CHEMISTRY OF THE DEGRADATION OF VINYL POLYMERS TO GIVE CARBON FIBRE PRECURSORS.

By

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SUMMARY

An investigation of the oxidative degradation of polyacrylonitrile, a precursor for carbon fibre manufacture, has been made by examining the oxidation of 'model' compounds of the polymer. During the attempted preparation of one of these 'models', 2,4-dicyanopentane, it became apparent that this compound was unstable in the presence of sodium cyanide.

Polyacrylonitrile was found to be unstable under similar conditions; refluxing a solution of the polymer in dimethylformamide with sodium cyanide produced a black nonflammable material with very similar properties to oxidatively degraded polyacrylonitrile. The initial product from the cyanide, polyacrylonitrile reaction is extremely sensitive to oxidation, absorbing oxygen at room temperature. This behaviour can not be explained by the formation of a hydrogenated naphthyridine structure by cyclisation of the nitrile groups in the polymer.

An alternative mechanism for the degradation under these conditions is proposed. Before cyclisation the propogating ketimine groups $(>C{=}NH)$ undergo tautomeric rearrangement to the enamine form $(>C{=}\overset{|}{C}{-}NH_2)$. Subsequent cyclisation results in a condensed 1,4-dihydropyridine structure which, by analogy with the known chemistry of 1,4-dihydropyridines, will oxidise on exposure to air to a fully aromatic condensed pyrinoid system.

This theory has been extended to cover the thermal and oxidative degradations of polyacrylonitrile in the solid state. It is concluded that the condensed 1,4-dihydropyridine is formed first and, under oxidative conditions, is transformed to a mixture of condensed pyrinoid and 4-pyridone sequences. Chain scission also occurs but hydrogen bonding through the 4-pyridone species prevents loss of orientation and damage to the fibre structure.

ACKNOWLEDGEMENT

I would like to thank Professor Scott for his encouragement and guidance during this project; Rolls-Royce Limited, Derby, for the award of a research grant; and the University of Aston in Birmingham for continuing the grant after the financial collapse of Rolls-Royce Limited.

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1. AN INTRODUCTION TO CARBON FIBRE

(i) INTRODUCTION

Carbon fibre is not a new material; it was first used by Edison for electric light filaments. This material was made by the pyrolysis of cellulose fibre and although its mechanical properties were not published they were probably poor.

Interest in carbon fibre as an engineering material arose in the early 1950's with the requirements by the aerospace industry for materials with high specific strength and modulus. Fibres with good mechanical properties were prepared from high tenacity rayons (regenerated cellulose) by a complicated heat treatment[1]. Typical mechanical properties of these fibres are 0.9 GN/M^2 for strength and 170 GN/M^2 modulus.

A promising precursor material was polyacrylonitrile (PAN) which has a high degree of orientation. Because of its polar nature it seemed likely that this orientation could be preserved through carbonisation resulting in a carbon fibre with improved structure and mechanical properties. Early attempts at the pyrolysis of PAN fibre were not too successful until Shindo[2] found that an initial oxidation of the fibre gave an improvement in the properties of the carbon fibre produced. Further development at RAE (Farnborough)[3] and Rolls Royce[4] resulted in further improvements. It was found that restraining the fibre during carbonisation, together with the use of copolymers of PAN could give fibres with strength of 1.7 GN/M^2 and moduli of 410 GN/M^2. Now fibres with values of 3.1 GN/M^2 and 450 GN/M^2 for strength and modules respectively are available, largely because of the development of an oxidative treatment prior to carbonisation.

The properties of some carbon fibres are reported in table 1 for comparison.

	Modulus GN/M^2	Tensile Strength GN/M^2
Carbon Fibre (Cellulose)	170	0.9
Carbon Fibre I (PAN 2,500°C)	380	1.7
Carbon Fibre II (PAN 1,000°C)	240	2.8
Typical Glass Fibre	69	1.7

TABLE 1: CARBON FIBRE PROPERTIES

(ii) MANUFACTURING PROCEDURE

A typical manufacturing procedure may begin with 3 denier Courtelle (PAN copolymer fibre manufactured by Courtaulds Limited). The fibre is stretched and heated in air at 220°C. Careful temperature control is required at this stage to prevent charing of the fibre. After oxidation the fibre, which is now black, is heated in an inert atmosphere (nitrogen, argon or vacuum) at a rate of 125°C/hour. The final temperature reached determines the physical properties of the carbon fibre produced: maximum modulus is attained at 2,500°C and maximum strength at 1,200°C. Figure 1 illustrates this effect.

The length of oxidation treatment has a large effect on the ultimate fibre properties. This can be seen in Table 2, together with the properties of a fibre carbonised without prior oxidation.

Pretreatment @ 220°C	Tensile Strength GN/M^2		Modulus GN/M^2	
	1,000°C	2,500°C	1,000°C	2,500°C
2 hours Air	1.21	1.26	152	282
22 hours Air	1.48	1.65	159	344
70 hours Air	1.52	1.57	165	413
16 hours N_2	1.21	0.72	97	207

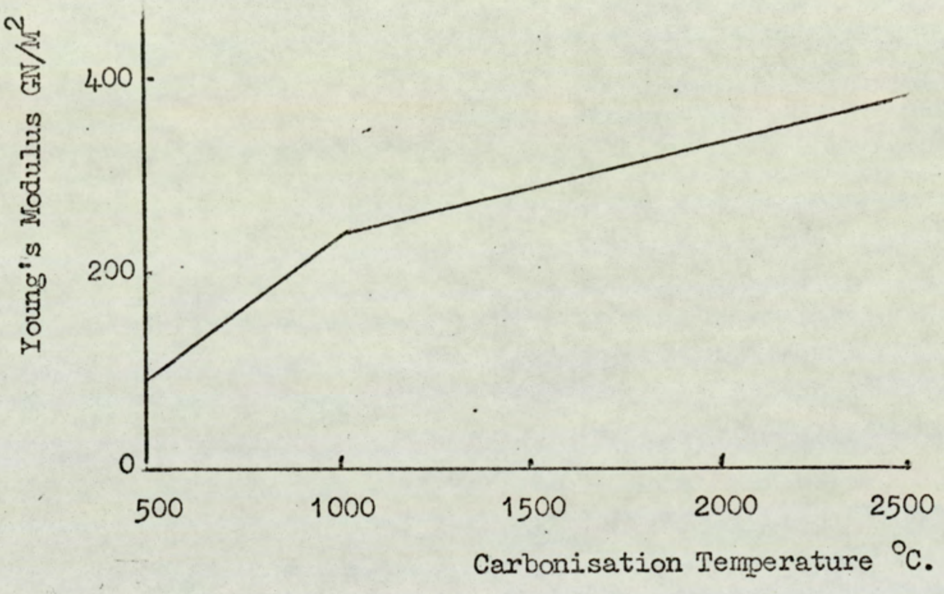
TABLE 2: EFFECT OF PREOXIDATION ON C.F. PROPERTIES

(iii) CARBON FIBRE STRUCTURE

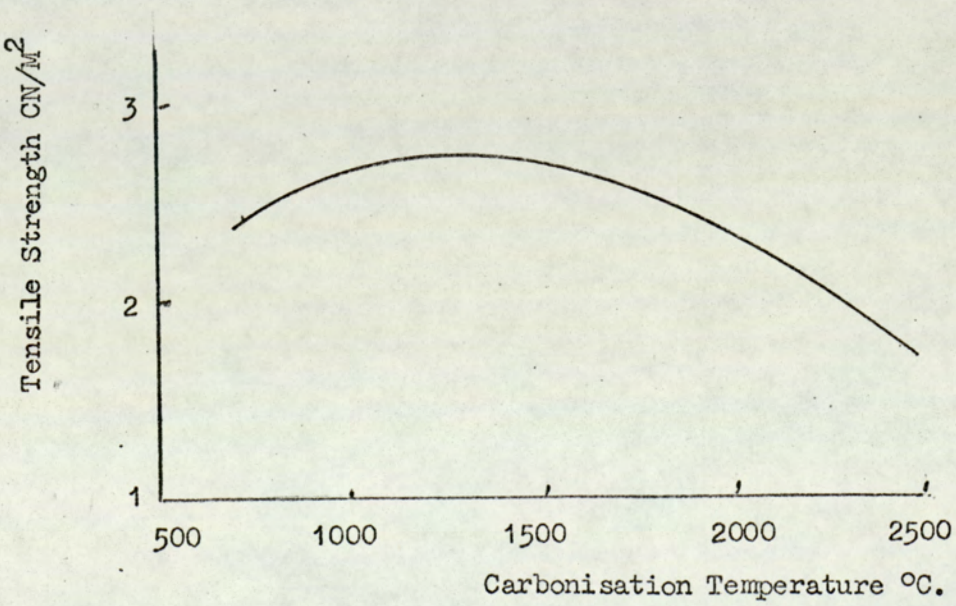
Carbon fibre has a fibrilar structure. The fibrils run parallel to the fibre axis and vary in width from 100 Å for high modulus fibre to 800 - 1,000 Å for the low modulus material. They are composed of

FIGURE 1: DEPENDENCE OF MECHANICAL PROPERTIES ON CARBONISATION TEMPERATURE

(a) Trend in Young's Modulus.



(b) Trend in Tensile Strength.

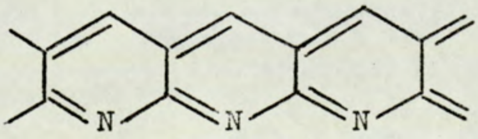


crystallites of graphite, these crystallites having a turbostratic structure. Normal graphite has a close packed structure with carbon atoms in alternate layers superposed resulting in an inter planar spacing of 3.44 Å. In turbostratic graphite the layers are randomly stacked, leading to a larger inter planar separation of 3.44 Å. Crystallite size varies with heat treatment; fibre heated to 2,500°C has crystals approximately 12 layer planes thick by 60 to 100 Å square whilst the material carbonised to 1,000°C has smaller crystals, approximately 30 Å square, with fewer layer planes. The basal planes of the crystallites are highly orientated in a parallel configuration with the fibre axis.

(iv) LOW TEMPERATURE DEGRADATION OF PAN

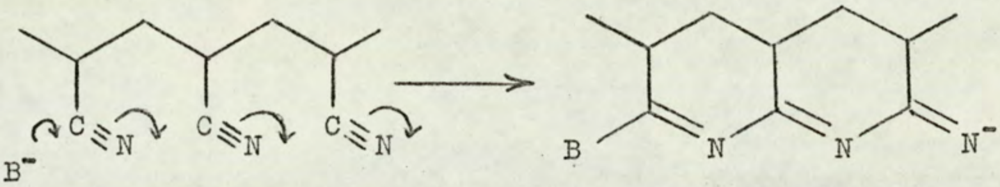
The thermal degradation of PAN has been extensively studied. Much of the early work however was concerned solely with the formation of colour at relatively low temperatures, this being related to the usefulness of the polymer in the textile industry. Despite the importance of the oxidation step in the manufacture of carbon fibre, relatively little work has been done on the rôle of oxygen in the degradation.

As early as 1950 Houtz[5] had observed that the rate of colouration of PAN was increased by heating in oxygen. The molecular weight remained constant and he observed no volatiles. From this he proposed a conjugated pyrinoid structure (I) formed by cyclisation through the nitrile groups.



I

This structure was modified by McCartney[6] after he had investigated the degradation of PAN by alkalis in NN'-dimethylformamide (DMF). Instead of the fully aromatic system he suggested a partially hydrogenated one formed by nucleophilic attack of the base on the nitrile group as outlines in Scheme 1.



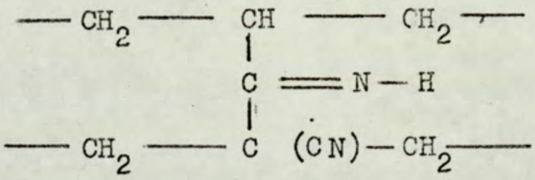
SCHEME 1

As well as the discolouration reaction McCartney observed an extensive reduction in molecular weight of the polymer which he attributed to random chain scission. The colour produced by the action of alkali was not very stable and could be readily bleached by dilute acid (e.g. hydrochloric acid).

At lower temperatures some type of initiation is essential. When the polymer is heated in a sealed tube at 100°C it remains white, even after 20 hours. The addition of a base, such as an amine, however initiates the discolouration at this temperature. Under inert conditions there is no appreciable colouration below 200°C. Above this temperature Burlant and Parsons[7] observed a progressive change from yellow to red, to dark red, to black accompanied by changes in the infra red (IR) spectrum of the polymer. The most noticeable change in the IR spectrum was the disappearance of the nitrile band at 2250cm^{-1}. A smaller band formed at 2180cm^{-1}, this being attributed to a nitrile group conjugated with a $C=C$. The residue had IR bands at 1634 and 1621cm^{-1}, assigned to unsaturation; 3623, 3448, 3356, 3205, 1634 and 1621cm^{-1}, assigned to amine or imine; and 2242 and 2179cm^{-1}, assigned to nitrile. The authors concluded that the hydrogenated naphthyridine structure II is formed first, and that this later dehydrogenates to give the fully aromatic Houtz structure (I).

As the temperature is increased further above 200°C what has been termed the "explosive degradation" of PAN occurs. This effect was first reported by Kennedy and Fontana[8] when the polymer was heated to 265°C at at pressure of 0.1 torr. It suddenly underwent a minute explosion and the colour changed abruptly from orange to brown. A number of other changes occurred: the nitrile band in the IR spectrum disappeared, solubility in DMF decreased, specific gravity increased, there was a decrease in hydrogen content and a weight loss of 31.6%. These observations are consistent with the formation of a system of naphthyridine rings, but there must have been considerable chain scission to explain the 31.6% weight loss. A similar effect has been reported in nitrogen[9].

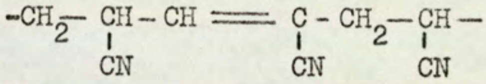
The fully aromatic pyrinoid structure of Houtz was questioned by Schurz[10] after he had considered differences in the UV and IR spectra between degraded PAN and pyridines and naphthyridenes. Instead he suggested that azomethine crosslinks (III) are formed.



III

Although this theory could explain the loss of solubility of the polymer in DMF it does not help with the problem of the chromophore. Grassie and McNeill[11] pointed out that much more conjugation was required to explain the intense colour of degraded PAN. They attributed the differences in the UV spectra between the degraded polymer and substituted naphthyridines to incomplete conjugation, supporting the partially hydrogenated structure of McCartney (II).

Another degradation scheme has been proposed by Conley and Bieron[12]. When they heated PAN at temperatures between 100° and 200°C in oxygen they noticed an increase in the IR band at $1600cm^{-1}$ but no accompanying decrease in the nitrile band at $2240cm^{-1}$. They interpreted the $1600cm^{-1}$ band as evidence for $-C{=}C-$ conjugated with a nitrile group. Other bands at $1710cm^{-1}$, $1685cm^{-1}$, $1380cm^{-1}$ and $810cm^{-1}$ were observed, the first two being interpreted as $C{=}O$ and the latter two as confirmation of $-C{=}C-H$. In the later stages the IR spectra became more complicated but from the early changes they proposed an oxidation scheme involving peroxidic intermediates, although these intermediates were not specified, leading to structure IV.



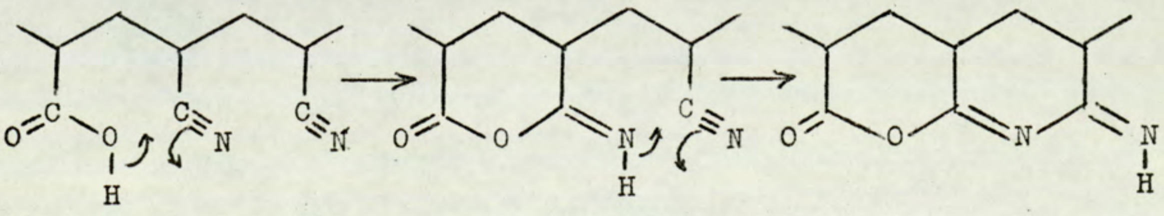
$$-CH_2-\underset{CN}{CH}-CH=\underset{CN}{C}-CH_2-\underset{CN}{CH}-$$

IV.

Support for this mechanism has come from Berlin et al.[13], and Fester[14]. Berlin and his co-workers conducted their oxidation experiments on dilute solutions of PAN in DMF and claim that the solvent has an activating effect on the α-hydrogen, although they do not discuss the nature of this effect or an oxidation mechanism.

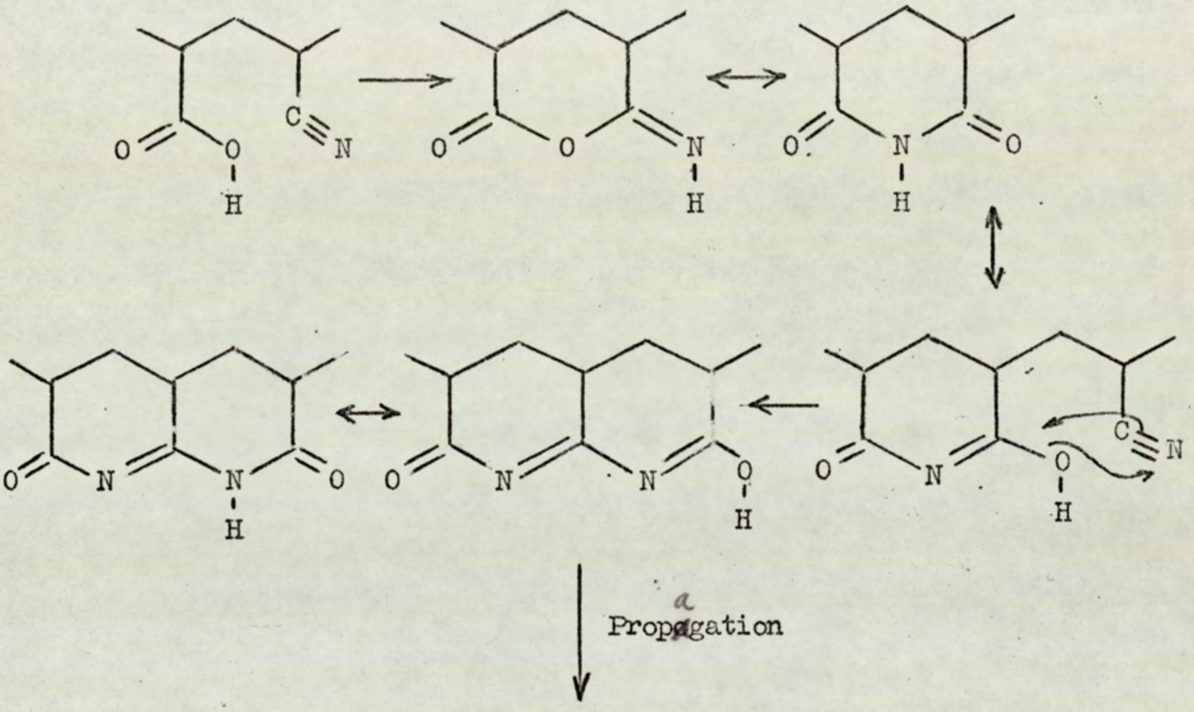
It is expected that the nitrile group conjugated with the $-C=C-$ in IV should have an IR absorption at lower wave number. Although in Conley and Bieron's work a band at 2215cm^{-1} appears which could be associated with a conjugated nitrile, this is not until much later when the C=C band at 1600cm^{-1} has attained a substantial intensity.

As mentioned previously there is little colouration below 200°C unless an initiating species is present. Grassie and Hay[15] found that nucleophiles, such as phenols and acids, acted as ~~initiations~~ initiators, particularly if copolymerised with acrylonitrile. They examined the thermal degradation in vacuum of acrylic acid, acrylonitrile copolymers and proposed an initiating mechanism involving hydrogen transfer as outlined in scheme II.



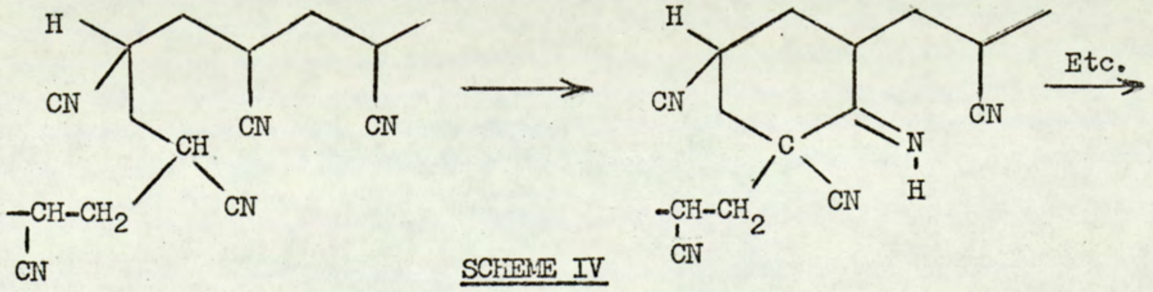
SCHEME II

Recently Grassie and McGuchan[16] modified this scheme after arguing that the carbonyl group in the cyclic compound should, by analogy with vinyl esters, have an IR absorption at higher frequencies. The observed carbonyl absorption is at lower frequencies in the degraded polymer, a fact which is best explained by the carbonyl group being part of a conjugated sequence. A mechanism to allow this has been proposed involving the transfer of an OH group instead of hydrogen (Scheme III).



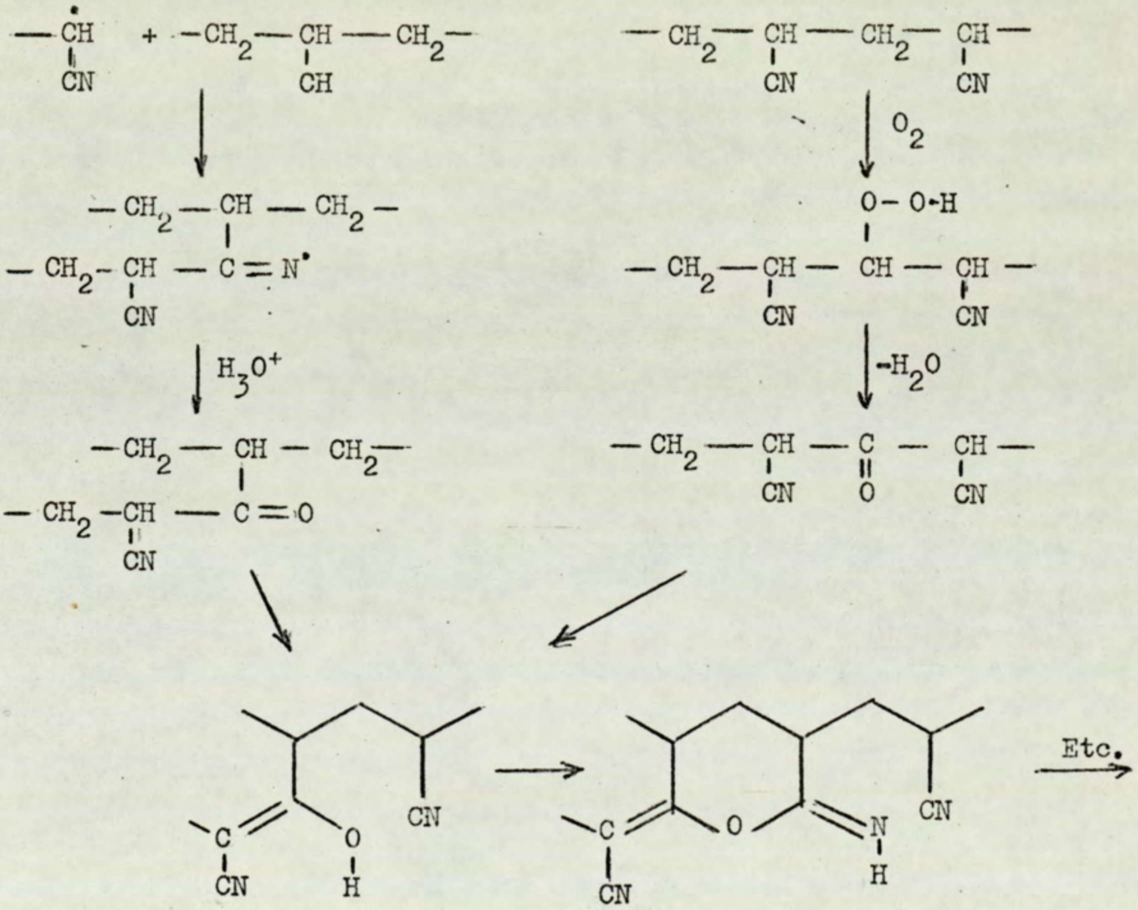
SCHEME III

A similar process to that outlined in scheme II has been suggested[15] to explain the self initiated colouration under inert conditions in the absence of nucleophilic species. It relies on the somewhat acidic nature of the hydrogen atom adjacent to the nitrile group to promote the cyclisation as shown in Scheme IV



SCHEME IV

Peebles et al.[17] have demonstrated that model compounds of PAN containing a 1,3 arrangement of nitrile groups are heat stable under nitrogen and explain the thermal instability of PAN in terms of defects present in the polymer, particularly β-ketonitriles. These species can be formed in two distinct processes; by hydrolysis of the cyanoenamine groups which arise by reaction between a propogating free radical and a nitrile group during the polymerisation of acrylonitrile, or by the oxidation of the polymer. It has been shown[18] that β-ketonitriles are capable of initiating the discolouration of PAN, presumably by nucleophilic attack on the nitrile groups through their enol form. The complete discolouration reaction is outlined in Scheme V.



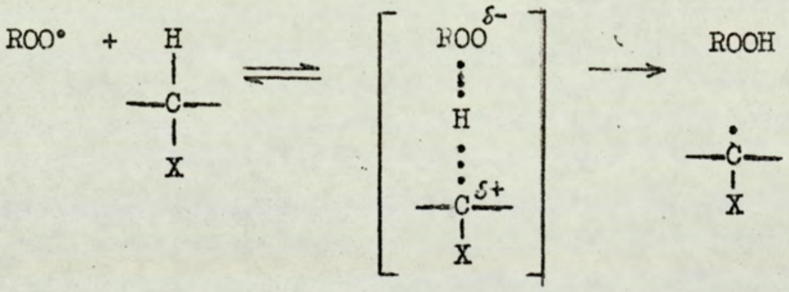
SCHEME V

It is interesting that Peebles and Brandrup found that the site of oxidative attack was the methylene hydrogens, not the tertiary hydrogens as had been previously supposed. They demonstrated this by showing that the rate of oxygen uptake in the series of compounds $CH_3\ CH(CN)(CH_2)_nCH/CN)CH_3$ (n = 0, 1, 2) increased with larger values of n. Obviously the nitrile group has a deactivating influence on the tertiary hydrogens, a fact explained by the nature of the oxidation mechanism which relies on the abstraction of a hydrogen atom by an alkylperoxy radical as a propogation step:

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

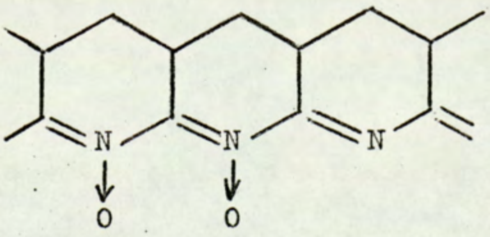
$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

The type of substituent group adjacent to a hydrogen atom can have a marked effect on the ease of abstraction of the hydrogen. This is because of the nature of the transition state:



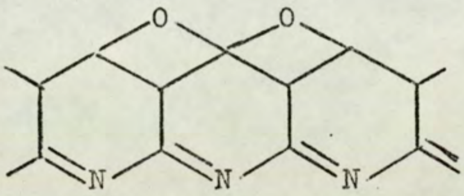
If X is electron withdrawing the transition state will be destabilised, preventing loss of the hydrogen. This is the case when X is a nitrile group and consequently the tertiary hydrogen atoms in PAN are deactivated with respect to oxidation.

