished work.
References (cont.)

33. M. Deane (U K A E A) unpublished work.
References (cont.)

70. Sadtler commercial spectra : polymers, Sadtler Research Laboratories.
75. German patent 1,929,849 (1970).
References (cont.)

76. British patent 1,264,026 (1972).
77. German patent 1,965,554 (1971).
79. German patent 2,130,403. (1972).
87. R.B. Beavers, Macromolecular Reviews 2 (1968) 204.
88. R. Morton, private communication.
95. A.J. Clarke, unpublished work.