To explain the oxygen content of PAN degraded under oxidative conditions Peebles and Brandrup propose the formation of a polynitrone $(\,-\!\!\!(\,C{=}\underset{\substack{\downarrow\\ O}}{N}\,)\!\!\!-\,)_2$ from the hydrogenated naphthyridene structure. They conclude[19] that degraded PAN is a random copolymer of polyimines and polynitrones (IV).

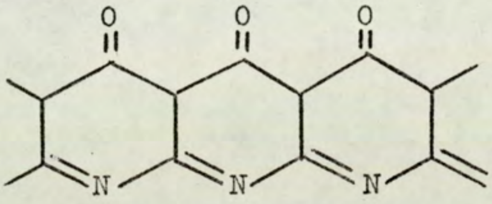


IV

Standage and Matkowsky[20] however found a correlation between the loss of hydrogen and oxygen uptake as PAN is being oxidised into the polymer and for every atom of oxygen absorbed, two atoms of hydrogen were lost. After examining the IR spectra of the oxidation products they decided that oxygen could be incorporated as either epoxide (VA) or carbonyl (VB) groups, favouring the epoxide structure on thermodynamic grounds.



VA



VB

They also report[21] that PAN fibre which had been heated under high vacuum at 290°C absorbed oxygen from the atmosphere subsequently at room temperature, changing in colour from a light or dark red to black as it did so. Even when pyrolysed at 335°C for 2 hours under nitrogen containing less than 50 p.p.m. of oxygen the product was found to contain 10% oxygen. This demonstrates the extreme sensitivity of thermally treated PAN to oxidation. None of the theories proposed so far can explain this ease of oxidation of the pyrolysed material.

(v) REACTION EXOTHERM

A very useful method of investigating thermal reactions of polymer is differential thermal analysis (DTA). The temperature of the sample is constantly compared to a reference while both are being heated at the same rate. Difference in temperature between the sample and the reference provide a measure of the thermal reactions occurring in the sample. If an endothermic process, such as melting, occurs the temperature of the sample will drop below that of the reference whilst in the case of an exothermic reaction the heat evolved will raise the temperature of the sample. Results are normally plotted as the difference in temperature ΔT against temperature.

Thermal analysis of PAN shows a sharp exothermic reaction occurring at c.a. 270°C. The actual temperature of the exotherm is strongly molecular weight dependent as shown by Thompson[9]. He prepared PAN samples with a wide range of molecular weights and found that the high exotherm temperatures were associated with higher molecular weight. The glass transition temperature (Tg) is related to the exotherm temperature (Tpk): Tpk - Tg is almost constant. In all cases Thompson found the exotherm was accompanied by a substantial weight loss (in nitrogen up to 40-50%).

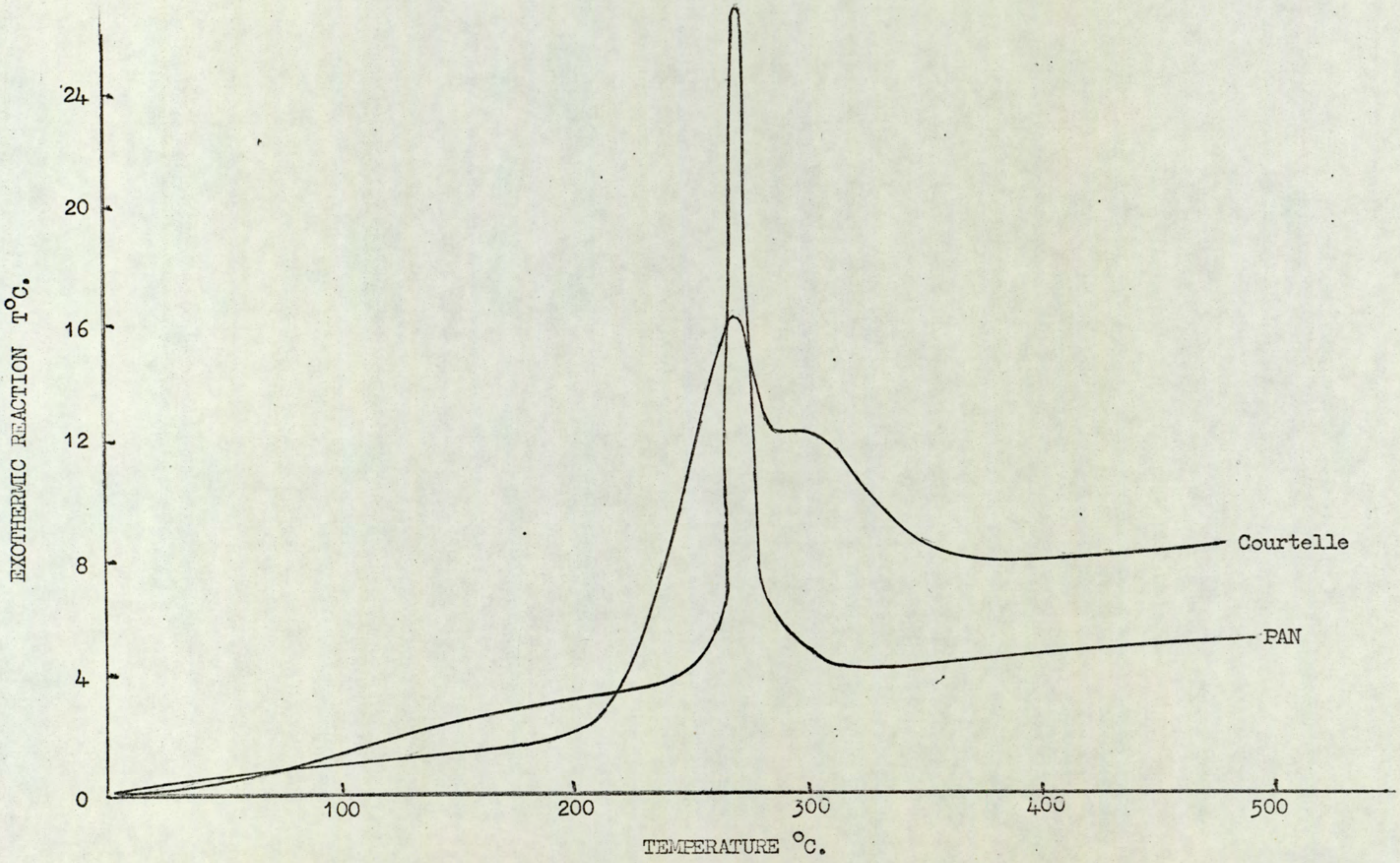
Polymer composition alters not only the exotherm temperature but also the shape of the exotherm. In general comonomer of the type usually found in commercial PAN fibres (acrylates, acrylic acid and itaconic acid) decrease the temperature at which the exotherm occurs and cause a broadening of the DTA trace. This is illustrated in figure 2 for Courtelle, a copolymer of acrylonitrile (91%), methyl acrylate (8%) and a small fraction of itaconic acid manufacturered by Courtaulds Limited. It is an excellent carbon fibre precursor since the broad nature of its exotherm reduces the problems associated with heat dissipation during oxidation.

Correlating the nitrile content of the polymer measured by IR spectroscopy during degradation with the extent of the exotherm shows that the exothermic reaction is associated with loss of nitrile[23]. Rose[24] has observed that some nitrile is lost before the exothermic reaction begins and, in the case of pure PAN, there is still a little nitrile remaining after it is complete. His results are summarised below:

1. Courtelle: 40% nitrile groups lost before the exothermic reaction. Remainder lost during the exotherm.
2. Dralon T: 40% lost before the exotherm, 40% during, and the final 20% after the exotherm is complete without further heat evolution.

Dralon T is a pure PAN fibre produced by Farben Fabriken Bayer,

FIGURE 2: REACTION EXOTHERM FOR PAN AND COURTELLE[22].



West Germany.

When subjected to rapid thermal treatment a small endotherm is observed by DTA immediately before the exotherm begins[24,25]. It has been proposed that this is a melting endotherm. PAN does not melt because thermal degradation occurs first and the polymer becomes intractable. Rapid heating can prevent this degradation occurring before the melting point is reached allowing the melting endotherm to be observed. This suggests that the reactions responsible for the exotherm take place at the melting point of the polymer.

Under isothermal conditions an exotherm is still observed after an induction period. The length of the induction period increases as the temperature is lowered. For example at 200°C Dralon T has an induction period of 11.6 minutes before any heat liberation is observed. Preoxidation increases the induction period considerably: after heating Dralon T in air to 250°C at 1°C/minute the induction period at 200°C increases to 31.53 minutes. This is contrary to what might be expected from Peebles' work[18,19]. He demonstrated that oxidation increases the concentration of initiating species within the polymer (β-ketonitriles). Therefore relaxation processes must be responsible for the isothermal induction period and not the formation of initiating species.

(vi) PHYSICAL CHANGES IN LOW TEMPERATURE TREATED PAN

Early work demonstrated that heating PAN fibre, particularly in air, produces a drastic reduction in tenacity and elongation at break, together with considerable shrinkage of the fibre[26,27]. With Courtelle however the situation is more complex; tensile strength passes through a maximum at c.a. 165° in air and 180° in nitrogen then decreases rapidly[28]. Rose[24] has carried out an intensive investigation of the changes in physical properties of PAN fibre heated in air and argon and his results show that above c.a. 260°C there is a marked divergence in the resultant properties of the fibre under these two conditions. Figures 3, 4 and 5 show clearly how under oxidative conditions tortion modulus, Young's

FIGURE 3: VARIATION OF TORTION MODULUS WITH HEAT TREATMENT.

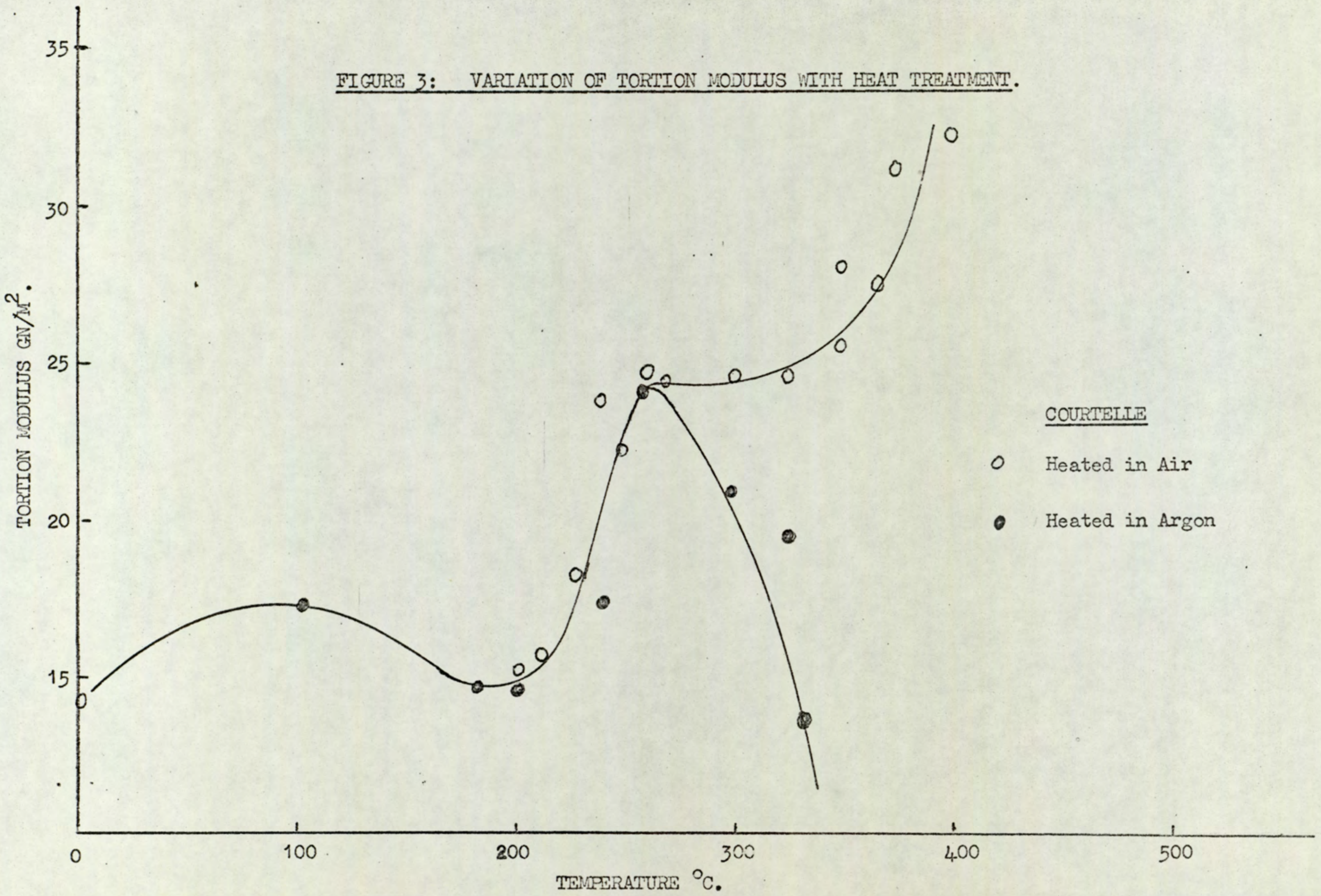


FIGURE 4: VARIATION OF YOUNG'S MODULUS WITH HEAT TREATMENT.

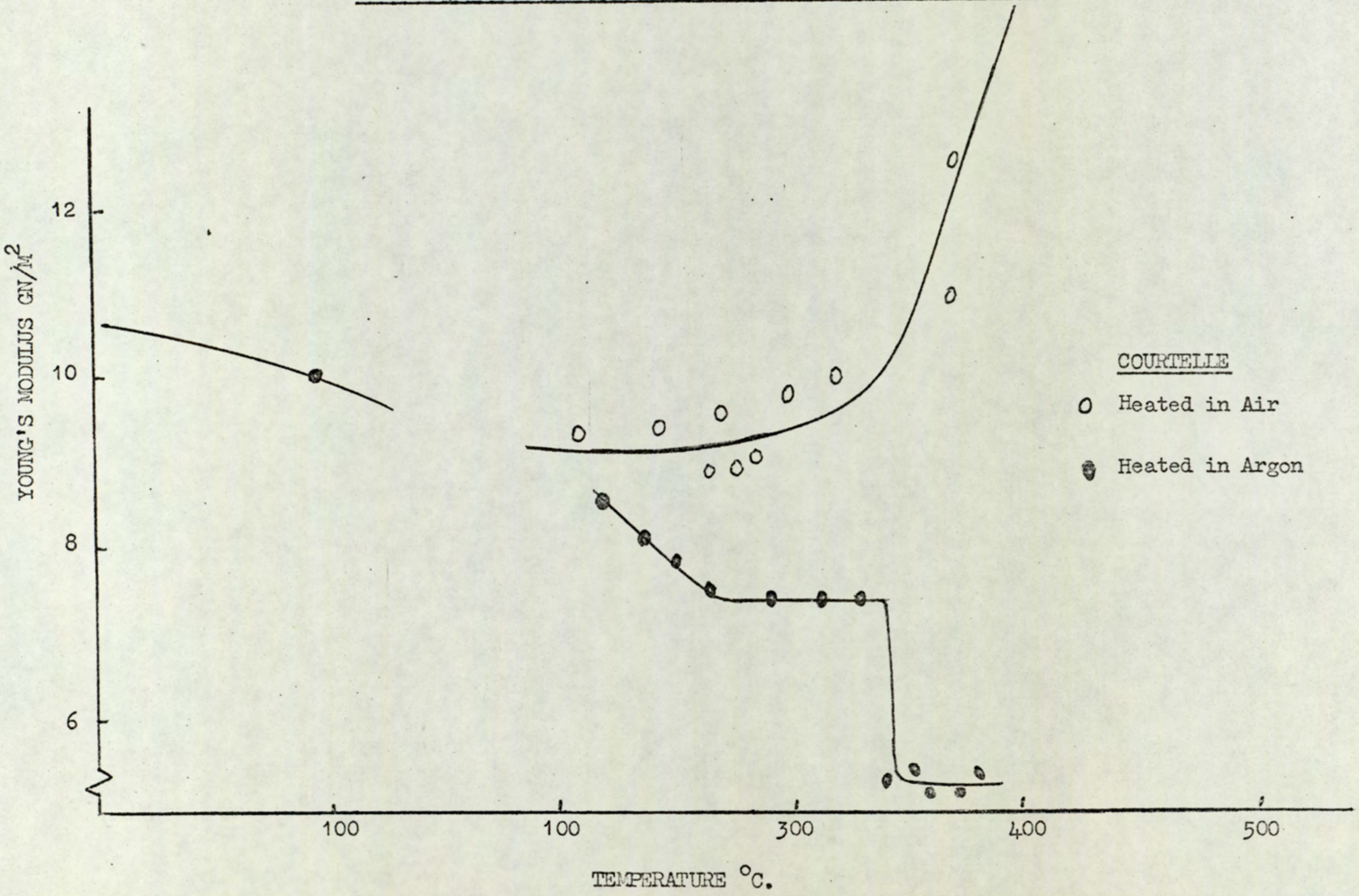
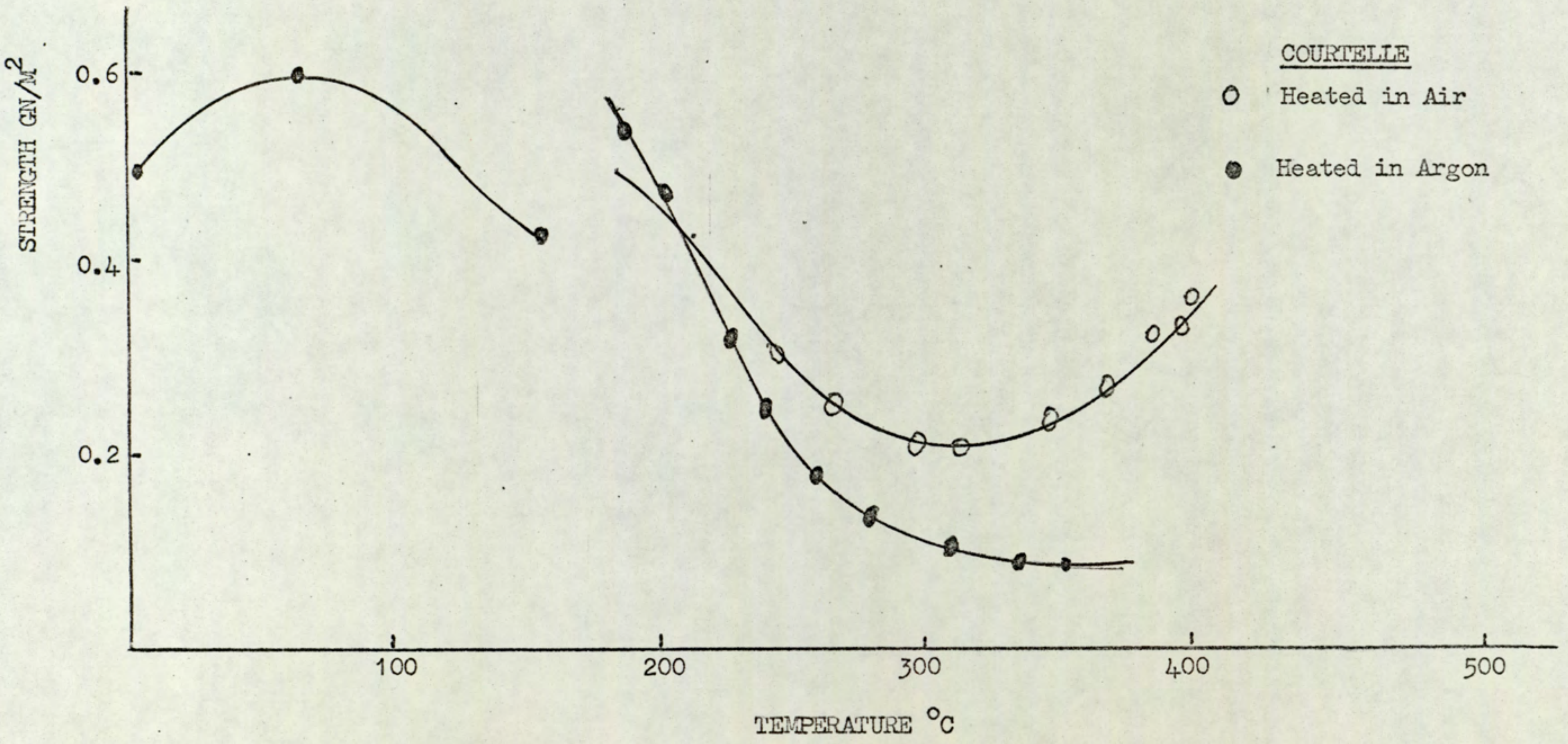


FIGURE 5: VARIATION OF TENSILE STRENGTH WITH HEAT TREATMENT.



modulus and tensile strength respectively begin to increase in value whilst in argon they continue to fall. The very significant influence of oxygen is clearly demonstrated.

Pre-oxidation also reduces the shrinkage observed when fibre is carbonised up to 1,000°C. In figure 6 the further contraction on carbonisation up to 1,000°C is plotted against the temperature and type of pre-treatment the fibre has received. Pre-oxidised samples only contract a further 10% on carbonising compared with 50% for fibres treated below 200°C. To achieve a comparable degree of stabilisation in an inert atmosphere requires pre-treatment at a higher temperature.

Pyrolysed PAN shows a considerable increase in hygroscopicity[26,27,28,29]. Again a marked difference is observed in the presence of oxygen, with moisture regain increasing continually up to 18% (Figure 7). The increase in hygroscopicity can be attributed to:

(i) An increase in the porosity of the fibre.

(ii) An increase in the number of hydrophilic groups, particularly under oxidative conditions (ketones and hydroxyls)

In all these examples the increase in physical properties associated with oxidation do not occur until after c.a. 280°C. Reference to Figure 8, a plot of residual exotherm against temperature of heat treatment shows that the exothermic reaction is over by 260°C suggesting that oxygen has no effect until this reaction ceases. This graph also demonstrates there is no significant differences between the exotherms observed under oxidative and inert conditions.

(vii) DEGRADATION OF POLYMETHACRYLONITRILE

It is interesting to compare the thermal behaviour of polymethacrylonitrile (PMAN) with that of PAN. Three different reactions are thought to occur, each at a different temperature:

FIGURE 6: FIBRE SHRINKAGE ON CARBONISATION TO 1,000°C

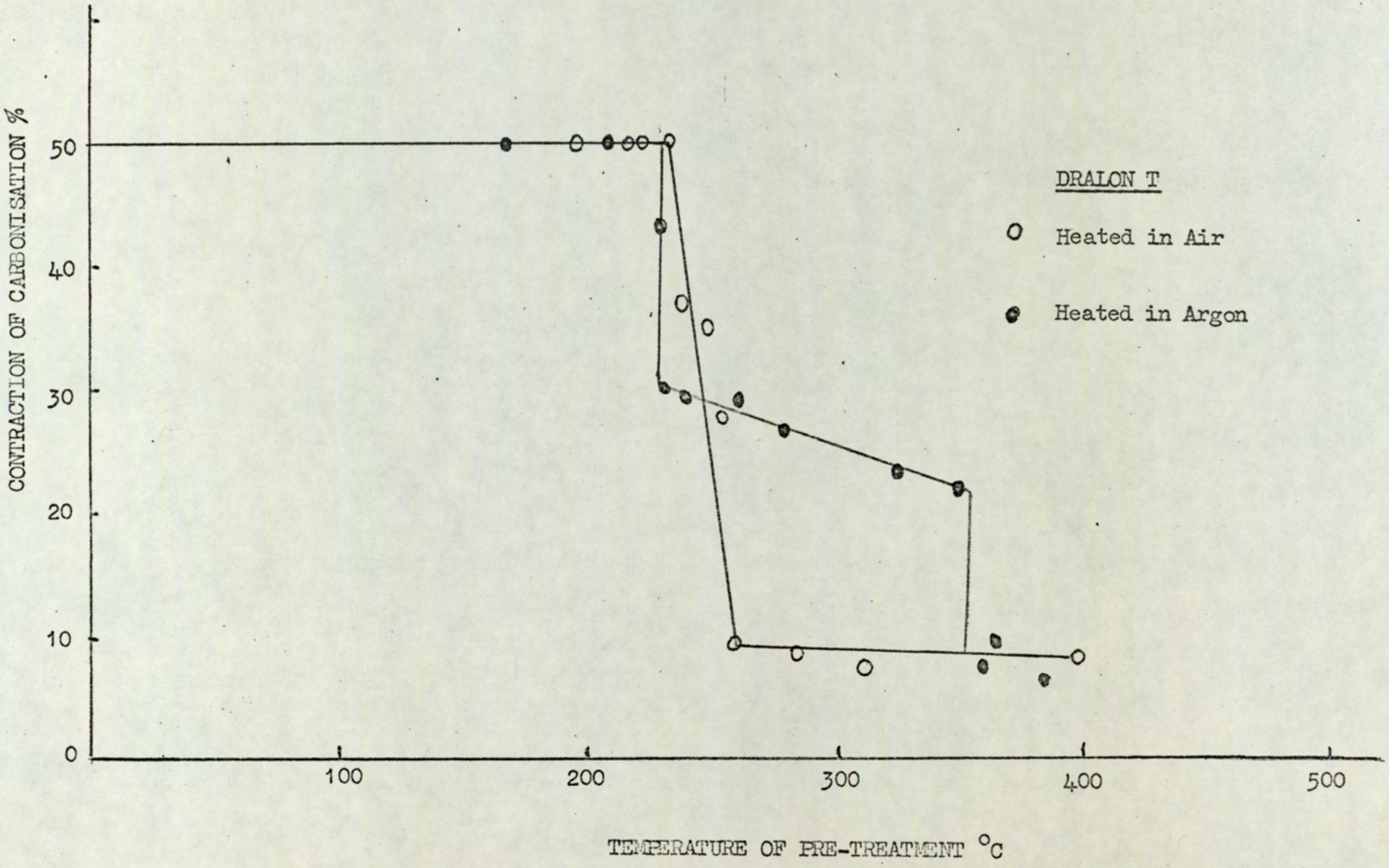


FIGURE 7: MOISTURE CONTENTS OF HEAT TREATED COURTELLE.

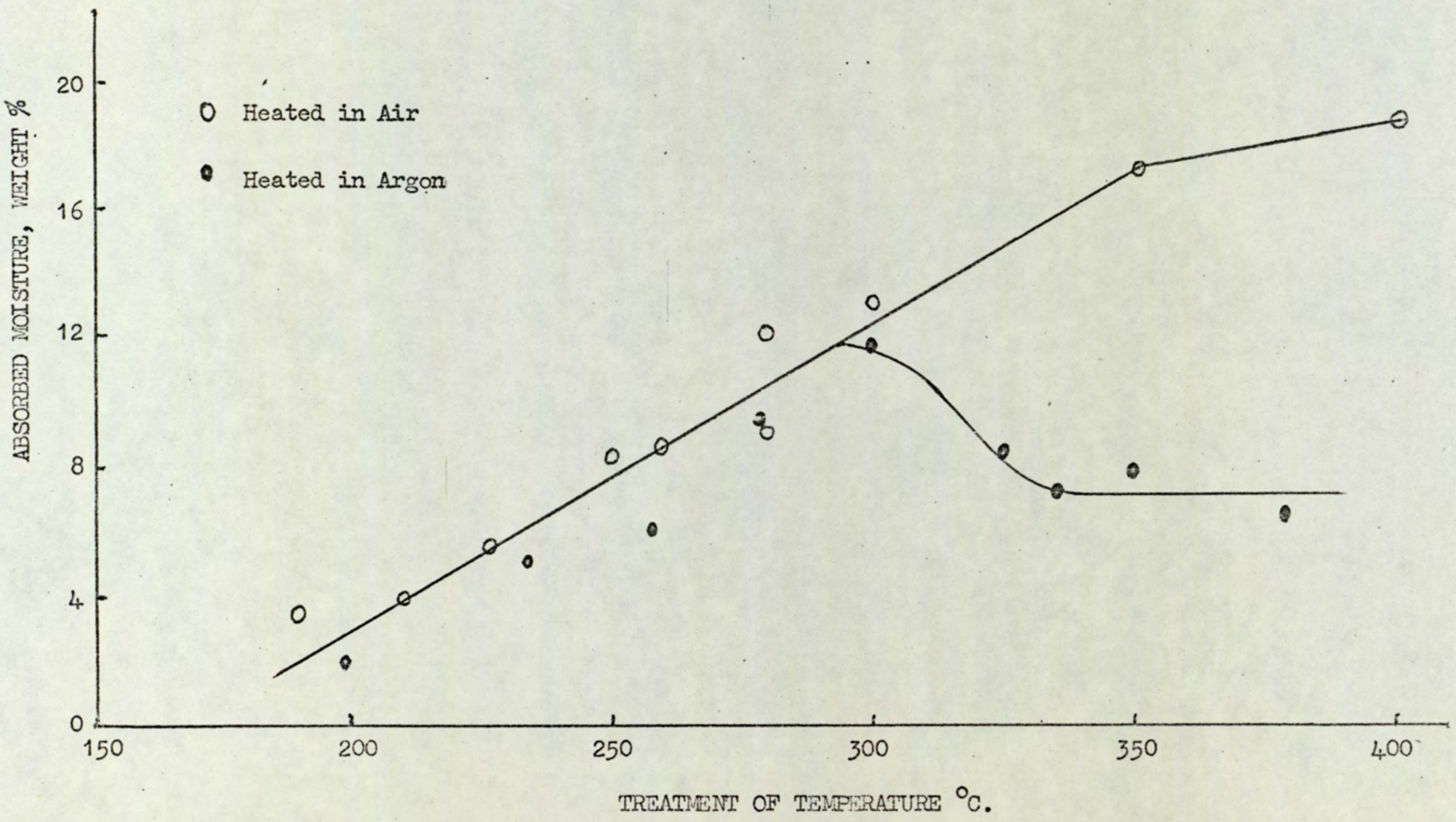
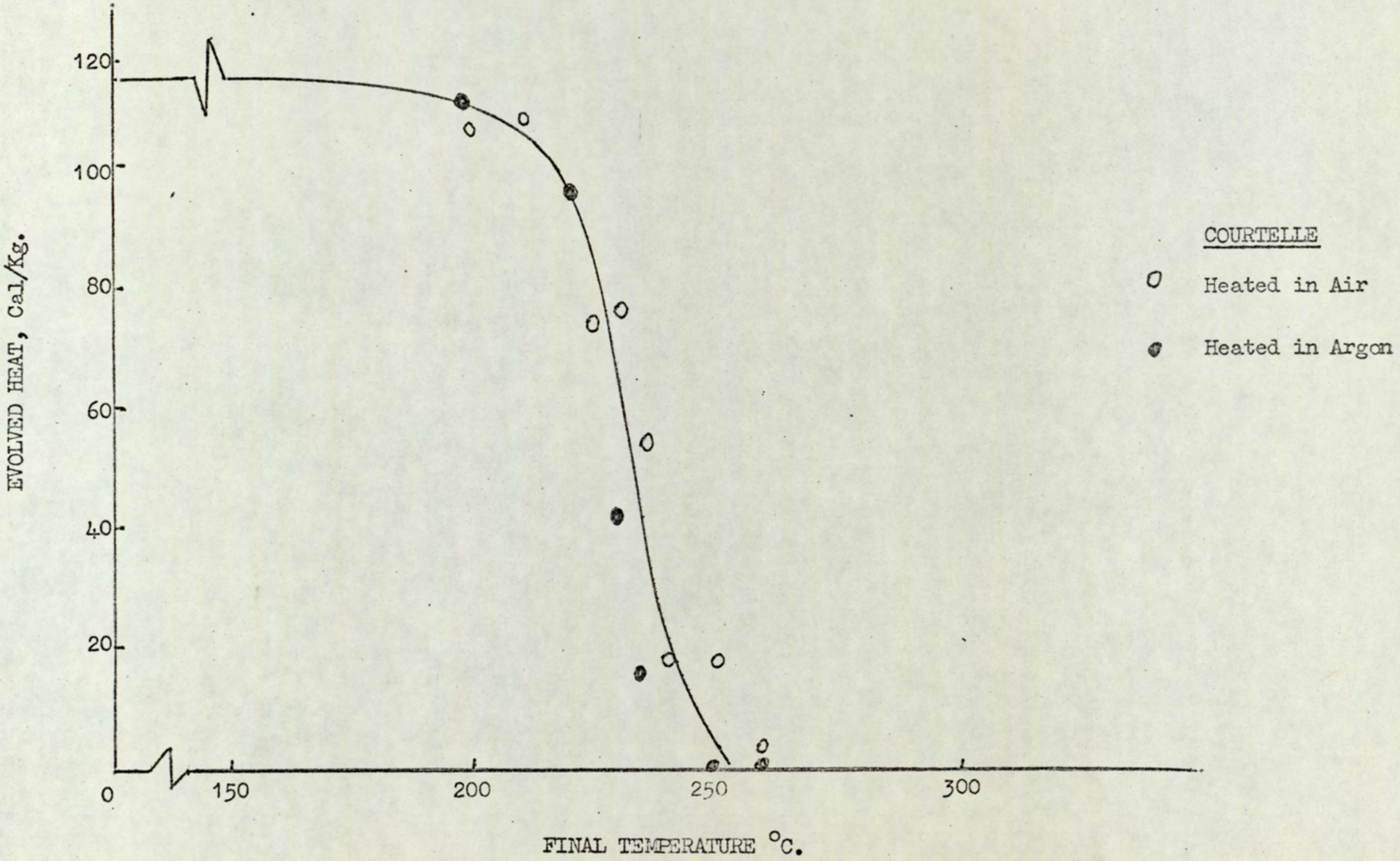


FIGURE 8: DECLINE IN RESIDUAL EXOTHERM WITH TEMPERATURE



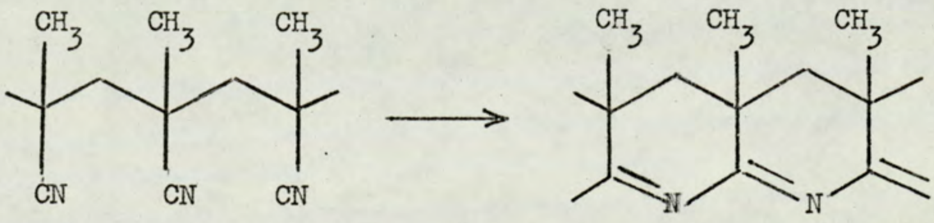
(a) Disappearance of ketene-imine linkages.

(b) Colour formation

(c) Depolymerisation.

As soon as the temperature rises there is a small but definite decrease in molecular weight and an IR absorption at 2012cm^{-1} is lost[30]. This IR absorption has been assigned to the ketene-imine structure (-C═C═N-) which is thought to be formed during polymerisation and its decomposition explains the initial fall in molecular weight. This reaction appears to be complete before there is any significant colouration of the polymer.

At temperatures of about 120° PMAN begins to discolour[31], changing through yellow and orange to a deep red. Simultaneously the polymer becomes insoluble in acetone and IR spectroscopy shows a decrease in the nitrile absorption at 2210 cm^{-1} with the appearance of broad bands in the 1693 - 1490 cm^{-1} region, thought to be $-(C{=}N)_n-$. Since there is no increase in molecular weight, the insolubility is not explained by crosslinking. It is assumed that the formation of colour and decrease in solubility is due to the cyclisation of the nitrile groups in a similar manner to PAN (Scheme VI)



SCHEME VI

The ease of discolouration is related to the purity of the original monomer and method of polymerisation. PMAN prepared under vacuum from purified methacrylonitrile, using αα' - azoisobutyronitrile as initiator, shows little discolouration at 160°C. An IR band at 1720 cm^{-1} is present in the impure polymer, the intensity of which parallels the ease of thermal discolouration. This is thought to be due to carboxylic acid groups formed during polymerisation and an initiation mechanism similar to that for the acid initiated discolouration of PAN (Scheme II) has been proposed. Since the purified polymer does not contain these groups its relative thermal stability can be readily understood.

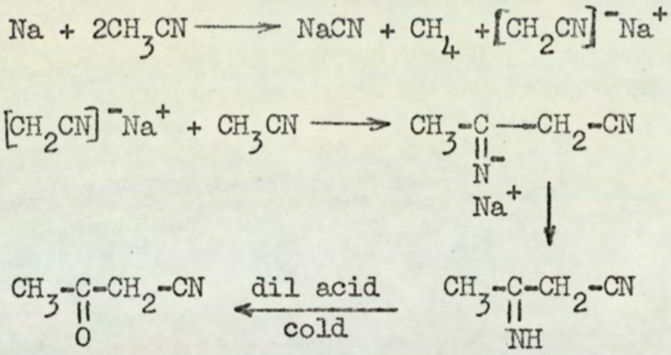
Above 220° PMAN undergoes depolymerisation to monomer. The yield of monomer depends on the extent of colouration of the polymer; cyclisation of the nitrile group appears to increase the thermal stability of PMAN. When the colouration reaction is prevented by using purified PMAN the monomer yield is almost 100% at 220°C[31]. It is thought that depolymerisation proceeds through a free radical unzipping mechanism.

In contrast to PAN the colouration of PMAN is a readily reversible reaction. Even on standing a solution of degraded PMAN in acetone or cyclohexanone is slowly bleached to a pale yellow and treatment with alkalis, acids or salts ($CaCl_2$) greatly accelerate this. The recovered polymer is spectroscopic~~ly~~ally similar to slightly discoloured PMAN.

(viii) SOME REACTIONS OF ORGANIC NITRILE COMPOUNDS

A mechanistic study of the degradation of PAN will obviously require a knowledge of the chemical properties of the nitrile group and some pertinent reactions will be reviewed here. Under basic conditions nitriles can undergo two types of reaction, proton abstraction from the α- carbon or nucleophilic attack on the nitrile group itself by the basic species.

Of the two, abstraction of the α- hydrogen is often faster, for example in the formation of the sodium salt of acetonitrile. These nitrile salts are very reactive and will condense with an original nitrile molecule in a reaction similar to the Claissen condensation of ketones (Scheme VII).



$$Na + 2CH_3CN \longrightarrow NaCN + CH_4 + [CH_2CN]^-Na^+$$

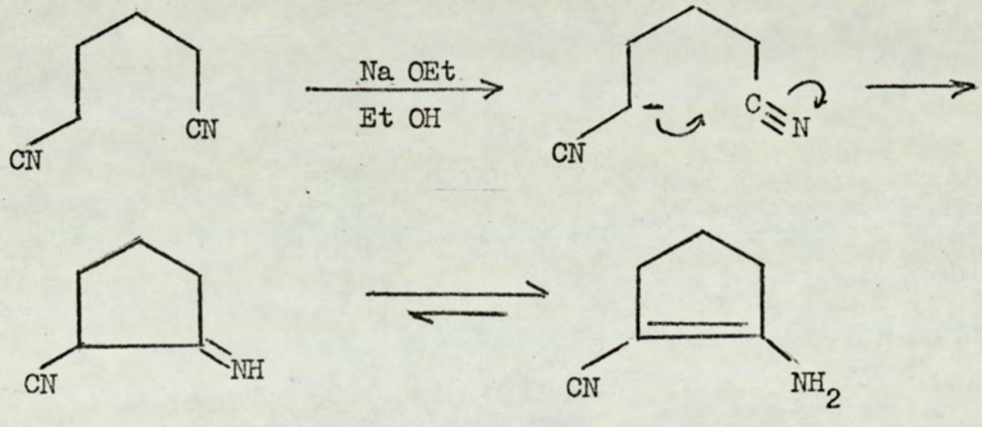
$$[CH_2CN]^-Na^+ + CH_3CN \longrightarrow CH_3\text{-}\underset{\underset{\textstyle N^-Na^+}{\|}}{C}\text{-}CH_2\text{-}CN$$

$$CH_3\text{-}\underset{\underset{\textstyle O}{\|}}{C}\text{-}CH_2\text{-}CN \xleftarrow[\text{cold}]{\text{dil acid}} CH_3\text{-}\underset{\underset{\textstyle NH}{\|}}{C}\text{-}CH_2\text{-}CN$$

SCHEME VII. CONDENSATIONS OF ACETONITRILE.

Further condensations are possible under more vigorous conditions i.e. benzyl cyanide can yield either 1,3-diamino-2-phenylnaphthalene or 4-amino-2,6-dibenzyl-5-phenylpyrimidine depending on the solvent, temperature and base used.

With dinitriles an intramolecular condensation can take place to give cyclic compounds. A well known reaction of this type is the cyclisation of adiponitrile reported by Thorpe[32]. (Scheme VIII)

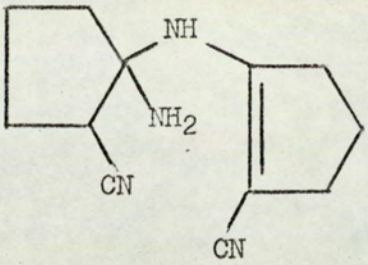


VI (a)

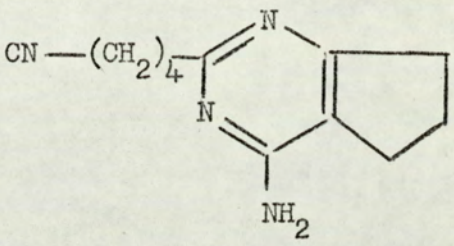
VI (b)

SCHEME VIII

The product was shown by Hammer and Hines[33] to exist in the enamine form (VIb). It is readily hydrolysed by dilute acid to 2-cyanocylopentanone. Under more rigorous conditions a dimer (VIII) is formed by combination of two 1-amino-2-cyano-1,2-cyclopentene molecules[34]. This dimer is readily converted by acid to pyrimidine (IX).

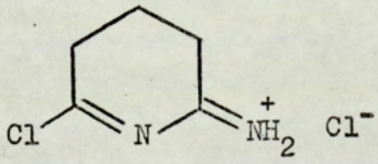


VIII



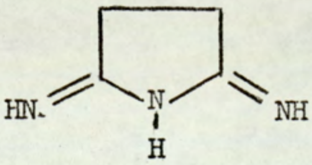
IX

A cyclisation reaction of more direct relevance to PAN is that of glutaronitrile which occurs under anhydrous acidic conditions to give a salt (X) which is readily hydrolysed by water to glutaromide[35].



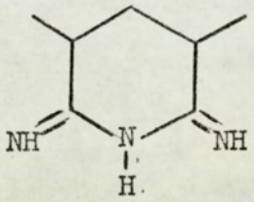
X

The similarity of this compound to the hydrogenated pyrinoid structure proposed for degraded PAN is easily seen. Another nitrile reaction that may be useful for comparative purposes is the formation of succinimidine (XI) from succinonitrile and sodamide[36].

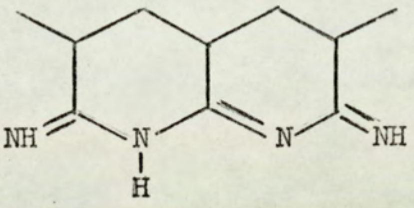


XI

Indeed this reaction has been extended to 2,4-dicyano-n-pentane and 2,4,6-tricyano-n-heptane by Takata et al.[37] and the products α,α'-dimethylglutaroimidine (XII) and octahydro-2,7-diimino-3,6-dimethyl-1,8-naphthyridine (XIII), were used as models of the degraded PAN chromophore in spectroscopic studies.



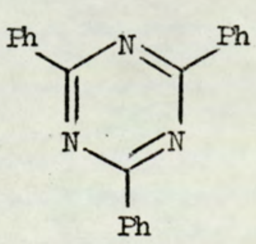
XII



XIII

It is interesting that the imidine structure ($HN{=}\overset{|}{C}{-}NH{-}\overset{|}{C}{=}NH$) is easily hydrolysed to the imide ($O{=}\overset{|}{C}{-}NH{-}\overset{|}{C}{=}O$), hence the hydrogenated naphthyridine structure proposed for the PAN chromophore should also be readily hydrolysable.

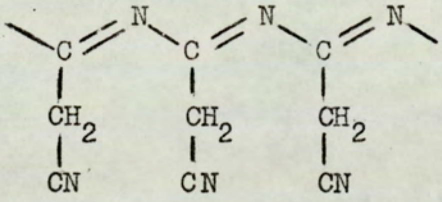
The polymerisation of nitriles containing no α-hydrogen is possible generally with the formation of triazines. Treating benzonitrile with sodium or organo lithium compounds yields 2,4,6-triphenyl-1,3,5-triazine. (XIV)[38].



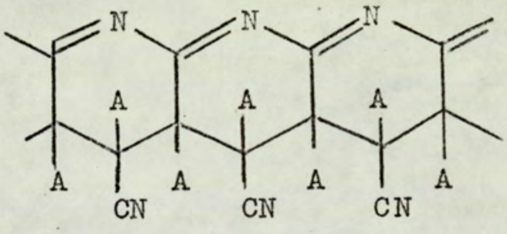
XIV

The formation of linear polymers from simple nitriles in a similar manner has been claimed by Kargin et al.[39]. They heated metal chloride complexes of the nitriles (acetonitrile, propionitrile, capronitrile and benzonitrile) to 250°C under vacuum to obtain black polymers which were assumed to be polyimines $\left(CR{=}N \right)_n$. In the early stages aminopyrimidines could be detected in the reaction mixture and it is thought that these later polymerised by a ring opening mechanism. Further investigation of the acetonitrile product by Peebles and Brandrup[19] did not confirm the polyimine structure and it is likely that the α- hydrogen is involved to some extent in the reaction.

Some dinitriles can be polymerised. Korshak et al[40] prepared heat resistant polymers from malononitrile, adiponitrile and methylcyanoacetate. They assigned structure XV to polymalononitrile and XVI to the polymers of adiponitrile and methylcyanoacetate.



XV

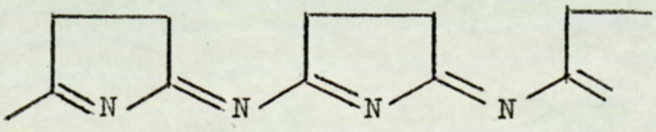


A = $-COCH_3$ (methylcyanoacetate)

A = $\left(CH_2 \right)_3 - CN$ (adiponitrile)

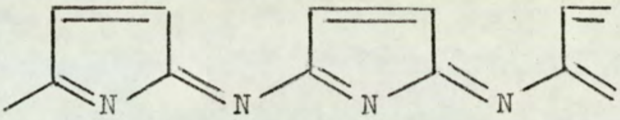
XVI

The polymerisation of succinonitrile has been brought about by base[19] and peroxides[41]. Ring closure is thought to occur in the polymerisation producing structure XVII.



XVII

Fumaronitrile and maleonitrile can be similarly polymerised by peroxides to give XVIII[41].



XVIII

The IR spectra of these polymers have a band at 2190cm^{-1} which Liepen assigns as a characteristic of the conjugated cyclic structure. He rules out the assignment of this band to conjugated nitrile, which seems most likely since almost only nitriles and acetylenes absorb in this region, because it is resistant to hydrolysis. However nitriles vary considerably with respect to ease of hydrolysis and some aromatic nitriles are particularly resistant.

(ix) CONCLUSION

It can be seen that there is considerable confusion over the structure of degraded PAN. No doubt this is due to some extent to the large variety of conditions and polymers employed by the different workers. The hydrogenated naphthyridine structure of McCartney has gained acceptance and probably is correct for PAN degraded under mild conditions. No mechanism has been postulated for the dehydrogenation of this structure to the fully aromatic ring system of Houtz which explains fairly well the properties of PAN degraded under more rigorous conditions.

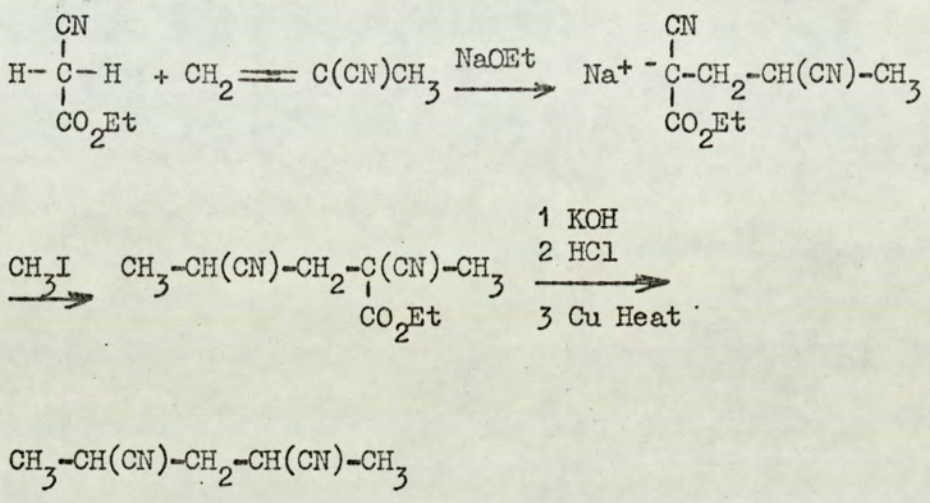
The role of oxygen in the oxidation step of carbon fibre manufacture is not apparent. It could initiate a cyclisation reaction, form cross-links or assist the aromatisation of cyclic intermediate. Originally this project was designed to learn more about this oxidation by studying the behaviour of 'model compounds', that is simple dinitriles with the same repeat unit as PAN, under oxidative and basic conditions. Whilst preparing these model compounds it became apparent that the cyanide ion was a very efficient initiator for the discolouration reaction. It was further found that the cyanide - PAN product contained oxygen and was very similar in properties to oxidatively degraded PAN, indicating that some oxidation must have taken place during the reaction.

It was felt that further investigation of the PAN-cyanide reaction, together with studies on model systems, should provide useful information on the degradation of PAN. The possibility also existed of finding a process based on the cyanide reaction which could be a substitute for the oxidation stage presently used in carbon fibre manufacture. The results and conclusions from these studies are presented in this thesis.

2. PREPARATION OF MODEL COMPOUNDS

(i) INTRODUCTION

An attempt to prepare 2,4-dicyanopentane, a model dimer of PAN, from acetylacetone was made. This compound had previously been prepared by Takata[42] and Clark[43] as follows:-



$$H-\overset{CN}{\underset{CO_2Et}{C}}-H + CH_2{=}C(CN)CH_3 \xrightarrow{NaOEt} Na^+\ {}^-\overset{CN}{\underset{CO_2Et}{C}}-CH_2-CH(CN)-CH_3$$

$$\xrightarrow{CH_3I} CH_3-CH(CN)-CH_2-\underset{CO_2Et}{C}(CN)-CH_3 \xrightarrow[3\ Cu\ Heat]{1\ KOH\ \ 2\ HCl}$$

$$CH_3-CH(CN)-CH_2-CH(CN)-CH_3$$

It was hoped that the development of a synthetic route from acetylacetone would also afford a convenient preparation of a model trimer, 2,4,6-tricyanoheptane, from diacetylacetone.

Acetylacetone was reduced to 2,4-pentanediol by sodium borohydride, this being the most convenient and efficient method found with yields claimed to be in excess of 90%[44]. Conversion of the diol to the dibromide was brought about by phosphorous tribromide but had this synthetic route proved successful the more economical method employing phosphorous and bromine would have been used subsequently. The preparation of the nitrile from 2,4-dibromopentane was attempted several times, all unsuccessfully. There was no evidence of a nitrile band in the IR spectrum of the residue although C.H.N. analysis showed a very high nitrogen content (34.8% against a theoretical 23%). It was concluded that 2,4-dicyanopentane could not be prepared by this route and Clark's method of preparation was reverted to.

Of the other nitrile compounds studied in this investigation succinonitrile and glutaronitrile were prepared and adiponitrile and maleonitrile were obtained from Koch-Light and B.D.H. respectively.

A similar route to that originally proposed for 2,4-dicyanopentane was used for the preparation of glutaronitrile, starting with propane - 1,3-diol, whilst succinonitrile was prepared from the reaction between acetone cyanohydrin and acrylonitrile[45].

EXPERIMENTAL

ATTEMPTED PREPARATION OF 2,4-DICYANOPENTANE

1. REDUCTION OF ACETYLACETONE. Ref: J. Dale[44].

To a solution of 200g of acetylacetone in 600ml of methanol a mixture of 50g sodium borohydride and 1g sodium hydroxide in 500ml of water was slowly added, keeping the temperature below 20°C by occasional cooling. After leaving over night the reaction mixture was distilled to remove the methanol and on cooling a sodium borate complex crystallised out. Further concentration of the solution yielded more of this complex. The diol was obtained by dissolving the complex in 2N sulphuric acid and extracting with chloroform. After removing the chloroform on a thin film evaporator distillation of the residue under vacuum gave 2,4-pentanediol (B.P. 97° - 98°/10 torr.)

2. 2,4-DIBROMOPENTANE

31.2g or 2,4-pentanediol was added slowly with constant stirring to 19g of phosphorous tribromide in 200ml of sodium dried benzene. Water was then added cautiously and the benzene layer separated. Evaporation to remove the benzene gave 18.6g of crude 2,4-dibromopentane which was purified by vacuum distillation (B.P. 60°/12 torr.)

3. ATTEMPTED PREPARATION OF 2,4-DICYANOPENTANE

A typical attempt at this preparation is given here. Sodium cyanide (6.5g) was dissolved in water (10ml) by gentle warming. 2,4-dibromopentane (15g) in IMS (30ml) was gradually added to the cyanide solution and the mixture was then refluxed. Normally a period of 24 - 36 hours under reflux is required to complete the reaction (see Preparation of Glutaronitrile) but after only one hour the mixture had become black and viscous. After removing the solvent on a rotary evaporator a small quantity of a viscous brown oil was extracted with ethyl acetate. There was no cyanide band ($\approx 2250\text{cm}^{-1}$) in the IR spectrum of this compound but analysis revealed a high nitrogen content (found: C, 41.6%; H, 4.0%; N, 34.8%. Calc: C, 68.8%; H, 8.7%; N, 23%).

PREPARATION OF 2,4-DICYANOPENTANE BY CLARK'S METHOD

1. ETHYL 2,4-DICYANOVALERATE

24g of 50% sodium hydride in oil was added to 113g of ethyl cyanoacetate in 300ml of dimethylformamide. After stirring for 3 hours at room temperature the solution was neutralised with hydrochloric acid, diluted with 400ml of water and extracted with ether.

After drying over $MgSO_4$ the extract was vacuum distilled to yield ethyl 2,4-dicyanovalerate (B.P. 120 - 126°/2 torr.)

2. 2-CARBETHOXY-2,4-DICYANOPENTANE

Methyl iodide (71g) was added drop-wise to a mixture of sodium hydride (12g) and ethyl 2,4-dicyanovalerate (90g) in ethanol (100ml). After the addition the solution was refluxed for 3 hours, the ethanol was evaporated off and the product extracted with ether. Distillation of the ether extract, after washing with water and drying over $MgSO_4$, gave 2-carbethoxy-2,4-dicyanopentane (B.P. 126° - 130°C/torr.)

3. 2,4-DICYANOPENTANE

Hydrolysis of 2-carbethoxy-2,4-dicyanopentane was brought about by adding 20g of it to a solution of 6g of KOH in 100ml of ethanol, keeping the temperature at about 15°C. After 2 hours the solution was neutralised with concentrated hydrochloric acid and the ethanol removed on a rotary evaporator. The 2-carboxy-2,4-dicyanopentane was extracted from the residue with ether and isolated by evaporation of the ethereal solution. The crude acid was decarboxylated directly by making a slurry with toluene and copper powder (1.0g) and heating under reflux for 1 hour. Copper compounds were removed from the reaction product by passing the solution through a short (C.10cm) column of silica gel M.F.C. (Hopkin and Williams), although a much shorter column (C.a. 1cm) could probably have been used (Clark recommends 10.50mm. of 60-100 mesh Florisil) crude 2,4-dicyanopentane was then obtained by evaporation of the toluene.

The combined products from several preparations were distilled to give four fractions boiling between 94°C and 104°C at 2 torr. No attempts were made to separate the two isomers of the dinitrile although crystals, presumably of the racemic compound (LIT. M.P. 50°C), formed in the two lower boiling fractions after several months.

PREPARATION OF GLUTARONITRILE

1. 1,3-DIBROMOPROPANE

To 500g of 48% hydrobromic acid a 150g of concentrated sulphuric acid was slowly and carefully added followed by 91g of propane-1,3-diol. A further 240g of concentrated sulphuric acid was carefully added and the mixture was refluxed for 3 hours. After refluxing a mixture of water and the dibromide was distilled from the product. The bromide layer was separated and washed in turn with water, concentrated hydrochloric acid, water, 5% sodium bicarbonate and water. After drying over magnesium sulphate it was distilled, the fraction boiling between 162° and 165° being collected.

2. GLUTARONITRILE

To a solution of sodium cyanide (147g) in 150ml of water a solution of 250g of 1,3-dibromopropane in IMS (500ml) was added over a period of 30 minutes. The mixture was then refluxed for 36 hours after which period the IMS was distilled off. The residue was then extracted with ethyl acetate (200ml), the extract filtered, dried over magnesium sulphate, and the ethyl acetate distilled off. Crude glutaronitrile so obtained was purified by distillation under vacuum (B,P, 139°-140°C/8 torr.)

PREPARATION OF SUCCINONITRILE

1. ACETONE CYANOHYDRIN

With constant stirring 30% sulphuric acid (334g) was added slowly to a solution of sodium cyanide (47g) and acetone (58g) in 200ml of water. The temperature was kept below 20°C by using an ice bath. After adding the acid the mixture was stirred for 15 minutes then extracted with ether. After drying over magnesium sulphate the ether was evaporated to yield crude acetone cyanohydrin.

2. SUCCINONITRILE

A mixture of the unpurified acetone cyanohydrin (9g), acrylonitrile (5.3g) and sodium carbonate (0.5g) in 3 ml of water was refluxed for 3 hours. Succinonitrile was extracted from the product with chloroform and purified by vacuum distillation (B.P. 158°-160°C/20 torr. M.P. 49°-50°C LIT. 53°-54°).

3. PAN, SODIUM CYANIDE REACTION

(i) INTRODUCTION

Following the failure of the preparation of 2,4-dicyanopentane from 2,4-dibromopentane it was decided to test the stability of PAN itself under similar reaction conditions. When sodium cyanide was added to a solution of PAN in DMF there was an almost immediate discolouration, the solution becoming a bright yellow, and on heating to reflux the colour rapidly deepened, passing through a reddish brown to black. After a period of reflux (c.a. 2 hours) a black, nonflammable material could be isolated from the reaction by either precipitation in ether or methanol, or removal of the DMF on a rotary evaporator.

(ii) REACTION CONDITIONS

The choice of solvent is critical; a compound with a high boiling point and dielectric constant appears to be necessary. Suitable solvents are DMF, dimethylsulphoxide (DMSO) and some alcohols and diols with high boiling points.

The reaction is easily inhibited, for example by water or traces of strong acid, and organic acids considerably reduce the rate of discolouration. The inhibiting effect of acids may be due to the formation of hydrogen cyanide from the cyanide salt. Experiments have shown that hydrogen cyanide has no appreciable initiating action when passed through a refluxing solution of PAN in DMF.

(iii) PROPERTIES OF CYANIDE DEGRADED PAN

The changes occurring in PAN during the cyanide reaction were followed by CHN analysis, IR spectroscopy and TGA (Thermogravimetric analysis).

The CHN analysis of a typical COURTELLE ~~PAN~~, cyanide reaction product is shown in Table 3, together with an analysis of a typical Courtelle sample which had been oxidised.

	C%	H%	N%	Residue %
PAN degraded by NaCN for 12 hrs. in DMF	55.9	3.9	21.4	18.9
Courtelle fibre oxidised for 7 hrs. @ 260°C	57.6	1.9	21.7	18.8

TABLE 3. COMPARISON OF OXIDISED AND CYANIDE TREATED PAN.

The similarity of these results for the oxidised and cyanide treated material is at once apparent, although the latter contains considerably more hydrogen. The large residue in the case of the PAN, cyanide product is difficult to understand but the overall similarity of the two sets of results suggest it may be due to oxygen. This implies that during the cyanide initiated degradation extensive oxidation must also be occurring.

IR spectroscopy provides a useful method of following the changes in chemical structure as PAN degrades, although detail is soon lost and at higher degrees of degradation only very broad bands are observed. The spectral changes are similar to those occurring in PAN during oxidation and can be seen in Figure 9. Also included for comparison is an IR spectrum of PAN oxidised in refluxing ethylene glycol.

The main changes are:

(a) The appearance of a broad band in the region 3200 to 3600cm^{-1}. This can probably be assigned to amine or amide formation, perhaps with some hydroxyl groups.

(b) A decrease in the aliphatic C-H stretch (νC-H) at 2940cm^{-1} together with some broadening.

(c) A decrease in the nitrile band at 2250cm^{-1}, with the appearance of a new absorption at approximately 2200cm^{-1}. This is almost certainly due to a conjugate nitrile group. A shoulder also appears in this region at 2610cm^{-1} suggesting a third nitrile absorption.

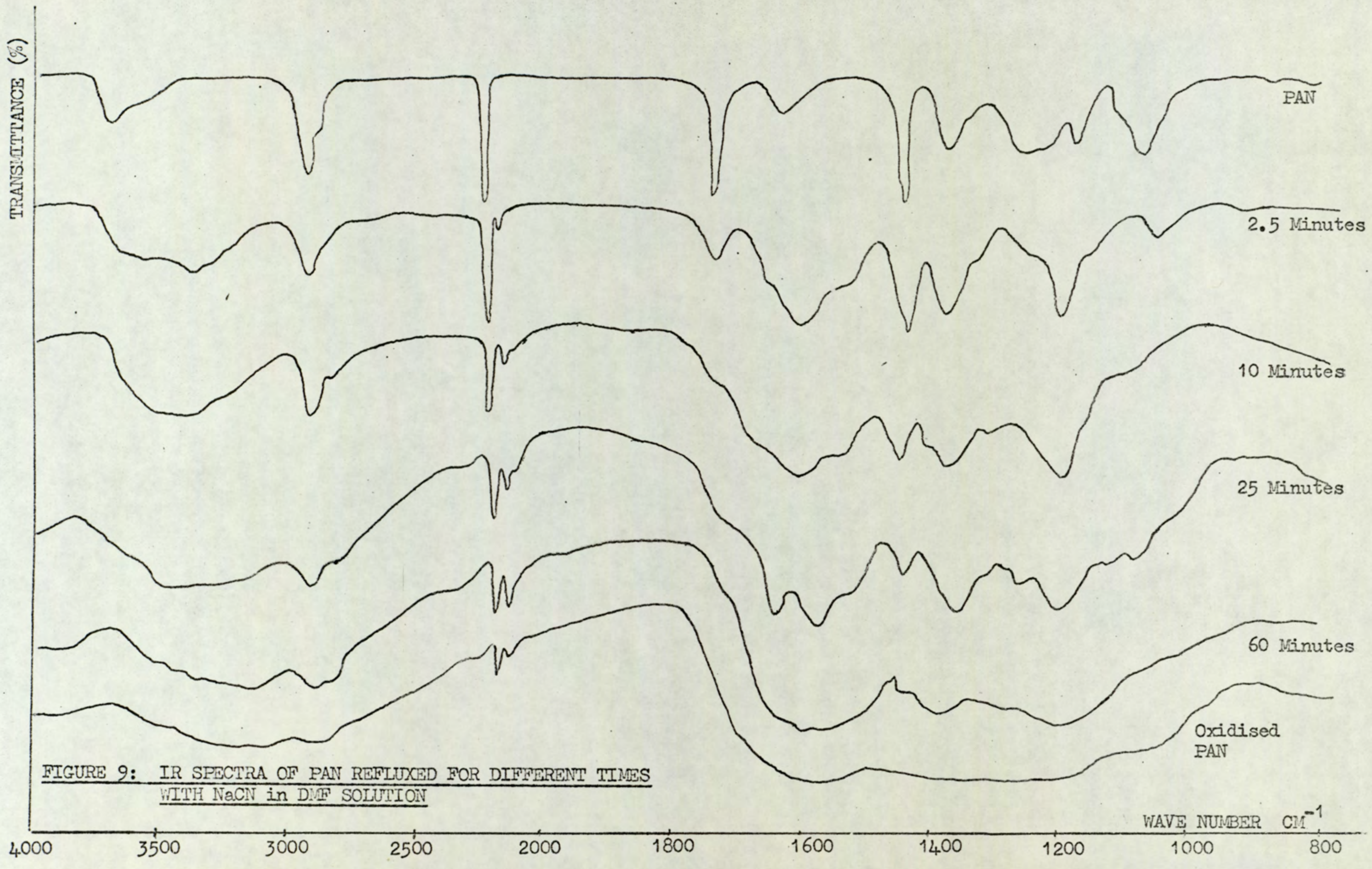


FIGURE 9: IR SPECTRA OF PAN REFLUXED FOR DIFFERENT TIMES WITH NaCN in DMF SOLUTION

(d) Absorptions appear in the double bond region (1550-1760cm^{-1}) which increase in intensity and gradually merge into a broad band. Two characteristic maxima appear at 1590-1600cm^{-1} and at 1660cm^{-1}. A band at 1740cm^{-1} already present in the polymer gradually decays.

(e) The band at 1460-1450cm^{-1}, which is almost certainly a methylene rocking mode (δCH_2), decreases continually with increasing extent of reaction, especially when compared to the adjacent band at 1370cm^{-1}. Although assignment of this band is doubtful, Liang and Krimm[46] suggest it may be caused by methyl group irregularities; it does appear to remain constant and provide a good internal reference for comparing the intensities of the 1450cm^{-1}band.

(f) A general increase in overall absorption and loss of detail as the extent of degradation increases.

Interpretation of these IR changes is difficult, particularly because of the broadness and lack of detail in the double bond region (1550-1800cm^{-1}). The following groups are likely to absorb in this region : $>C=C<$, $>C=N$, aromatics, carbonyls, and amines. There is good reason to expect all of these groups to be present to some extent in degraded PAN. To complicate matters even more there must be considerable conjugation present to explain the intense colour of degraded PAN. Therefore, the basic absorption frequencies of these groups will be considerably shifted, making the unambiguous assignment of bands impossible.

The disappearance of the nitrile group, together with the appearance of bands in the double bond region suggest that cyclisation is occurring, but the apparent loss of methylenic hydrogens probably indicates that dehydrogenation, or oxidation, is also taking place and fully aromatic structures are being formed. This is similar to what is thought to happen during the oxidation of PAN[5] and it is likely that similar structures are being formed.

Further comparison between the cyanide, PAN product and oxidised PAN is possible by the use of thermogravimetric analysis (TGA). As PAN is heated up to c.a. 1,000°C, the weight loss curve is characteristic of the pre-treatment the polymer has received. This can be seen in Figure 10, where the different shapes of the curves for untreated PAN and a preoxidised Courtelle fibre is at once evident. In the same graph the similarity between the TGA curve for a sodium cyanide treated sample of PAN and the preoxidised material's curve can be seen.

After carbonising to 1,000°C in the thermobalance a CHN analysis was carried out on the residue and this is shown in Table 4 together with an analysis of a residue produced by heating preoxidised Courtelle under similar conditions. Again the results from the two different pre-treatments are in fair agreement, suggesting close similarities in their structures.

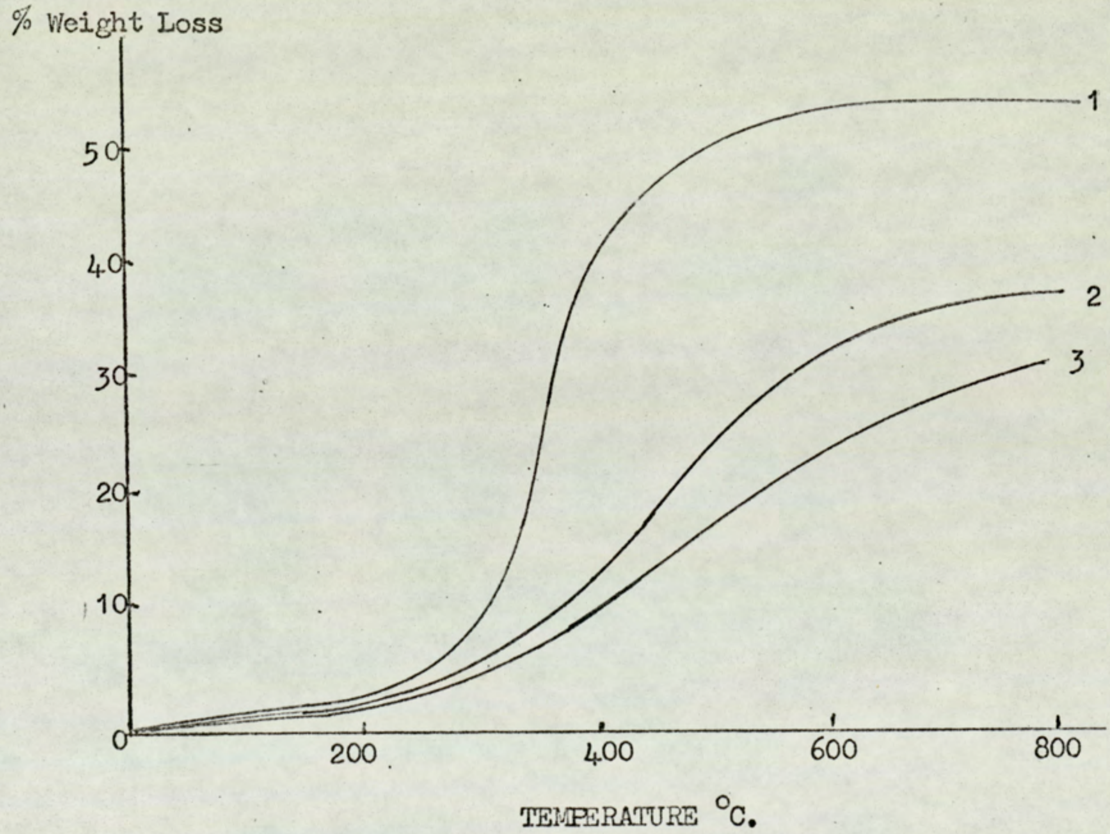
	C%	H%	N%	Residue %
PAN/NaCN/DMF heated to 1,000°C	81.0	0.3	12.0	6.7
Courtelle Preoxidised @ 220 heated to 1,000°C	89.3	0.3	10.9	0.5

TABLE 4: PREOXIDISED AND CYANIDE TREATED COURTELLE AFTER PYROLYSIS TO 1,000°C

(iv) METHOD OF CYANIDE ION INITIATION -

The role of the cyanide ion in the discolouration reaction was determined by reacting an excess of sodium cyanide with PAN. The most likely reaction on a theoretical basis is the nucleophilic addition of the cyanide ion to a polymer nitrile group and therefore the

FIGURE 10: THERMOGRAVIMETRIC ANALYSIS OF PAN



1. PAN
2. PAN/DMF/NaCN
3. PAN Oxidised.

initiating cyanide ion should be detectable by IR spectroscopy. The IR spectra of the degraded material isolated from the reaction between PAN and an equimolar concentration of sodium cyanide is shown in Figure 11. A new and very intense nitrile absorption is present at 2160cm^{-1} which must be associated with the initiating cyanide ion. In the IR spectra of other cyanide degraded PAN samples there is usually a shoulder at this wavenumber which is to be expected with the small concentration of sodium cyanide (c.a. 5% with respect to polymer) employed in these cases. There is no evidence of this band in samples of PAN and Courtelle which have been oxidatively degraded.

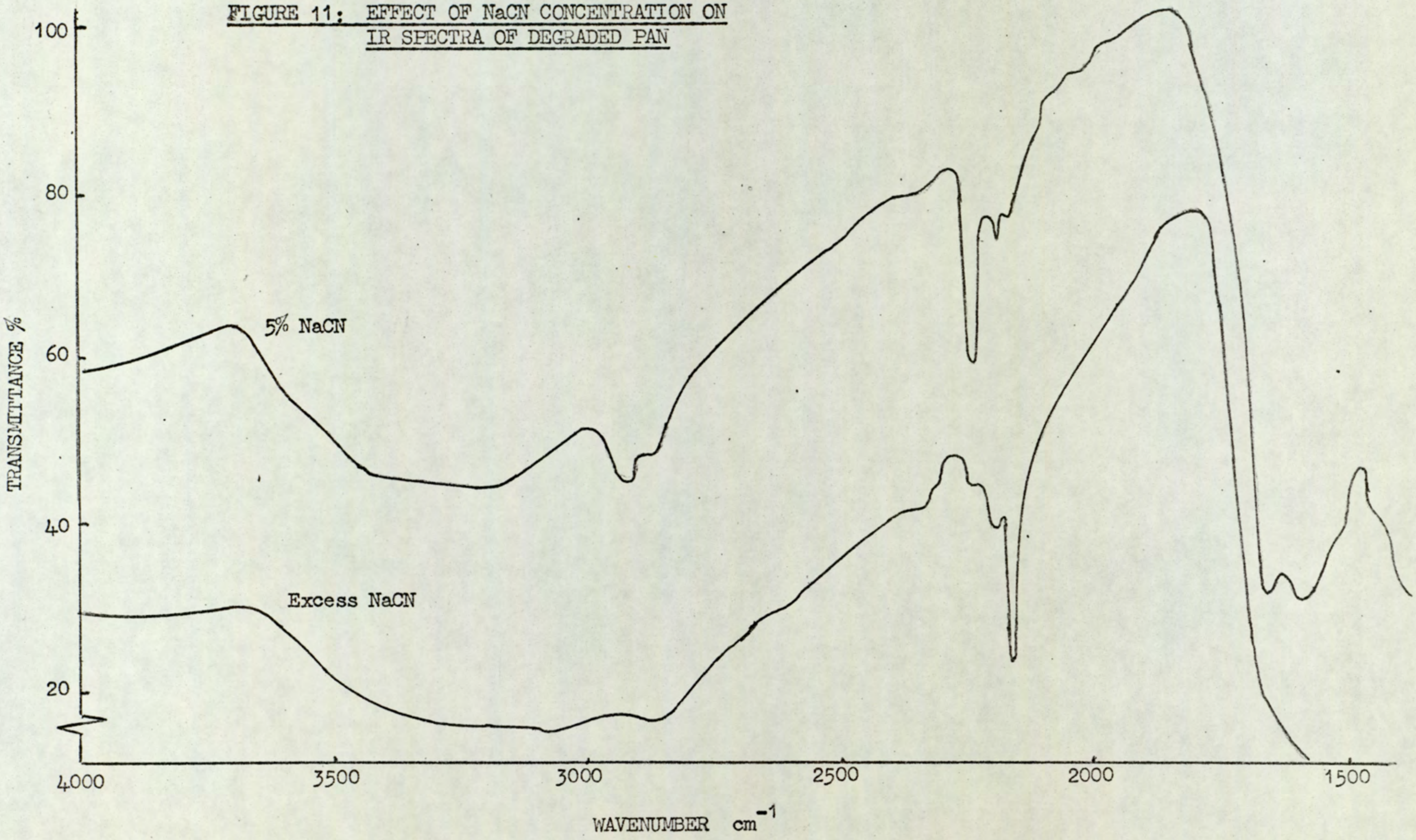
The low frequency of the absorption associated with the initiating nitrile group suggests a high degree of conjugation since it is well below that normally expected for even unsaturated alkyl nitriles (2235-2215cm^{-1}). In fact the band falls in the region associated with isonitriles (2180-2130cm^{-1}) but the very reactive nature of this group makes such an assignment very unlikely. There is also no mechanistic reason to justify the interpretation of this band as evidence of isonitrile formation.

The possibility of sodium cyanide contaminating the reaction product is very small; isolation of the sample for IR spectroscopy was by precipitation in an excess of water followed by several washes with clean water so any excess salt should have been removed. Since sodium cyanide absorbs at 2080cm^{-1} in the IR, any impurity should be detectable and the 2160cm^{-1} band can not be the result of contamination by the salt.

(v) INFLUENCE OF OXYGEN ON THE CYANIDE, PAN REACTION

The marked similarity between cyanide and oxidatively degraded PAN has already been discussed, together with the analysis figures which suggest that oxygen is present in the reaction product. The oxygen absorption of a PAN solution in DMF containing sodium cyanide at 60°C

FIGURE 11: EFFECT OF NaCN CONCENTRATION ON IR SPECTRA OF DEGRADED PAN



is shown in Figure 12. In contrast an identical solution showed no appreciable absorption under similar conditions in the absence of the cyanide. Quantitative measurements of the volume of oxygen absorbed in this reaction were not made.

To determine whether the presence of oxygen was essential to the cyanide initiated degradation attempts were made to exclude oxygen from the system, but discolouration still occurred when the reaction was carried out under nitrogen or under vacuum after rigorous degassing. It was concluded from this that the cyanide ion promotes oxidation, but that this oxidation is not essential to the degradation mechanism.

There are two possible ways in which oxidation can proceed during the cyanide, PAN reaction:

(a) By oxidation of an active intermediate formed as part of the propagating step, e.g. the combination of oxygen with a carbanion.

(b) By oxidation of the reaction product, assuming that this is oxidatively unstable.

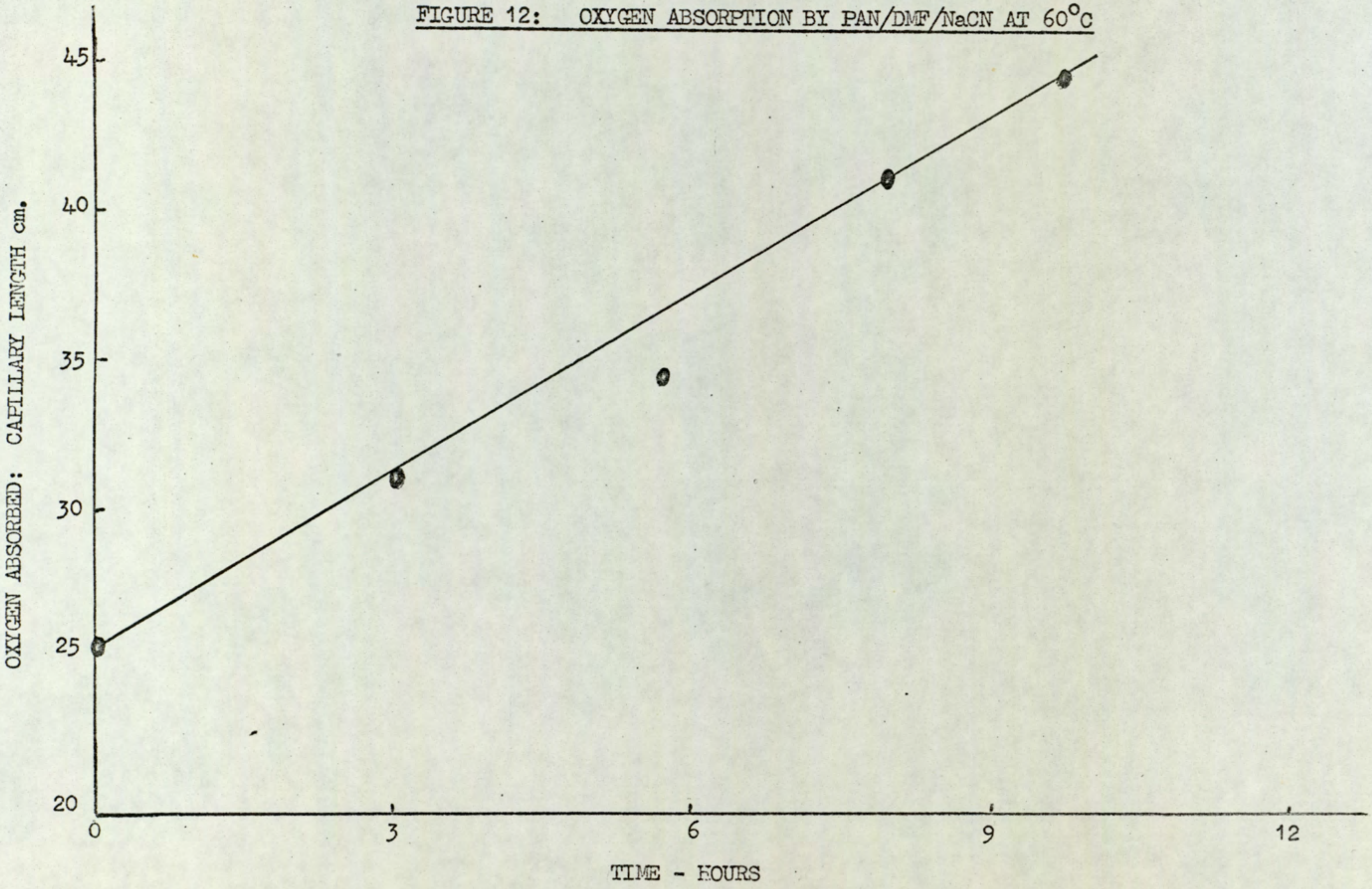
To distinguish between these two possibilities oxygen absorption measurements were carried out on PAN which had previously been degraded in solution by sodium cyanide under oxygen free conditions. Results indicate that the degraded material is very easily oxidised, absorbing up to approximately half a molar equivalent of oxygen in a few days at room temperature. Clearly the oxidation can not proceed by a mechanism of the first type (a); the product from the cyanide, PAN reaction must itself oxidise, and do so very readily.

(vi) STABILISATION OF THE CHROMOPHORE WITH OXIDATION

It is well-known that the ketimine group ($-\overset{|}{C}=N-$) is readily hydrolysed under acidic conditions :

$$(R)_2C{=}N{-}R' \xrightarrow[H^+]{H_2O} (R)_2C{=}O + H_2NR'$$

FIGURE 12: OXYGEN ABSORPTION BY PAN/DMF/NaCN AT 60°C



Since the colouration in degraded PAN has been attributed to the formation of polyimine $-(C{=}N)_n-$ sequences, it should be possible to bleach the discoloured polymer with mineral acids. For this reason the action of hydrochloric acid on PAN samples degraded by oxidation and cyanide treatment was investigated. No bleaching of these materials was observed, but it was found that if oxygen had been excluded during the PAN, cyanide reaction, the resulting product was instantly bleached on the addition of a few drops of hydrochloric acid. After standing and absorbing oxygen before the addition of acid the product became stable and no bleaching was observed. It was concluded from this result that oxidation brings about a stabilisation of the chromophoric group.

(vii) APPLICATION OF CYANIDE REACTION TO PAN FIBRE

The conventional method for manufacturing carbon fibre is a two stage process, the first stage being a carefully controlled oxidation of PAN fibre. The many similarities between oxidised and cyanide treated PAN suggested that the oxidation step may be replaceable by a treatment with cyanide salts, provided a suitable solvent system could be found. Such a solvent system would probably require a high boiling point and dielectric constant by analogy with solvents in which the PAN, cyanide reaction occurs (DMF and dimethylsulphoxide) yet neither dissolve nor damage the fibre. It was decided to investigate the alcohol series first to try and find such a solvent.

Ethylene glycol was one of the earliest solvents used. Discolouration of the fibre, a sample of Courtelle, proceeded quickly in a solution containing 2% sodium cyanide but considerable swelling of the fibre occurred and its structure was damaged to some extent. In an attempt to reduce the fibre-solvent interaction recourse was made to a long chain monohydric alcohol, n-octanol. In this solvent discolouration of Courtelle fibre was much slower and incomplete compared to ethylene glycol under equivalent conditions of cyanide concentration and temperature, but no swelling or damage to the fibre occurred.

Further experiments using mixtures of the two solvents or consecutive treatments in n-octanol first followed by ethylene glycol were carried out until it was found that stretching the fibre on a frame during treatment considerably reduced fibre damage. Results from these treatments were very encouraging (see Experimental Section): degraded fibres with very similar properties to oxidised PAN fibre as shown by TGA and chemical analysis were produced.

With the fibres supported and under the correct conditions of temperature and sodium cyanide concentration fibre damage was considerably reduced, even in pure ethylene glycol. To obtain uniform black fibres however long reaction times of up to 24 hours were necessary. A much better solvent was found to be propane-1,3-diol; providing the fibre was supported on a frame uniform discolouration was produced with no apparent damage to the fibre. For example, at 165°C and 1g sodium cyanide per 150ml solvent, 1g of Courtelle fibre was converted into silky, black fibre in three hours.

EXPERIMENTAL

All IR spectra were obtained on a Perkin Elmer PE 237 spectrophotometer. Solid materials were pressed into 13.0 mm diameter discs as a 3% mixture with patassium bromide. DTA was carried out at Aston University on a Du Pont 900, DTA and TGA on a Du Pont 950 TGA. The TGA of fibre was carried out at Rolls-Royce Limited, Derby, on a Stanton thermobalance.

TYPICAL PAN, SODIUM CYANIDE REACTION

To a solution of 2g PAN powder in 100ml of DMF was added 0.5g of sodium cyanide. An almost instantaneous yellow colouration occurred. The solution was refluxed and within half an hour had become black. After further refluxing for 12 hours a black nonflammable material was precipitated by pouring the reaction mixture into water.

IR SPECTRA OF DEGRADED PAN (FIGURE 9.)

A mixture of 2g PAN, 100ml DMF and 0.2g sodium cyanide was refluxed. Samples were removed after different reaction times and the reaction was stopped by adding water (c.a. 10 ml sample + 2ml water). The polymer was precipitated by excess ether, collected, washed with water and dried at 80°C in an oven. The IR spectrum of each sample was obtained.

INITIATION OF HYDROGEN CYANIDE

Hydrogen cyanide was generated by allowing sulphuric acid to drip onto a paste of sodium cyanide and water. The gas, after passing through a splash head, was led into a gently refluxing solution of PAN in DMF. No rapid discolouration was observed, but after several hours the solution became yellow. It was concluded that no significant initiation of the discolouration reaction was occurring.

DISCOLOURATION BY SODIUM CYANIDE UNDER INERT CONDITIONS

(1) Under Nitrogen

Nitrogen was passed through a solution of 1g PAN in 50ml of DMF for several hours. Sodium cyanide was added to the mixture and nitrogen was continued through the solution for a further twelve hours. After this time a bright yellow colouration had formed. On raising the temperature to reflux discolouration through red to a dark red occurred and within fifteen minutes the solution was almost black with polymer precipitating.

(2) In Vacuum

A solution of PAN in DMF was placed in a tube (5ml of 1% solution) and rigorously degassed by the following procedure:

(a) The mixture was frozen (liquid nitrogen) and the tube evacuated then sealed with a tap.

(b) The mixture was allowed to thaw, with bubbles of gas forming as it did so.

(c) The mixture was refrozen and the liberated gas evacuated off.

This was repeated several times until no more bubbles formed on thawing.

With the solution frozen sodium cyanide was added to the tube (0.05g) which was then again evacuated, this time backing the rotary pump with a mercury diffusion pump until a 'sticky' vacuum was achieved on a "Vacustat" manometer. The tube was then sealed.

Heating the mixture in a furnace to 150°C produced, within fifteen minutes, a deep red, brown discolouration which turned black on further heating. It was concluded that oxygen was not necessary for the discolouration reaction.

OXYGEN ABSORPTION MEASUREMENTS

Initial measurements of oxygen absorption were made by the use of inverted glass tubes, 1m long and approximately 4mm diameter. A small thread of liquid, usually water, sealed the tube and volume changes were measured by noting the position of this thread. When it was realised that considerable gas absorption was occurring, simple mercury U tube manometers were used for qualitative work and gas burettes for quantitative (Figure 13).

Before reading the volume in the gas burette the internal pressure was adjusted to atmospheric by positioning the height of B so the liquid levels in A and B were equal.

For all oxygen absorption measurements the flasks containing the material under investigation were flushed with oxygen and placed in a constant temperature bath. To ensure adequate mixing of the liquid with oxygen the flask contents were stirred with magnetic stirrers.

(1) OXYGEN ABSORPTION DURING PAN CYANIDE REACTION

10ml of a 1% PAN solution was placed in a 25ml flask together with c.a. 0.05g sodium cyanide. The flask was placed in a bath at 60°C and oxygen absorption followed by an inverted tube. The graph of oxygen uptake against time is recorded in Figure 12. No significant oxygen absorption was observed for a similar solution without sodium cyanide over the same period.

(2) OXYGEN ABSORPTION AFTER INERT PAN, CYANIDE REACTION

Solutions of PAN in DMF (concentration 1-2%) were degraded by refluxing with sodium cyanide under nitrogen. After several hours reflux the solutions were cooled to room temperature, transferred to an apparatus for measuring oxygen absorption and the oxygen uptake recorded. Initial results using simple inverted tubes demonstrated that large oxygen uptakes were occurring (Figure 14). Further work using gas burettes showed that approximately half molar equivalents

FIGURE 14: OXYGEN ABSORBED BY CYANIDE DEGRADED PAN FOLLOWED BY CAPILLARY TUBE

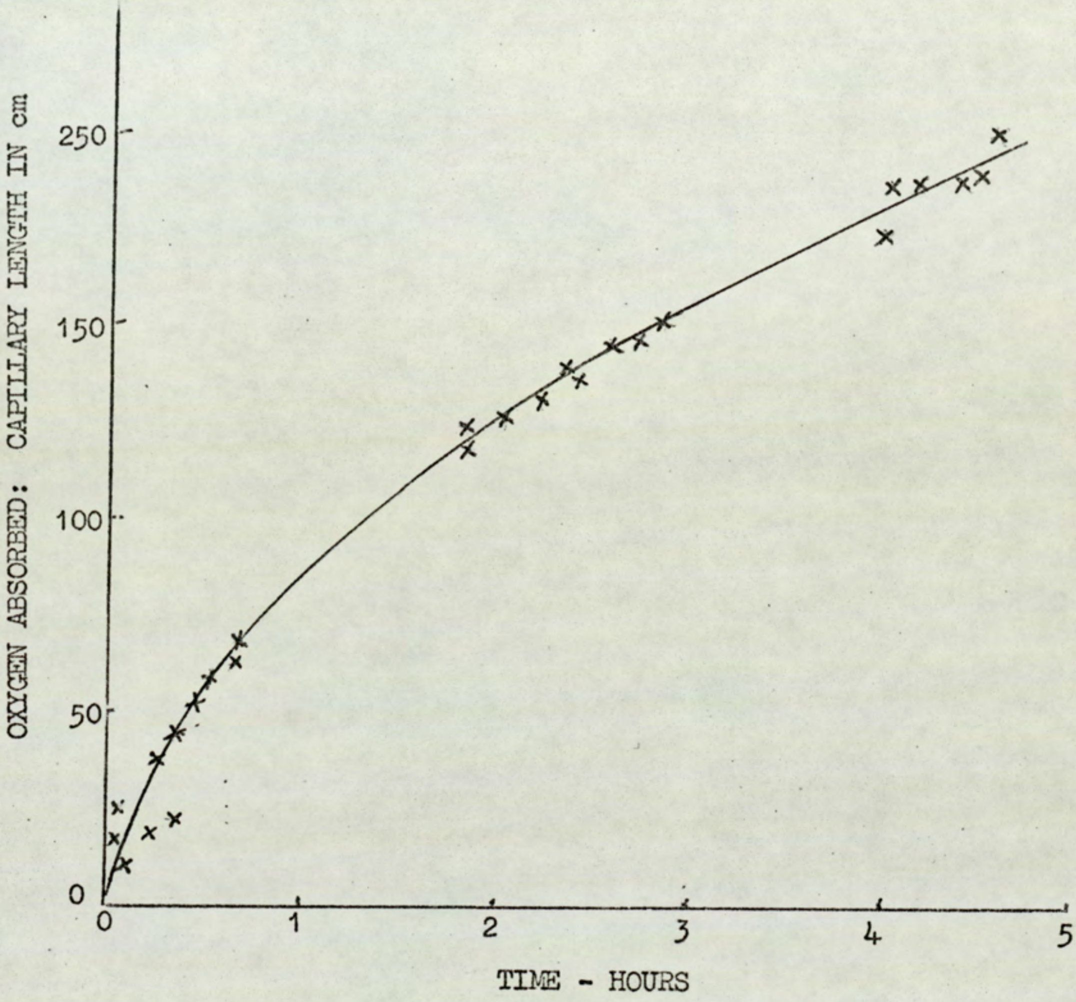
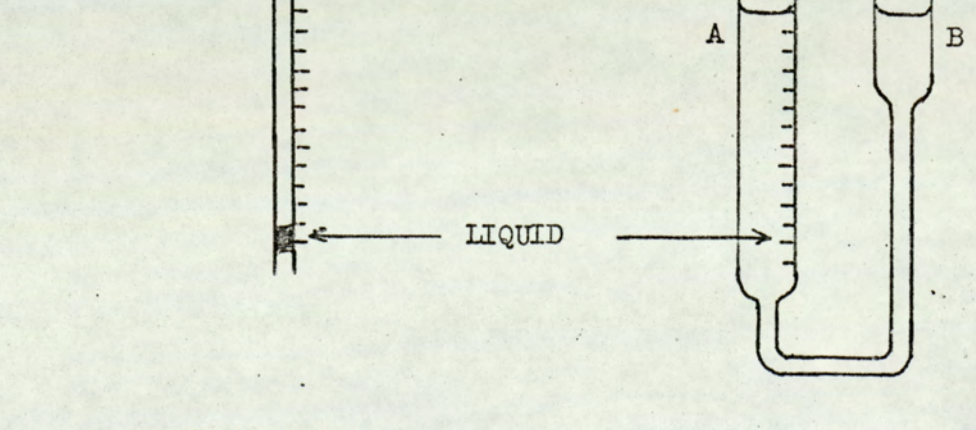


FIGURE 13: OXYGEN ABSORPTION APPARATUS



of oxygen were absorbed. Figure 15 shows the oxygen absorption curve for 0.3002g of PAN over a 80 hour period. Approximately 60ml of oxygen has been absorbed during this time. Although these results were obtained on solutions of degraded PAN it was found that oxygen absorption still occurred after removing the solvent (DMF) under vacuum on a rotary evaporator. Solutions of PAN in DMF refluxed for several hours in the absence of sodium cyanide were used as blanks. These solutions, which had become bright yellow, absorbed no significant quantities of oxygen, confirming that the degraded polymer was responsible for the observed oxygen absorption.

DEGRADATION OF PAN FIBRE

(1) Ethylene Glycol and n-Octanol

Courtelle fibre was used for all these experiments. In a typical experiment 1g of fibre was placed in 50ml of solvent with 0.5g sodium cyanide and the mixture was gently refluxed. After a period of time the fibre was removed, washed well with water and dried in an oven at 80°C.

It was found that fibre treated for 30 minutes in ethylene glycol, sodium cyanide formed a gel on soaking in water. This could be prevented by supporting the fibre on a frame before treatment. Figure 16 shows the TGA and elemental analysis of six Courtelle samples treated with sodium cyanide as follows:

1: 5 minutes reflux in ethylene glycol/NaCN.

2: 5 minutes reflux in n-octanol/NaCN.

3: 14 hours in n-octanol/NaCN.

4: 14 hours reflux in ethylene glycol/NaCN under restraint.

5: 12 hours reflux in 20% ethylene glycol, 80% n-octanol/NaCN.

6: 2½ hours reflux in n-octanol/NaCN followed by
14 hours reflux in ethylene glycol/NaCN.

It can be seen that samples 4 and 6 have a preoxidised type of TGA trace and elemental analysis shows close similarities to oxidised Courtelle.

FIGURE 15: OXYGEN ABSORBED BY CYANIDE DEGRADED PAN FOLLOWED BY GAS BURETTE.

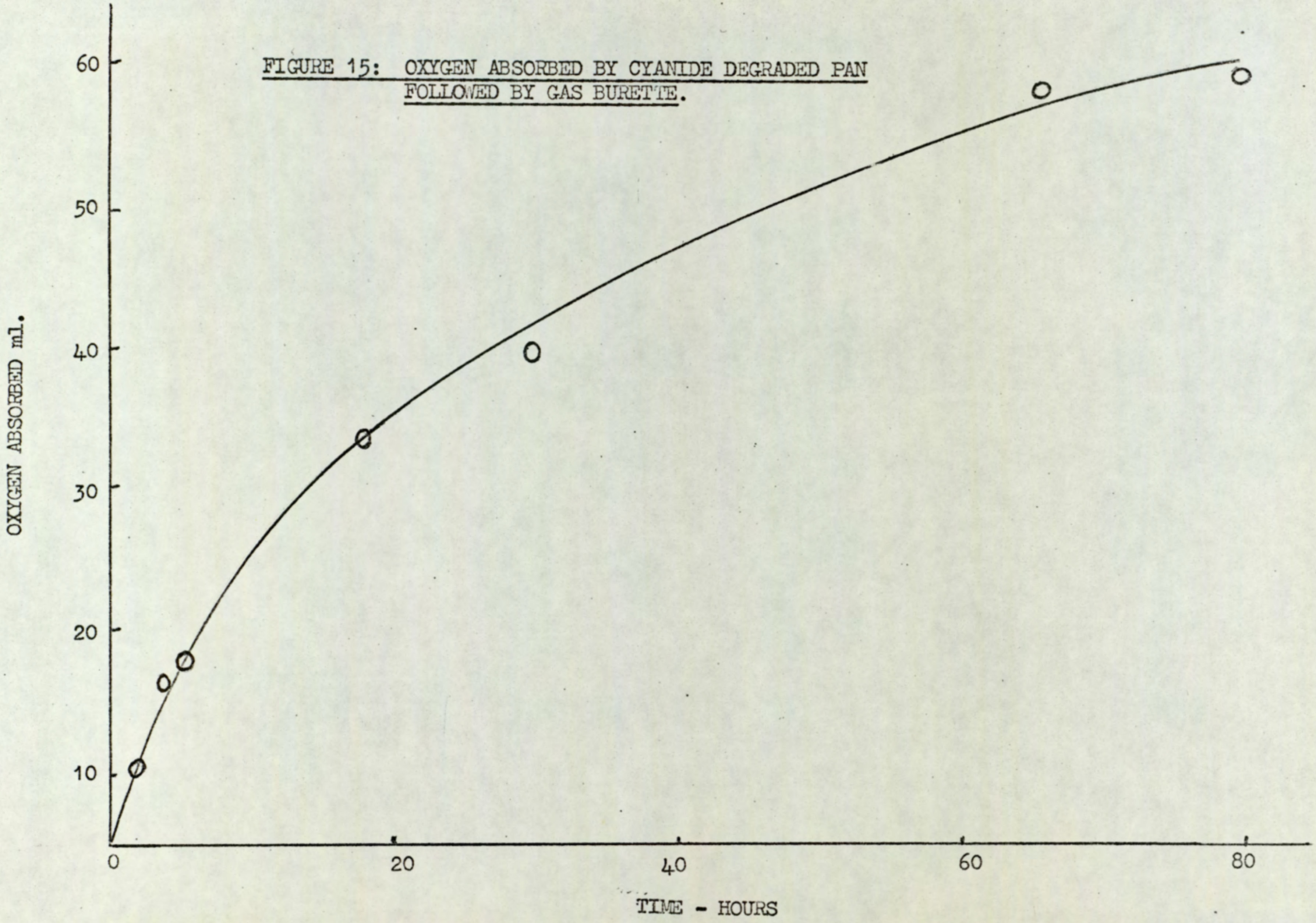


FIGURE 16a: THERMOGRAVIMETRIC ANALYSIS OF COURTELLE FIBRE AFTER VARIOUS TREATMENTS.

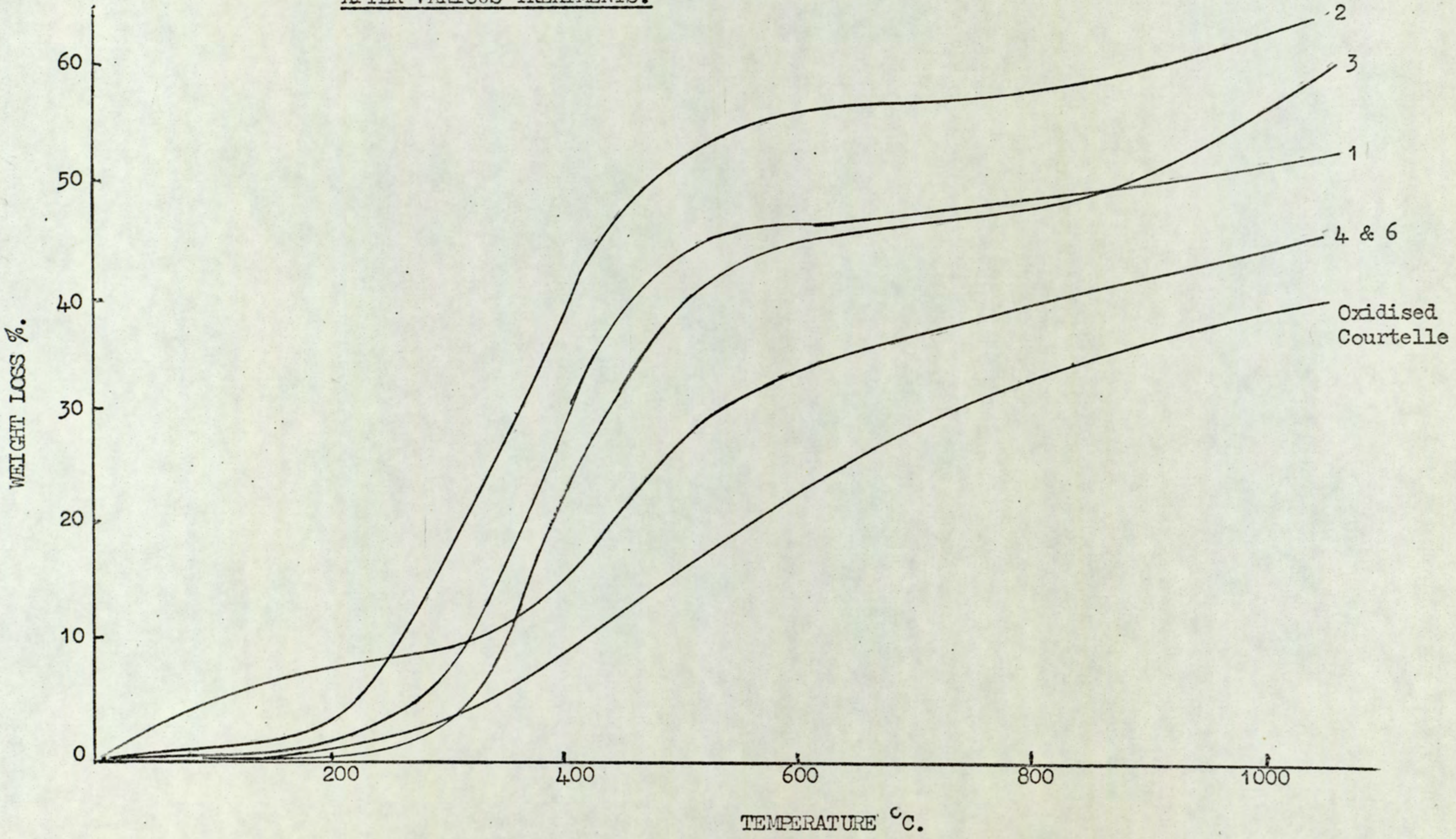


FIGURE 16b: ELEMENTAL ANALYSIS OF COURTELLE FIBRE AFTER VARIOUS TREATMENTS.

Sample	Carbon %	Hydrogen %	Nitrogen %	Remainder (Oxygen)
1	64.7	5.5	23.1	6.7
2	63.3	5.4	22.4	8.9
3	63.8	5.5	22.0	8.7
4	59.6	4.9	16.0	19.5
5	58.7	4.9	17.1	19.3
6	61.0	4.6	15.9	18.5
Courtelle Oxidised for 7 hrs. @ 260°C	57.6	1.9	21.7	18.8

(2) Pentane-1,3-diol.

Further work established pentane-1,4-diol as a better solvent. In a typical reaction 1g of Courtelle stretched on a glass frame was placed in a mixture of 150ml of the diol with 1g of sodium cyanide at 165°C. After 3 hours the now black fibre was removed, washed well with water and dried in an oven at 80°C. Black silky fibres were obtained.

At this stage the work on developing fibre treatments based on the PAN, cyanide reaction was dropped following the financial collapse of Rolls-Royce Limited and the loss of suitable facilities to study the carbonisation of these fibres.

4. CHAIN SCISSION REACTION

(i) INTRODUCTION

McCartney[6] reported a large reduction in the molecular weight of PAN when treated with base in solution. A similar reduction is observed when PAN in DMF solution is heated with sodium cyanide, although the extent of the reduction in molecular weight is not as great as reported by McCartney. A typical graph of solution viscosity versus time of heating is shown in Figure 17. It is possible that this fall in viscosity does not reflect a similar change in molecular weight; changes in molecular structure or configuration could also be responsible. However the magnitude of the viscosity change, especially in the McCartney case where it was reduced to 5-10% of its original value, does suggest that chain scission is occurring.

Pyrolysis also causes molecular weight reduction although this is often impossible to detect because the polymer becomes insoluble. Rose[24] however found some Courtelle samples sufficiently soluble in 60% nitric acid to enable viscosity determinations to be carried out. Starting with an original molecular weight of 70,000 he found:

(1) Courtelle heated at 15/12°C/minute to 260°C in argon reduced to 2,100.

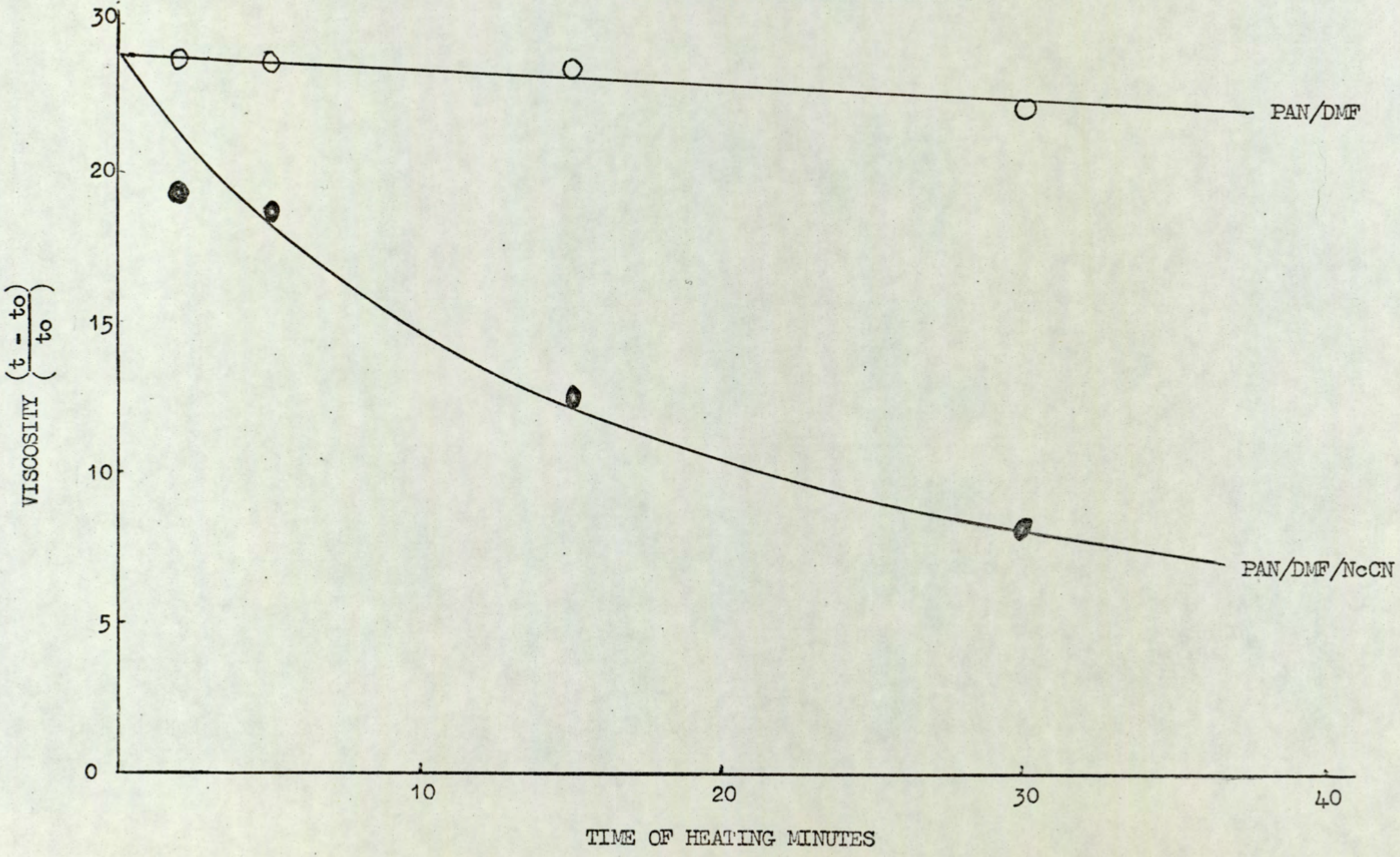
(2) Courtelle heated @ 1°C/minute to 290°C in air reduced to 3,500.

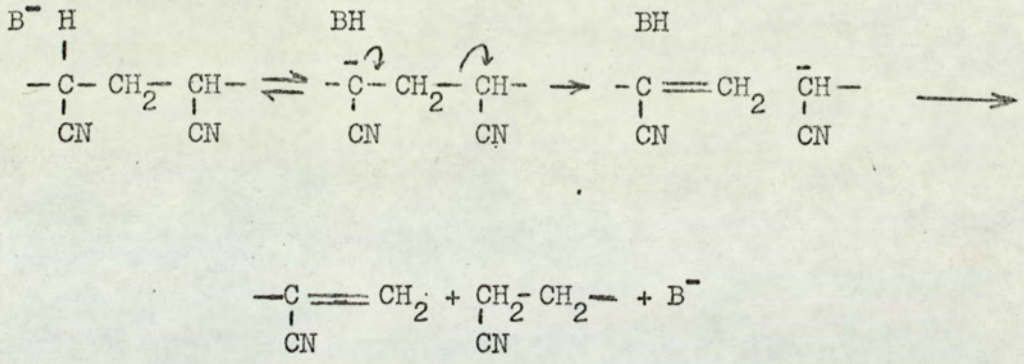
Again results may be suspect because of changes in the viscosity, molecular weight relationship but extensive chain scission on thermal treatment is suggested.

(ii) Mechanism

A probable mechanistic scheme for a chain scission reaction under these conditions is outlined below:

FIGURE 17: VARIATION OF VISCOSITY OF A PAN/DMF/NaCN SOLUTION WITH TIME OF HEAT TREATMENT

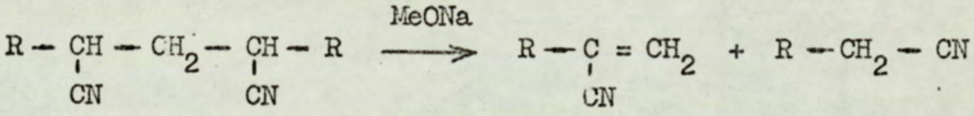




$$\overset{B^-}{}\ -\underset{CN}{\overset{H}{C}}-CH_2-\underset{CN}{CH}- \rightleftharpoons \overset{BH}{-\underset{CN}{\overset{-}{C}}}-CH_2-\underset{CN}{CH}- \rightarrow \overset{BH}{-\underset{CN}{C}}=CH_2\ \underset{CN}{\overset{-}{CH}}- \longrightarrow$$

$$-\underset{CN}{C}=CH_2 + \underset{CN}{CH_2}-CH_2- + B^-$$

Evidence that this does occur has been obtained after studies on the reactions of 2,4-dicyanopentane and glutaronitrile with bases. Both these compounds are model dimers of PAN and if they react as suggested above should yield the following products:



$$R-\underset{CN}{CH}-CH_2-\underset{CN}{CH}-R \xrightarrow{MeONa} R-\underset{CN}{C}=CH_2 + R-CH_2-CN$$

(R = H: Glutaronitrile
R = CH_3: 2,4-dicyanopentane)

Traces of acrylonitrile and acetonitrile in the case of glutaronitrile, and methacrylonitrile in the case of 2,4-dicyanopentane were detected by gas-liquid chromatography (GLC) on the distillates obtained by refluxing the dinitriles with sodium methoxide. Neither acrylonitrile nor methacrylonitrile could be detected in the reaction mixture in each case, but it was later shown that these compounds polymerise rapidly under such basic conditions. Some methanol was also detected providing further evidence for this mechanism.

During the reaction between these model compounds and sodium methoxide considerable discolouration occurred, the mixtures eventually becoming black and viscous.

(iii) CONCLUSION

In the presence of bases a chain scission reaction occurs with reduction in the molecular weight of the polymer. An intermediate carbanion is formed by loss of the somewhat acidic α-hydrogen and it is this carbanion which is responsible for the chain scission reaction.

EXPERIMENTAL

VISCOSITY CHANGES DURING THE PAN,CYANIDE REACTION

A standard solution of 2.5545g PAN in 250ml DMF was prepared and filtered through a No. 3 glass sinter. 50ml of this solution was added to 0.05g of sodium cyanide; an immediate yellow discolouration was formed. After shaking for several minutes to dissolve some sodium cyanide the solution was filtered. Samples of the solution before and after addition of cyanide were heated in an oil bath at 100°C. At regular intervals alliquots were removed from each sample and their viscosity determined in a Ubbelohde viscometer at 25°C. A plot of specific viscosity (t-to)/to versus time for both samples is shown in Figure 17. The clear reduction in viscosity on heating in the presence of cyanide ion can be seen.

REACTION OF MODEL DIMERS WITH STRONG BASES

Glutaronitrile and 2,4-dicyanopentane were refluxed separately with sodium methoxide, the vapour from the reaction being condensed and collected. Analysis of the distillate was carried out by a gas chromatography using a Perkin Elmer F30 gas chromatograph. A silicone gum SE30 column was used with a flame ionisation detector and nitrogen as the carrier gas. Analysis for volatile substances was carried out at 45°-50°C. (This was the lowest stable temperature available without a special cooling unit) and the column was then cleared of higher boiling materials, such as the dinitriles, by temperature programming up to c.a. 150°C.

(1) GLUTARONITRILE

At 50°C a 0.2 l sample of distillate had peaks at 2.59 (large), 2.92 (medium), and 3.72 (small) cm.

The retention times of methanol, methyl cyanide and acrylonitrile were 2.02, 2.62 and 2.95 cm. respectively when run singly and 1.92, 2.50 and 2.87 cm when run as a mixture. The 2.59 and 2.92 peaks in the glutaronitrile distillate correlate well with methyl cyanide and acrylonitrile.

At 45°C the distillate gave four peaks at 2.2 cm (very small), 2.90 (large), 3.30 (medium) and 4.25 (small). The retention times for a mixture of methanol, methyl cyanide and acrylonitrile were respectively 2.10, 2.90 and 3.32. Again there is very good agreement that the 2.90 and 3.30 peaks are methyl cyanide and acrylonitrile, and some evidence that the small 2.2 peak is methanol.

Adding samples of methyl cyanide and acrylonitrile to the distillate still gave three peaks at 2.93, 3.33 and 4.2 cm, the last being very small. This is good evidence for the formation of methyl cyanide and acrylonitrile in the reaction between strong bases and glutaronitrile.

(2) 2,4-DICYANOPENTANE

At 45°C, 0.2 1 of the distillate from 2,4-dicyanopentane gave two peaks at 3.30 cm and 4.80 cm. Methacrylonitrile, an unexpected product, gave a peak with a retention time of 4.75 cm. (This peak and the 4.80 cm one in the distillate were less sharp than the others and slightly asymmetric so measurements were made to the bases of the peaks, not the maximum peak heights). Addition of methacrylonitrile to the distillate still originated in two peaks at 3.35 and 4.70. This suggests that methacrylonitrile is formed in the reaction between base and 2,4-dicyanopentane.

(3) POLYMERISATION OF ACRYLONITRILE AND METHACRYLONITRILE

Attempts to detect acrylonitrile in the reaction between sodium cyanide and glutaronitrile by GLC on the reaction mixture failed. Similarly in the case of 2,4-dicyanopentane no methacrylonitrile could be detected. It was realised that both these monomers could polymerise rapidly on heating with sodium cyanide to give black polymer. In both cases a solvent was found to be essential, for example DMF. Thus a solution of acrylonitrile (1ml) in DMF (5ml) with 0.05g sodium cyanide was heated until a vigorous exothermic reaction began. The solution became black and the polymer was precipitated by pouring the mixture into excess ether. In the case of methacrylonitrile the reaction was slower and considerably less exothermic.

(4) CONCLUSION

It is realised that the short retention times observed in these experiments makes unequivicable identification of the reaction products very difficult. Although longer retention times were obtained using other columns resolution was very poor in these cases: broad chromatogramms were produced making specific identification impossible. The gas chromatograph used was chosen because of its excellent resolution and repeatability. The results obtained do support the identification of the expected products from the model compound reactions and provide some evidence for the proposed chain scission mechanism.

5. POLYMETHACRYLONITRILE, A COMPARISON

(i) INTRODUCTION

Polymethacrylonitrile (PMAN) is discoloured by heat, but the colouration is different in several respects to that of PAN.

(ii) DISCOLOURATION BY SODIUM CYANIDE

A solution of PMAN in DMF discolours when refluxed with sodium cyanide, although the discolouration is much slower and less complete than in the case of PAN. After several hours the solution becomes bright orange and some precipitation of polymer occurs.

Figure 18 shows the IR spectra of ~~PAN~~ PMAN before and after the cyanide treatment. The same general changes noted the IR spectra of cyanide treated PAN can be seen; bands tend to broaden and merge with a loss of detail.

There is a decrease in the nitrile band and a change in the relative intensities of the aliphatic νC-H bands at 2,980cm^{-1} and 2920cm^{-1}, suggesting some change in the configuration of the methylene or methyl groups. A broad absorption between c.a. 1500cm^{-1} and 1700cm^{-1} has formed without any definite maxima in this region.

(iii) OXYGEN ABSORPTION

Unlike cyanide treated PAN, degraded PMAN does not show any evidence of absorbing oxygen. A possible explanation of this is that the extent of reaction in PMAN is so small that only slight oxygen absorption occurs. Deeply coloured products have not been produced so little oxygen absorption has been expected. However the chromophore does not stabilise on standing in air or oxygen and can still be readily bleached by hydrochloric acid. A bright orange sample 2½ years old was bleached to a light yellow instantly by a few drops of dilute acid.

FIGURE 18a: IR SPECTRUM OF POLYMETHACRYLONITRILE/NaCN 4000-1500 cm^{-1}

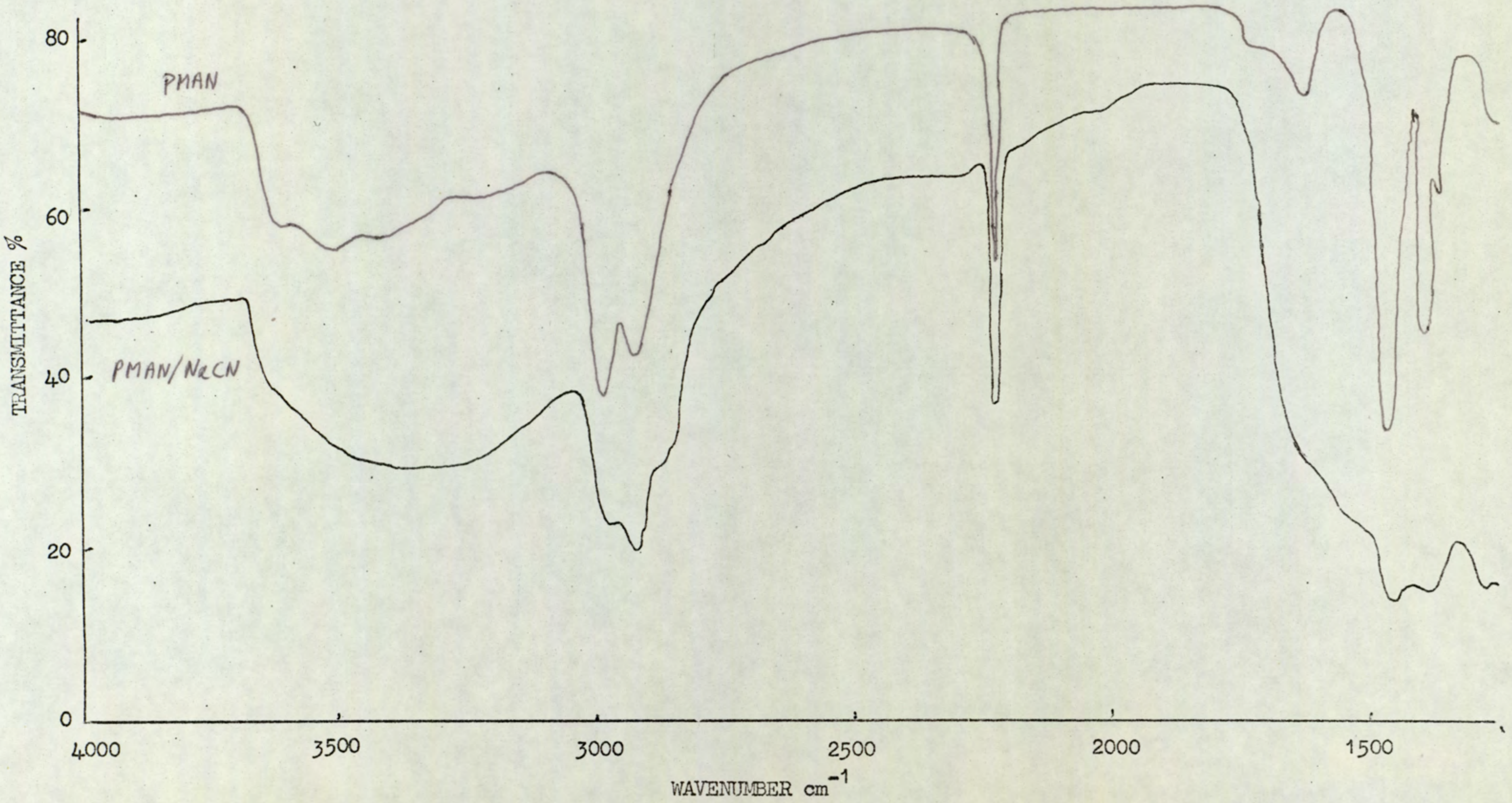
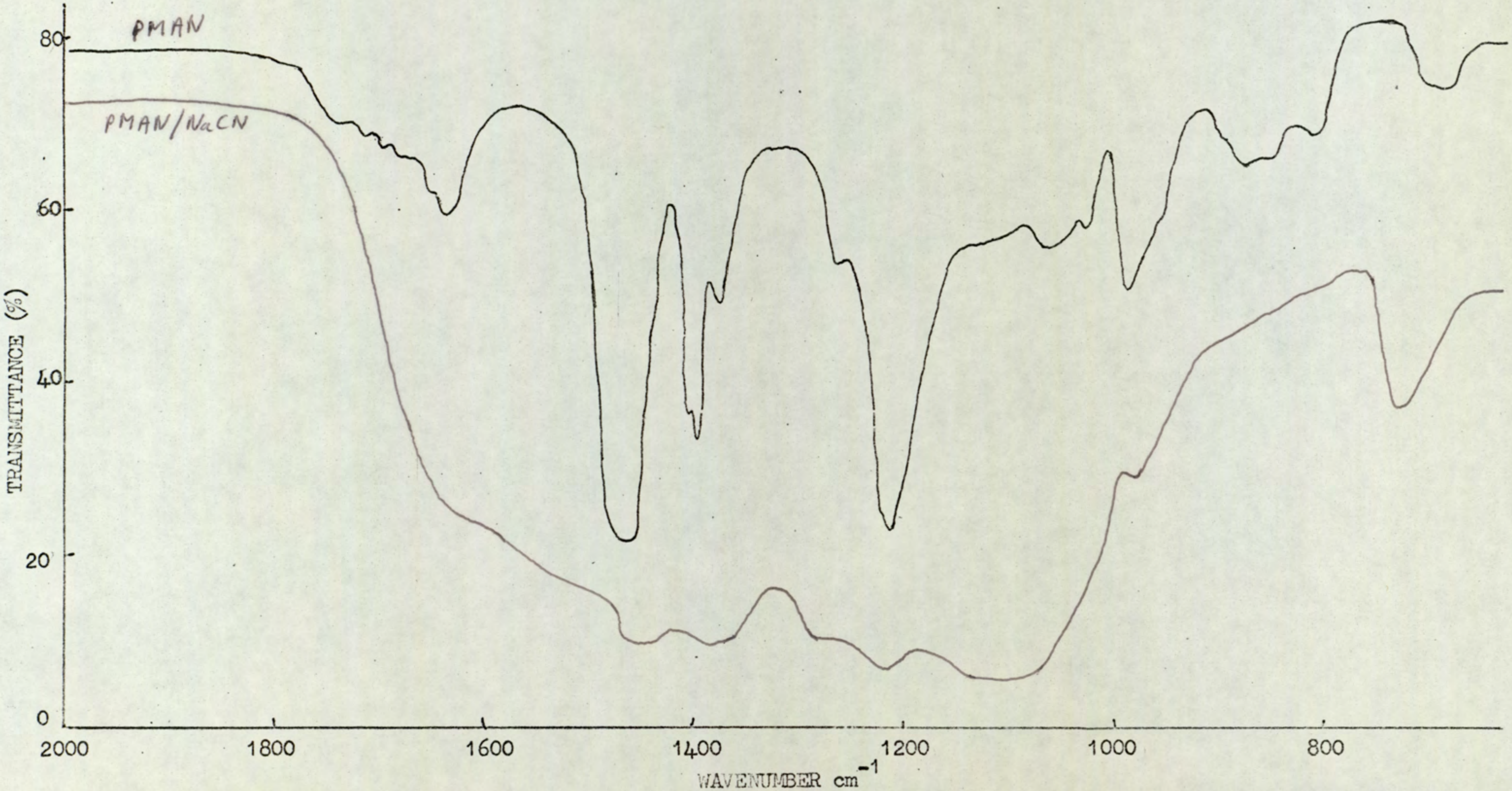


FIGURE 18b: IR SPECTRUM OF POLYMETHACRYLONITRILE/NaCN 2000-800 cm^{-1}



(iv) INTERPRETATION

One obvious explanation for the differences in behaviour between PMAN and PAN could be the increased steric hinderance caused by the methyl group. This would explain the slower rate of discolouration of the polymer and the instability of the chromophore. However discolouration does occur and the degraded material behaves exactly as expected for a polyimine, that is instant hydrolysis occurs under acidic conditions. Since no stabilisation of the chromophore is apparent when the polymer is exposed to oxygen there are probably major differences between its structure and that of degraded PAN.

Another difference between the thermal degradation of PAN and PMAN is the lack of an exotherm during DTA on the latter[47]. This could be explained by increased steric hinderance to the cyclisation of PMAN caused by the methyl group rendering the reaction energetically unfavourable. Alternatively it could be that the exotherm observed in the degradation of PAN is due to a more complicated reaction than the proposed cyclisation reaction and may involve the α-hydrogen atoms.

It can be concluded that the reaction between PMAN and sodium cyanide produces a hydrogenated naphthyridene structure of the type proposed in the introduction but there are differences in properties between this product and the PAN, cyanide product.

EXPERIMENTAL

PREPARATION OF POLYMETHACRYLONITRILE

Freshly distilled methacrylonitrile (20ml) and 150ml of water previously degassed by boiling were placed in a flask. 0.3g sodium thiosulphate and 0.3g of sodium persulphate were added and the mixture stirred vigorously under nitrogen at 50°C. After 14 hours the mixture was coagulated with a few drops of hydrochloric acid and the polymer filtered off.

Crude polymethacrylonitrile was purified by dissolving in DMF, filtering the solution, and precipitating by pouring into excess methanol. After washing with fresh methanol the product was vacuum dried.

REACTION OF POLYMETHACRYLONITRILE WITH SODIUM CYANIDE

Polymethacrylonitrile was dissolved in DMF (5% solution) and sodium cyanide was added (C.A. 10% with respect to polymer). After refluxing for several hours the solution had become a bright orange and polymer had begun to precipitate. After a further 14 hours the reaction was stopped and the orange polymer filtered off, washed with water and dried.

OXYGEN ABSORPTION

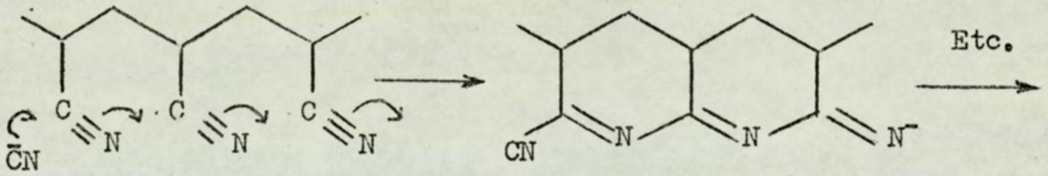
The above experiment was repeated under nitrogen and the degraded solution transfared to an oxygen absorption apparatus. Oxygen uptake was followed on a mercury manometer but after several days no gas absorption had been observed. It was concluded that PMAN treated with cyanide does not absorb oxygen.

At all times the orange colouration could be readily bleached by adding a few drops of hydrochloric acid.to the solution. Even a discoloured sample of PMAN 2½ years old instantly became a yellow colour on shaking with dilute acid. Obviously no stabilisation of the PMAN chromophore occurs in oxygen.

6. MECHANISM OF PAN, CYANIDE REACTION

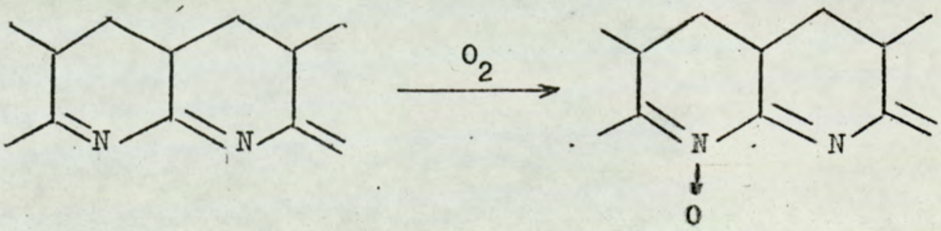
(i) INTRODUCTION

It is difficult to explain the results obtained from the cyanide, PAN reaction in terms of the present theories of PAN degradation. A cyclisation initiated by the nucleophilic attack of a free cyanide ion on a pendant nitrile group could take place leading to the formation of a hydrogenated naphthyridine structure.

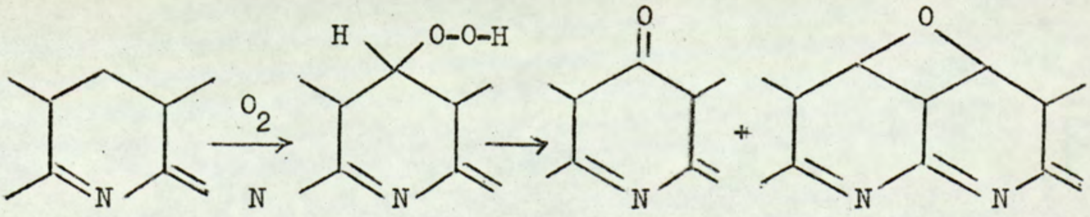


This scheme can not explain the subsequent oxidation of the cyanide, PAN reaction product since there is no reason why the above hydrogenated naphthyridine should be so reactive towards oxygen. Three possible oxidation processes can be considered with respect to the structure.

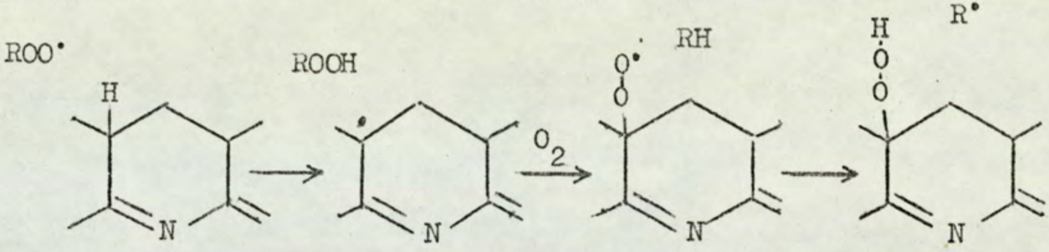
(1) Nitrone formation suggested by Peebles and Brandrup[19].



(2) Ketone or epoxide formation as suggested by Standage and Matkowsky[20] via hydroperoxidic intermediates:



(3) Autoxidation involving the α-hydrogen:



None of these schemes can explain the observed behaviour of the PAN, cyanide reaction product.

(1) Nitrones and N-oxides are formed only under very stringent oxidative conditions, usually in the presence of hydrogen peroxide or peracids, not on exposure to air. Neither of the two IR absorptions associated with nitrones at 1,290cm^{-1} and 980cm^{-1} are observed in oxidatively degraded PAN. Nitrones and N-oxides are reactive species and decompose on heating, so their formation can not explain the stabilisation of the degraded polymer observed during oxidation. As evidence of nitrone formation Peebles and Brandrup claim that no changes in the IR spectrum of polysuccinonitrile, a model polyimine, occur during oxygen absorption[19]. However in a published spectrum the methylene absorption at c.a. 2800cm^{-1} can be clearly seen to disappear after exposure to oxygen. This, together with other spectral changes, suggests that nitrones are not being formed and the oxidation is more complex.

(2) Oxidation of the methylene groups by a radical chain process to form hydroperoxide and ketones may occur but since there is no activation of the methylene group, such an oxidation could not be as rapid and as quantitative as the one observed at room temperature.

(3) The presence of the polarised imine groups ($\overset{\delta+}{\supset C} = \overset{\delta-}{N}-$) will, as explained earlier, reduce the probability of oxidation at the tertiary hydrogen by their electron withdrawing nature. So oxidation by a radical chain process at this site should be slower than at the

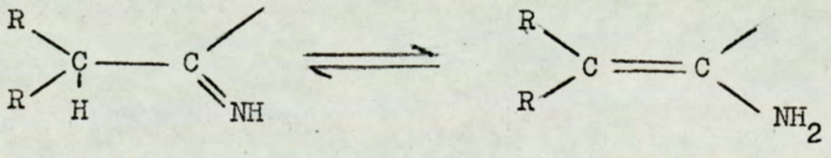
methylene bridge.

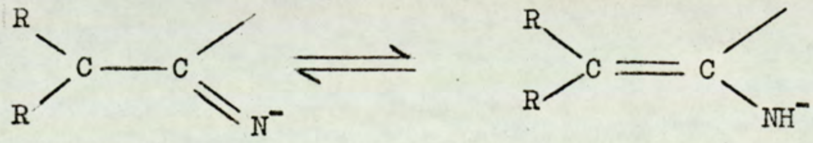
The product from the reaction of PMAN with sodium cyanide does not appear to absorb oxygen or become resistant to bleaching by acids on exposure to oxygen. Since it can be assumed that this material has a hydrogenated naphthyridine structure, it provides further evidence that this structure is not oxidised by mechanisms one and two. Of course oxidation by mechanism three is not possible in the case of PMAN because of the absence of the tertiary hydrogen.

It is concluded that an alternative mechanism is required to explain the reaction between PAN and sodium cyanide and the subsequent oxidation of the product. Such a mechanism is very likely to involve the α-hydrogen present in PAN to account for the differences in behaviour between itself and PMAN.

(ii) AN ALTERNATIVE MECHANISM

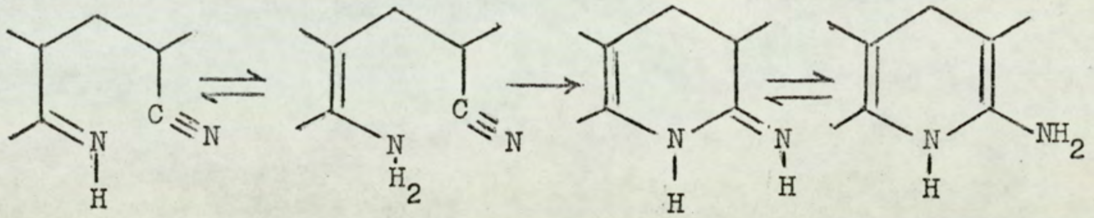
In solution there is a possibility of the intermediate anion, or ketimine if protonation has occurred, rearranging to the enamine tautomer before cyclisation:



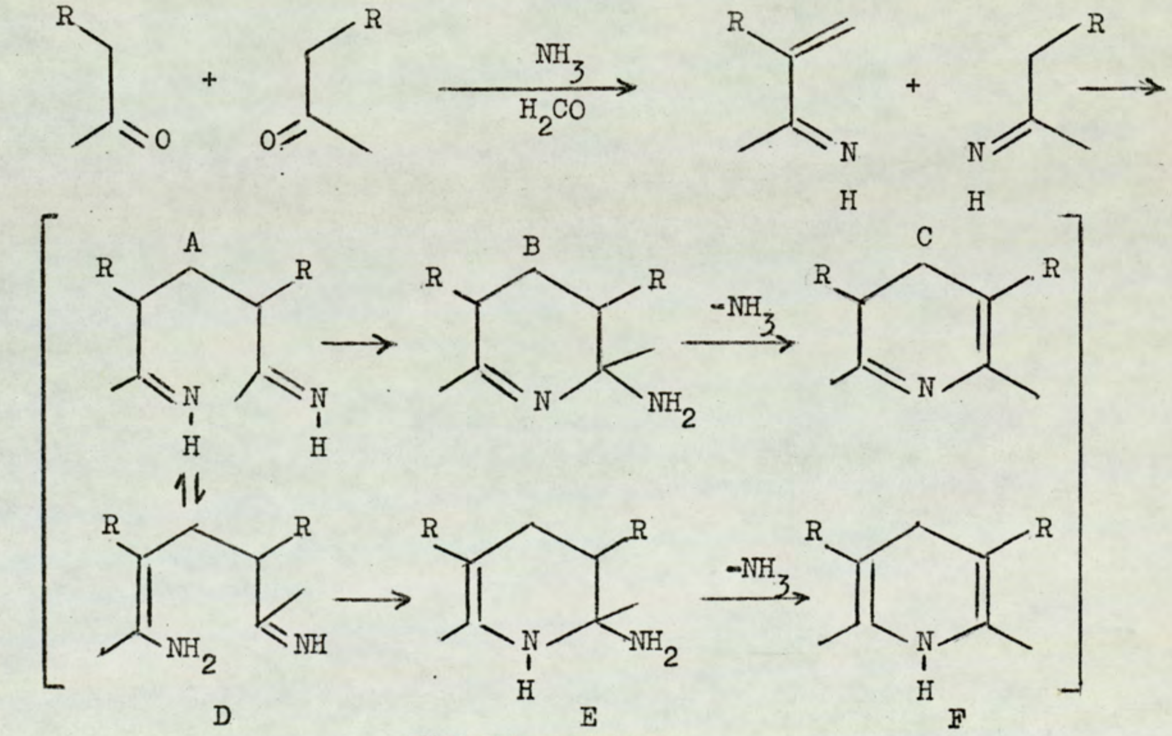


This tautomerism is analogous to the keto, enol tautomerism with the ketimine being the most stable state. However, stabilisation of the enamine by resonance readily occurs as typified in the Thorpe cyclisation[32] of adiponitrile where the product is 1-amino-2-cyano-1,2-cyclopentene and not the ketimine as was first thought[33].

If the enamine tautomer is formed before cyclisation a 1,4-dihydropyridine structure will result on subsequent cyclisation:



This scheme is similar to mechanism proposed for the Hantzsh synthesis of dihydropyridines from 1,3-diketones or β-ketonic esters by reaction with an aldehyde and ammonia[48].

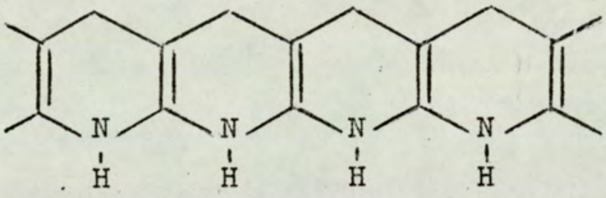


HANTZSH SYNTHESIS

The intermediate A could cyclise directly, giving B and subsequently a 3,4-dihydropyridine C. This is analogous to the Grassie type cyclisation mechanism for the degradation of PAN. Alternatively reaction could occur through tautomer D forming, via E, a

1,4-dihydropyridine F. The group R is usually a ketone or a carbalkoxyl so the enamine tautomer D should be the more stable isomer. In practice 1,4-dihydropyridines are produced, suggesting that this scheme is correct. However, since of the two dihydropyridine isomers under consideration the 1,4 is the more stable, even if the 1,3 were formed by the first mechanism it would tautomerise under the prevailing reaction conditions and a 1,4-dihydropyridine would still be the product.

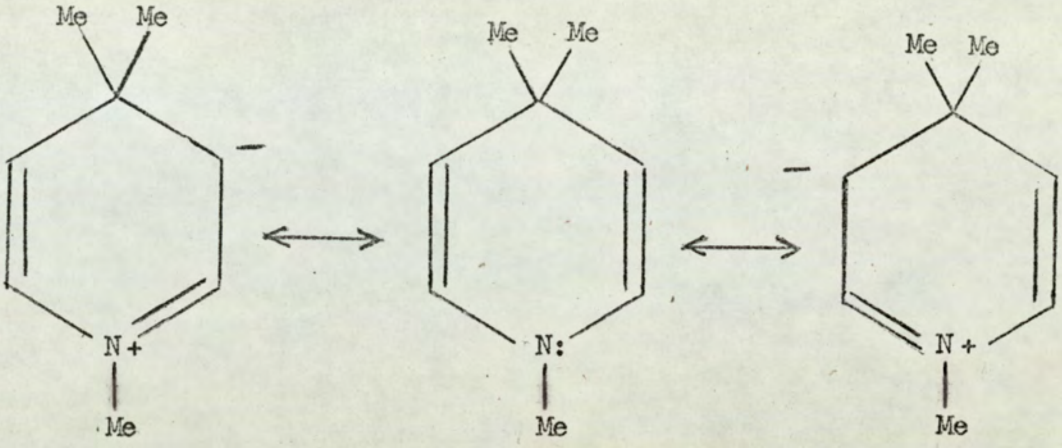
By analogy with the Hantzsh synthesis it is reasonable to expect a 1,4-dihydropyridine structure from the cyanide, PAN reaction in solution. In fact a sequence of adjacent dihydropyridines would be formed as shown in structure XIX.



XIX. CONDENSED 1,4-DIHYDROPYRIDINE STRUCTURE FOR PAN,CYANIDE PRODUCT.

(iii) PROPERTIES OF 1,4-DIHYDROPYRIDINES

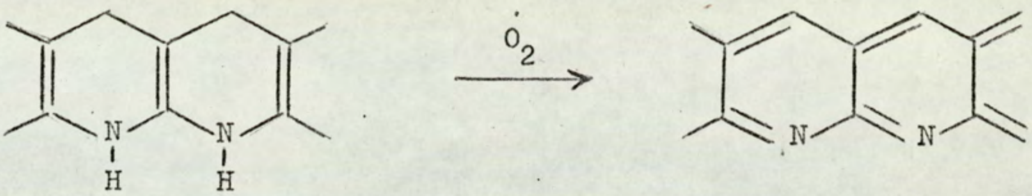
Although the parent compound of the series 1,4-dihydropyridine itself is extremely reactive and unstable in the presence of air[49], stability can be increased by substitution in the 3 and 5 positions by groups capable of conjugating with the ring. Such compounds are well known as intermediates in the Hantzsh synthesis of pyridines. Another stable dihydropyridine has been prepared by Sorensen and Kosower[50]; it is 1,4,4-trimethyl-1,4-dihydropyridine. The authors report that the ring is planar with a small stabilisation energy, c.a. 4 Kcal mol^{-1}. This stabilisation arises out of resonance between the carbon-carbon double bonds and the nitrogen lone pair:



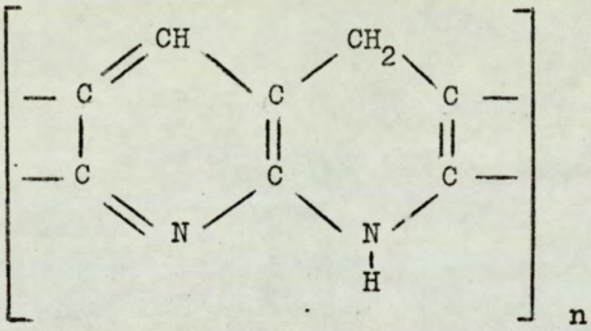
The IR spectrum of this compound has bands at 1662-1668cm^{-1} and 1600cm^{-1} in the double bond region, hence the postulated dihydropyridine structure XIX is compatible with the observed IR spectrum of cyanide treated PAN.

Chemically 1,4-dihydropyridines are reactive species, their most outstanding property being their ability to oxidise to the corresponding pyridine. Often this occurs simply on exposure to air. The presence of such structures in the PAN , cyanide reaction product could at once explain its extreme ease of oxidation.

Since the ring is planar many of the steric problems associated with the McCartney hydrogenated naphthyridine structure are eliminated and the strain induced by adjacent rings will be minimal. The loss of conjugation associated with the polyimine is compensated by the ring stabilisation of the dihydropyridine. Therefore the condensed 1,4-dihydropyridine structure is likely to be more stable, provided oxygen is excluded, than the hydrogenated naphthyridine. In the presence of oxygen a fairly rapid oxidation is to be expected with the formation of a more stable fully aromatic naphthyridine structure of the type proposed by Houtz[5].



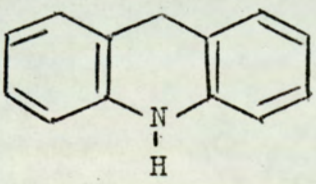
It is interesting that just such a mixture of pyridine and 1,4-dihydropyridine rings has been proposed by Monahan[51] after elemental and spectrophotometric analysis of degraded PAN:



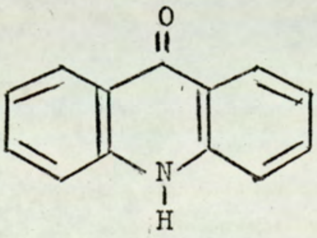
(iv) MODEL FOR A CONDENSED 1,4-DIHYDROPYRIDINE STRUCTURE

To study the properties of the condensed 1,4-dihydropyridine structure a suitable model was required. An obvious choice is 1,4,5,8-tetrahydro-1,8-naphthyridine but this compound has not been reported in the literature. Only the decahydro, 1,2,3,4-tetrahydro, and the 4a,8a-dihydro, 1,8-naphthyridines are known.

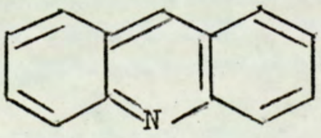
A useful model is the acridan, acridone, acridine system:



Acridan



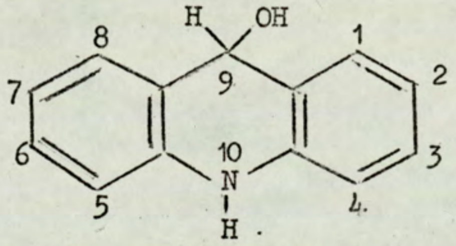
Acridone



Acridine

Although acridan might be expected to be more stable than the suggested structure for PAN treated with cyanide, all acridans can be readily oxidised to acridines[52]. Preparatively oxidation is usually brought about by dichromate but it can be accomplished with hot air, particularly if the acridan is in a basic solution. Heating a mixture of alumina and acridan for 48 hours at 120°C yields 50% acridine, together with 4% acridone[53]. Treating the alumina with sodium methoxide prior to the reaction considerably increases the rate of conversion; a 78% yield of acridine is obtained in 24 hours at only 55°C. This demonstrates that the oxidation is clearly base catalysed.

The mechanism by which acridan is oxidised to acridine is not known but it may proceed through a 9-hydroxyacridan:



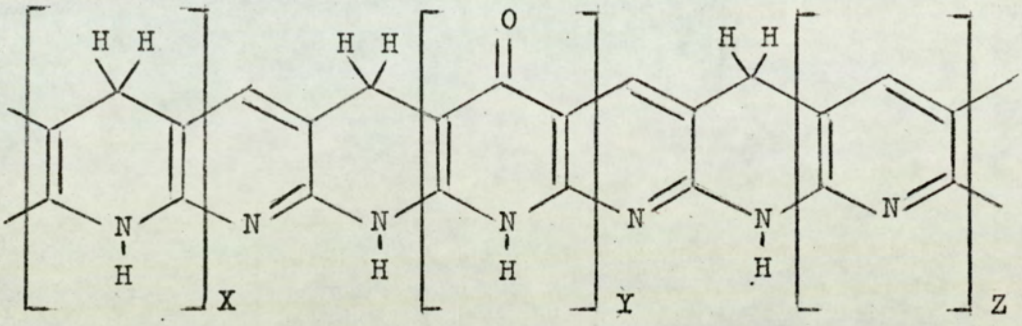
Amine substituents on the 3 and 9 positions tend to facilitate the oxidation. By comparison therefore the condensed 1,4-dihydropyridine structure proposed for cyanide treated PAN should be readily oxidised.

(v) CONCLUSION

In the reaction of PAN with sodium cyanide in solution a cyclisation reaction occurs via an enamine tautomer producing a condensed 1,4-dihydropyridine type of structure. This structure is more stable than the dehydrogenated structure of McCartney on a thermodynamic basis for two reasons.

1. There is considerably more electron delocalisation since the lone electron pairs on the nitrogen atoms can participate in resonance.
2. The ring is planar so steric hinderance is considerably reduced.

On the other hand the condensed 1,4-dihydropyridine will be very reactive chemically. On exposure to oxygen rapid oxidation to a fully aromatic pyrinoid system will occur and the molecule will be stabilised. The ultimate product will be a random mixture of condensed pyridine, 1,4-dihydropyridine and 4-pyridone units (Structure XX).



STRUCTURE XX. CYANIDE DEGRADED PAN AFTER OXIDATION

Before stabilisation by oxidation the condensed 1,4-dihydropyridine system will be susceptible to hydrolysis, particularly under acidic conditions. The bleaching of the PAN, cyanide reaction product before exposure to oxygen by hydrochloric acid is therefore explained by this mechanism.

7. EVIDENCE FOR THE CONDENSED 1,4-DIHYDROPYRIDINE STRUCTURE.

(i) INTRODUCTION

Obtaining direct evidence for the condensed 1,4-dihydropyridine structure has proved very difficult. Because of its reactive nature the probability of detecting it in the material isolated from the PAN, cyanide reaction is very small and, since such a detection could only be made by IR spectroscopy, would probably be inconclusive because of the poor resolution of such spetra.

It was hoped that studies on model compounds, e.g. 2,4-dicyanopentane, might provide confirmation of this mechanism by the isolation of either pyridines or 1,4-dihydropyridines from their reactions with strong bases or sodium cyanide. As will be explained later all such attempts failed, probably because the model compounds polymerised before or during cyclisation. Some indirect evidence has been found however.

(ii) BASE CATALYSIS OF OXIDATION

By analogy with the known 1,4-dihydropyridines and acridans the oxidation of the PAN, cyanide reaction intermediate should be base catalysed. Experiments to detect this were made. It was found that the rate of oxygen uptake could be increased by the addition of a strong base such as sodium methoxide to a DMF solution of cyanide treated PAN.

Oxygen absorption could be inhibited by the addition of water or weak acids. This can be explained by hydrolysis of the reactive dihydropyridine structure with the probable formation of amide groups. No discolouration was observed during this process, probably because extensive oxidation or dehydrogeneration had already taken place.

(iii) ROOM TEMPERATURE DISCOLOURATION

The ketimine tautomer is thermodynamically more stable, although once a 1,4-dihydropyridine unit has been formed it may stabilise an adjacent enamine in preference to the ketimine. At room temperature therefore tautomerisation may be prevented and the hydrogenated naphthyridine structure proposed by McCartney formed. Under such conditions no oxygen absorption should occur.

Although at low temperature the discolouration of PAN by sodium cyanide is slow, after approximately one week a black solution was obtained. During this period very little oxygen absorption occurred. The degraded polymer isolated from this reaction was dark brown. The colour was not stable and could be readily bleached to a pale yellow by dilute acids. Its IR spectrum (Figure 19) is similar in many respects to PAN degraded by other methods with the usual loss of detail but a well defined band at 1670cm^{-1} has appeared. Unlike PAN reacted with sodium cyanide at higher temperatures no diminution of the δCH_2 band at 1460cm^{-1} has occurred indicating little loss of methylene groups. This spectrum supports the McCartney hydrogenated naphthyridine structure, assigning the 1670cm^{-1} absorption to the ketimine stretching mode (ν C=N), and is evidence that PAN degraded by sodium cyanide at room temperature has this structure.

On dissolving the degraded polymer in DMF and refluxing for a short period major changes occurred in the IR spectrum (Figure 20). Although the nitrile absorption at 2250cm^{-1} has changed little in intensity the band at 1460cm^{-1} has disappeared and absorptions in the 1750-1600cm^{-1} region have merged into one band. These changes can be explained by the rearrangement of McCartney type structures to the more stable condensed 1,4-dihydropyridine, followed by its oxidation to the fully aromatic Houtz form with loss of methylene.

(iv) CONCLUSION

No direct evidence has been found for the condensed 1,4-dihydro-

FIGURE 19a: IR SPECTRUM OF PAN/NaCN ROOM TEMPERATURE REACTION 4000-1500 cm^{-1}

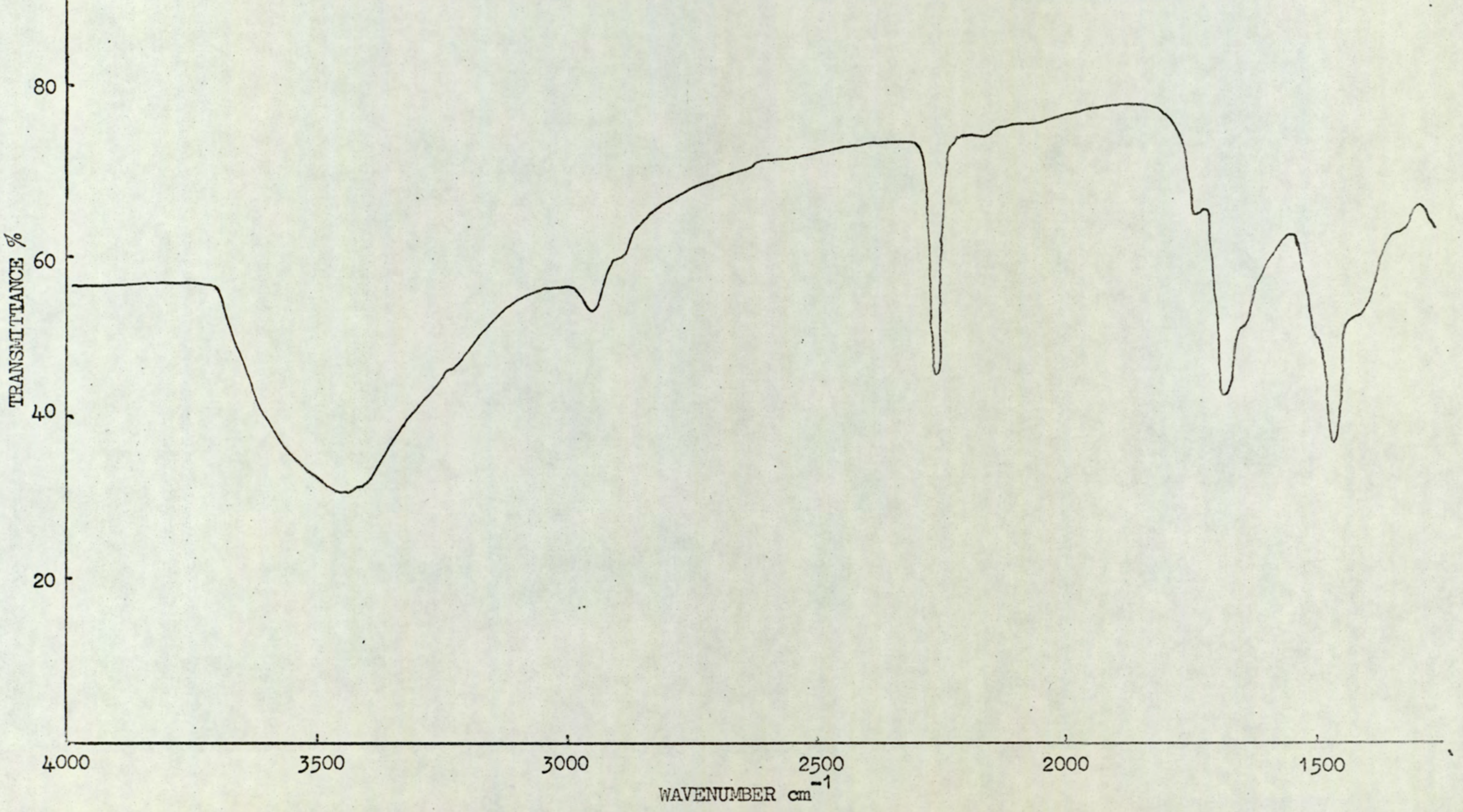


FIGURE 19b: IR SPECTRUM OF PAN/NaCN ROOM TEMPERATURE REACTION 2000-800 cm^{-1}

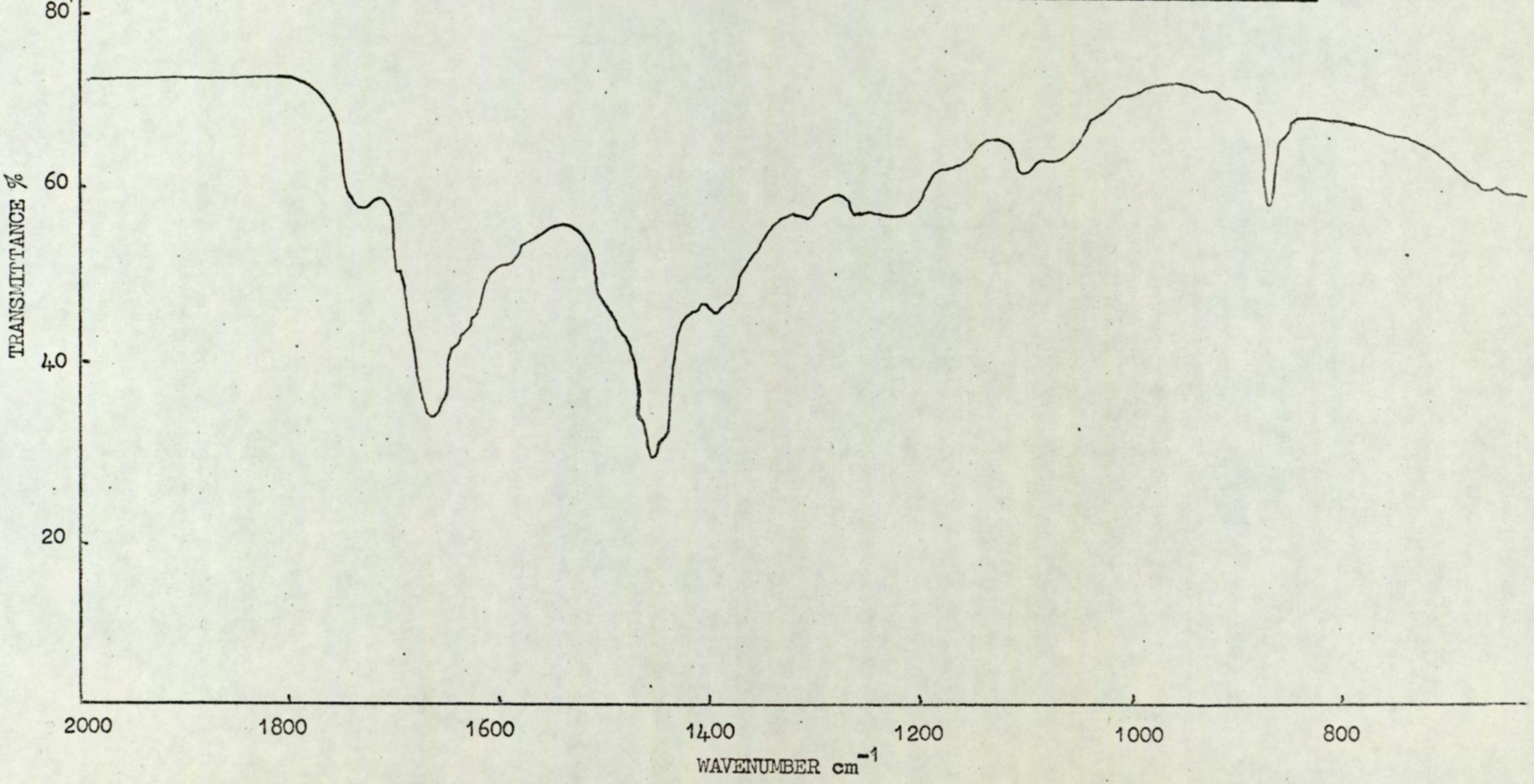


FIGURE 20a: IR SPECTRUM OF PAN/NaCN ROOM TEMPERATURE REACTION AFTER 30 MINUTES REFLUX 4000-1500 cm^{-1}

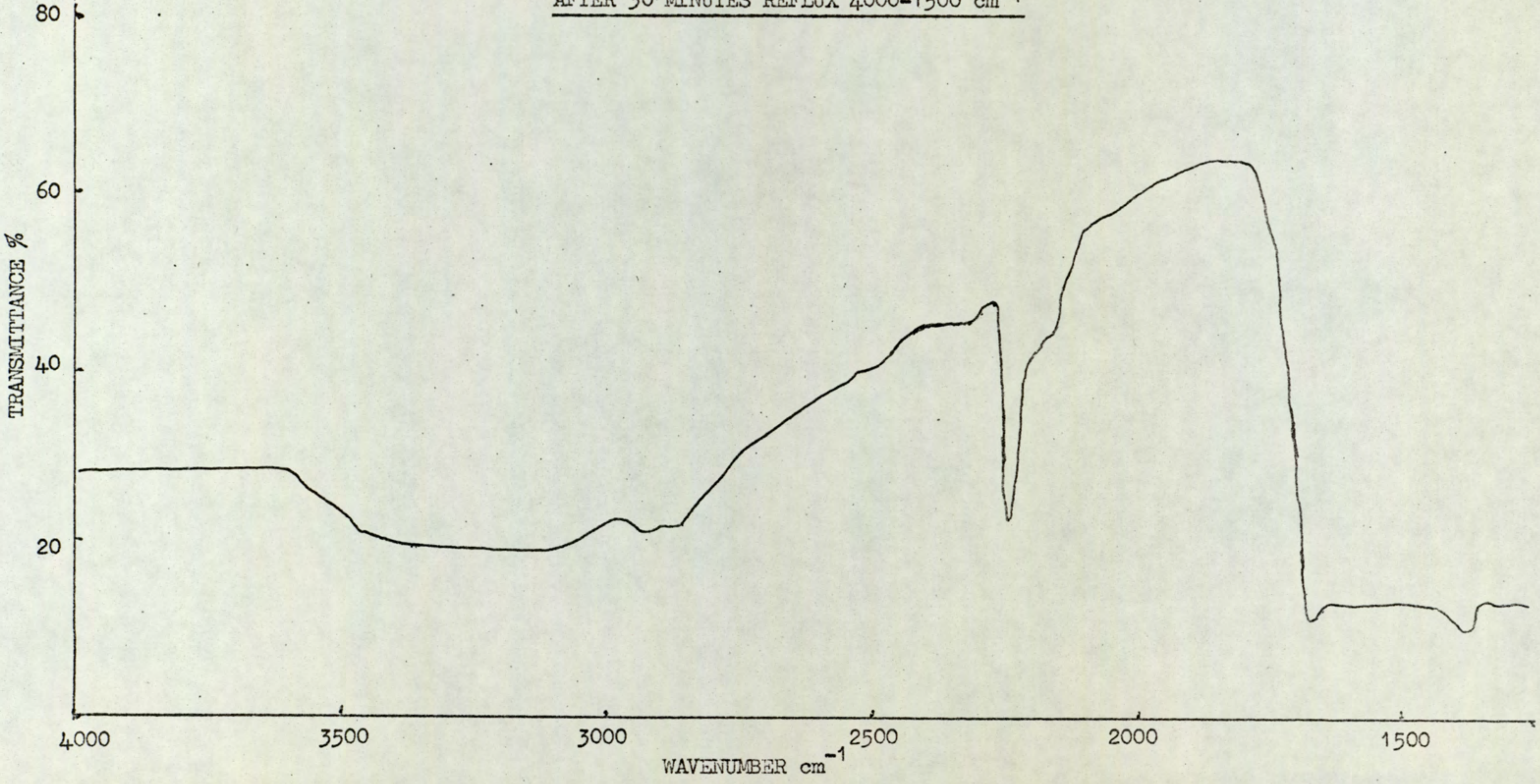
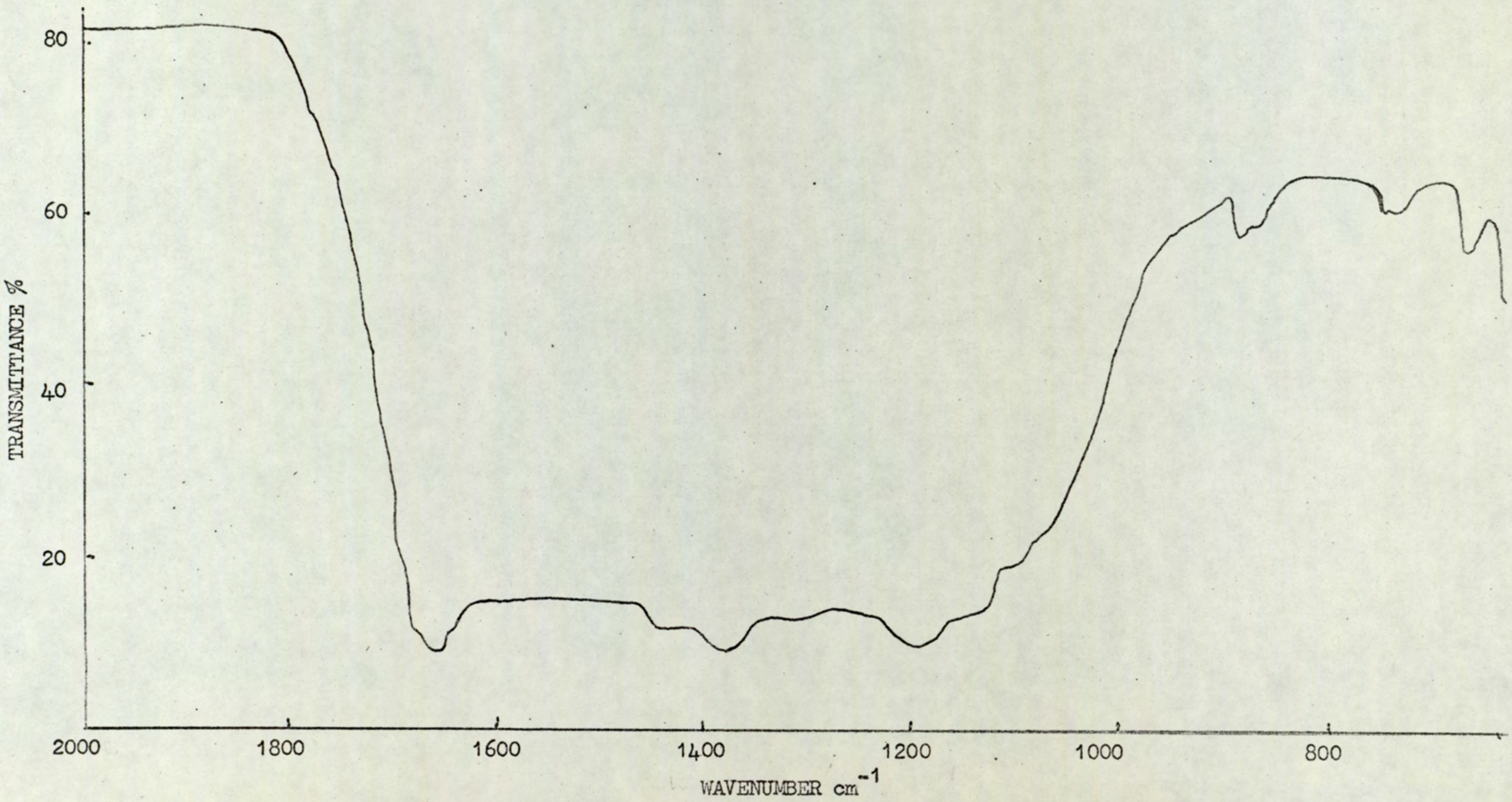


FIGURE 20b: IR SPECTRUM OF PAN/NaCN ROOM TEMPERATURE REACTION AFTER 30 MINUTES REFLUX 2000-800 cm^{-1}



pyridine structure of cyanide degraded PAN but the following indirect evidence is presented:

1. A hydrogenated naphthyridine can not explain the properties and reactions of PAN treated with sodium cyanide at high temperatures. The dihydropyridine can give very satisfactory explanation, particularly of the post-oxidation and differences between the behaviour of PAN and PMAN under similar conditions.

2. The assumption of a condensed 1,4-dihydropyridine structure enabled the prediction to be made that the post-oxidation of cyanide treated PAN is base catalysed and inhibited by weak acids.

3. The low temperature reaction between PAN and sodium cyanide demonstrates that two forms of degraded PAN exist, one stable to oxygen and the other readily oxidisable. Conversion from the oxygen stable to the oxidisable form can readily be brought about by heating in DMF and changes in the IR spectra of these compounds support oxidation by loss of methylene.

EXPERIMENTAL

BASE CATALYSIS OF OXIDATION

In a typical experiment a 2% solution of PAN in DMF was refluxed under nitrogen with sodium cyanide for 4 hours. Two 20ml. alliquots were placed in 50ml. flasks and to one was added 0.25g of sodium methoxide. The oxygen uptake of these mixtures was followed by measuring the internal pressure with mercury manometers. The graph of pressure against time (Figure 21) clearly demonstrates that the presence of base is causing a greater rate of oxygen uptake.

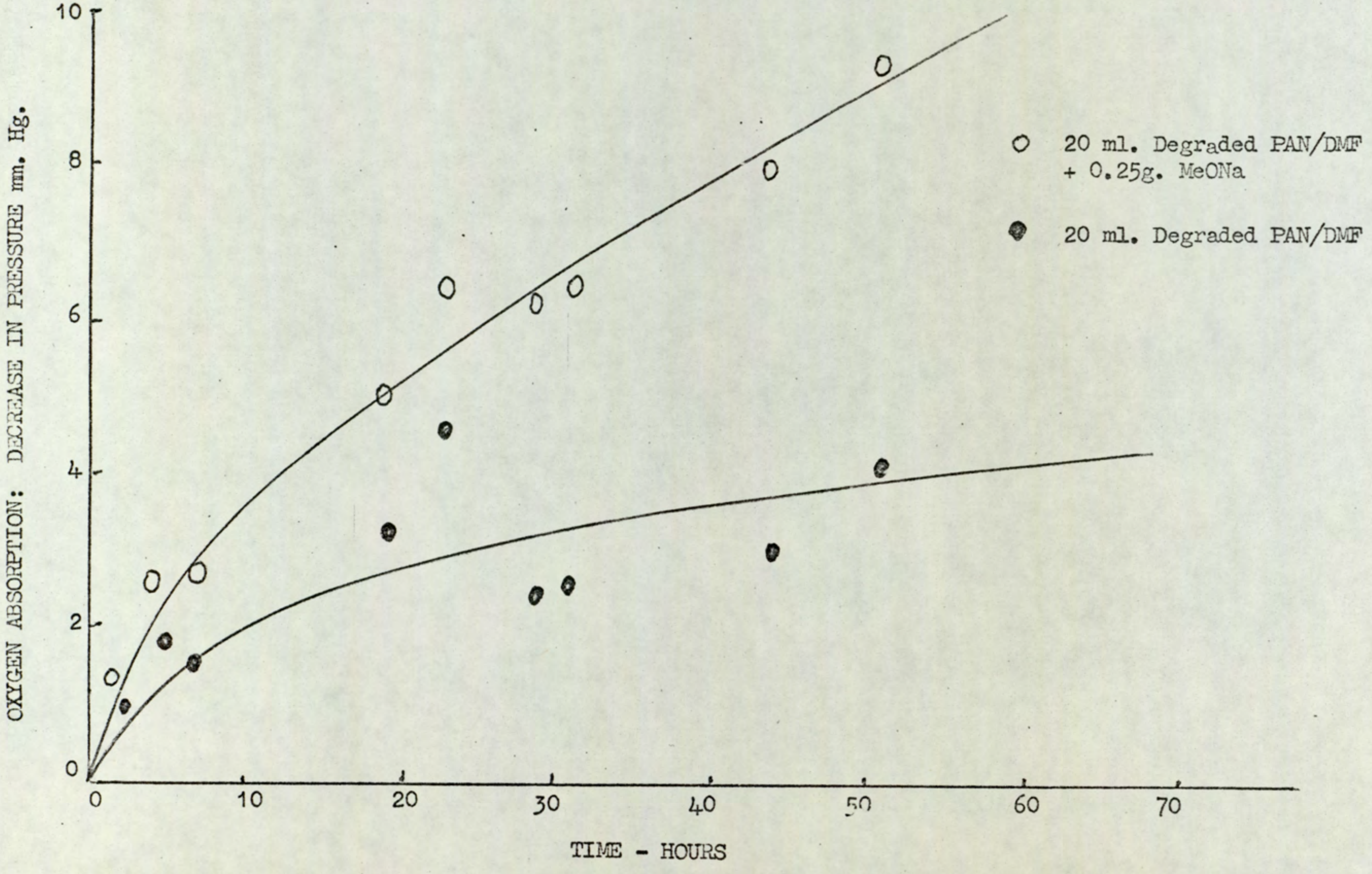
Addition of weak acids (acetic acid) or water (c.a. 1 ml.) to similar solutions considerably inhibited the oxygen absorption reaction and occasionally some gas evolution occurred.

LOW TEMPERATURE PAN, CYANIDE REACTION

A solution of PAN in DMF (2%) was placed in a flask and 0.05g of sodium cyanide was added. The mixture was well mixed and left for several weeks at room temperature. Within one week the solution was a very dark red but there was no apparent pressure drop within the vessel recorded on a manometer. After a month the solution was black. The colour could be instantly discharged by adding hydrochloric acid to the solution.

The polymer was precipitated as a dark brown powder by pouring the solution into an excess of ether and its IR spectrum was obtained from a 3% mixture with patassium bromide. The degraded material was redissolved in DMF and heated to reflux gently. After 30 minutes the solution was cooled and the polymer again precipitated in ether and its IR spectrum obtained.

FIGURE 21: OXYGEN ABSORPTION OF CYANIDE DEGRADED PAN UNDER BASIC CONDITIONS



8. EXPLANATION OF THE OXIDATIVE DEGRADATION OF PAN IN TERMS OF A CONDENSED 1,4-DIHYDROPYRIDINE STRUCTURE.

(i) INTRODUCTION

The marked similarity between oxidatively degraded PAN and PAN treated with sodium cyanide in solution has already been noted. A similar mechanism to that proposed for the cyanide, PAN reaction could explain a great many of the experimental facts about the oxidative degradation, particularly the post oxidation reported by Standage and Matkowsky[21]. PAN heated to 290°C under high vacuum absorbs oxygen at room temperature on subsequent exposure to air. An identical effect has also been observed by Rose[24] with samples of pure PAN fibre (Dralon T) heated to 252°C under inert conditions. After treatment the fibre was a light orange but exposure to air brought about a darkening of the sample to dark brown and an increase in the oxygen content:

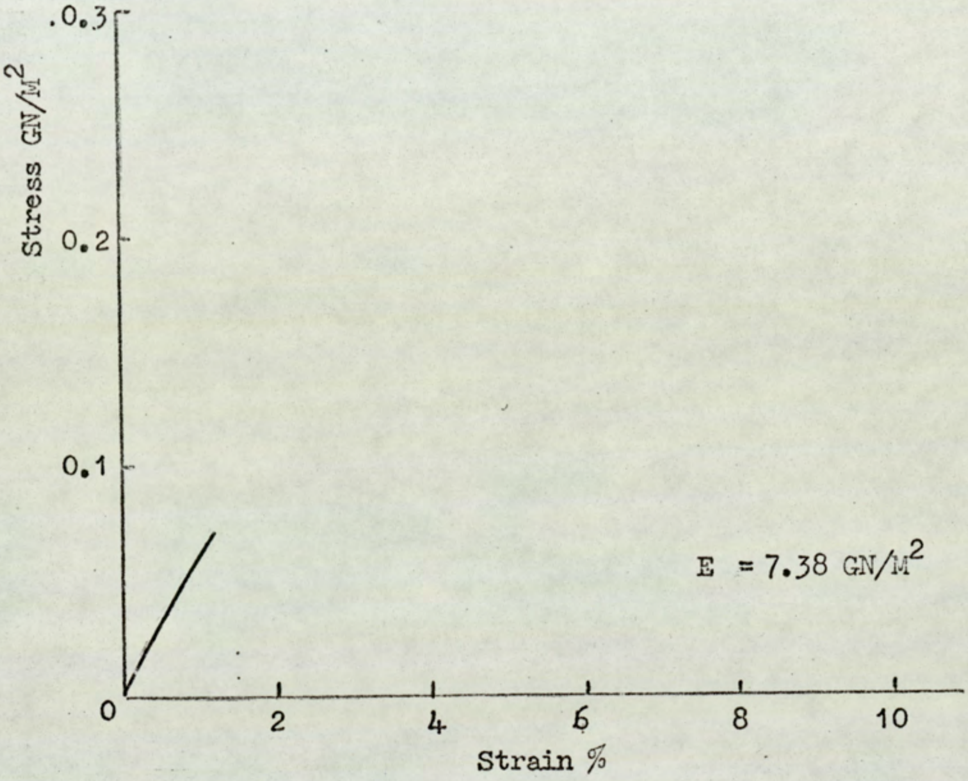
Pyrolysed to 252°C	Carbon %	Nitrogen %	Hydrogen %	Remainder (Oxygen)
Unexposed to Air	68.4	23.9	5.9	1.5
Exposed to Air	65.7	22.7	5.0	6.3

It is difficult to detect detailed changes in the IR spectra before and after exposure because of the poor resolution obtained with degraded materials but there is an increase in the absorption at $1600cm^{-1}$ with all bands merging into one. Increases also occur in the $3200cm^{-1}$ region, possibly because of hydroxyl formation. There is a dramatic change in the stress, strain curve for the pyrolysed fibre on post oxidation (Figure 22).

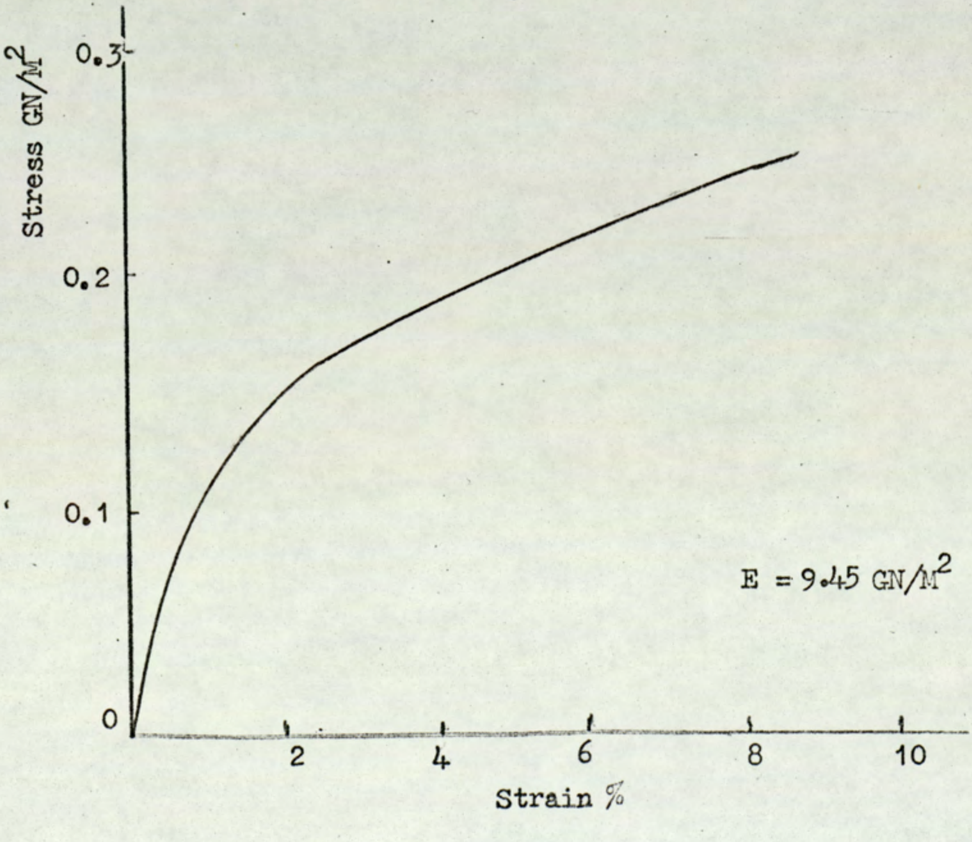
These results cannot readily be accommodated by the hydrogenated naphthyridine structure but are readily explained by a condensed 1,4-dihydropyridine as in the case of cyanide treated PAN.

FIGURE 22: EFFECT OF POST OXIDATION ON THE INERT DEGRADED FIBRE.

Heated in Argon to 333°C, Under Restraint



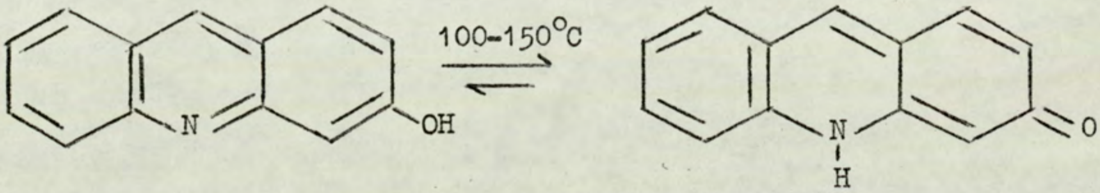
Heated in Air to 333°C, Unrestrained



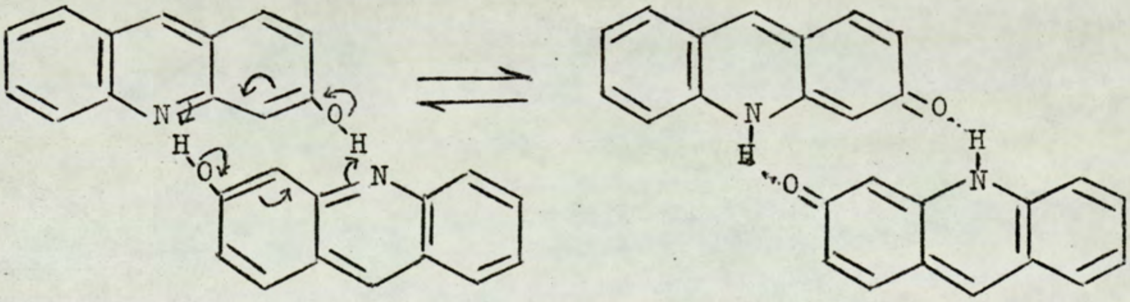
(ii) FORMATION OF A CONDENSED 1,4-DIHYDROPYRIDINE UNDER OXIDATIVE CONDITIONS.

The formation of a condensed 1,4-dihydropyridine structure under oxidative conditions necessitates the ketimine, enamine tautomerism occurring in the solid state. Examples of tautomeric rearrangements in the solid state are very rare, although it is well known that they can occur on melting, for example in the case of 1,3-diketones.

One possible solid state rearrangement is that of 3-hydroxyacridine which is thought to occur at 100-135°C[54]:

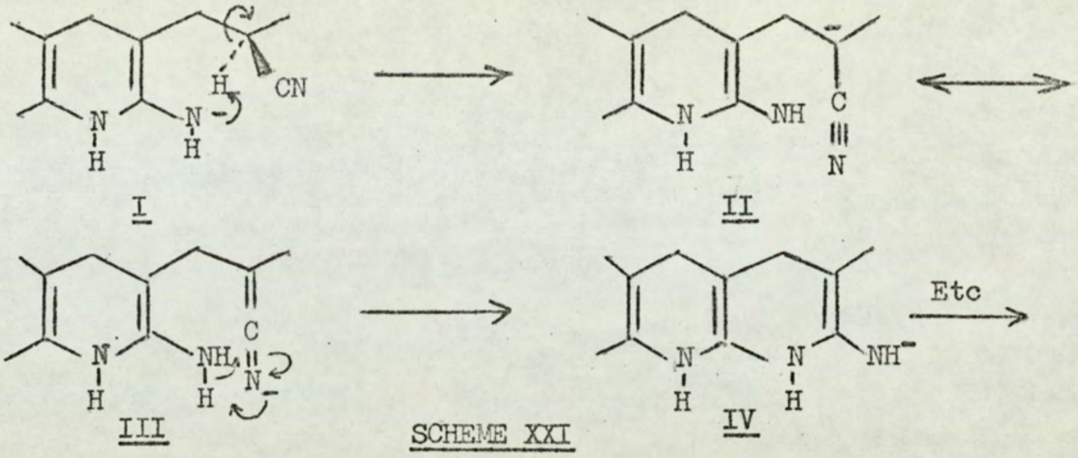


Cairns-Smith[55] suggests that the rearrangement is facilitated by hydrogen bonding, transfer of the bonded hydrogens causing the rearrangement.



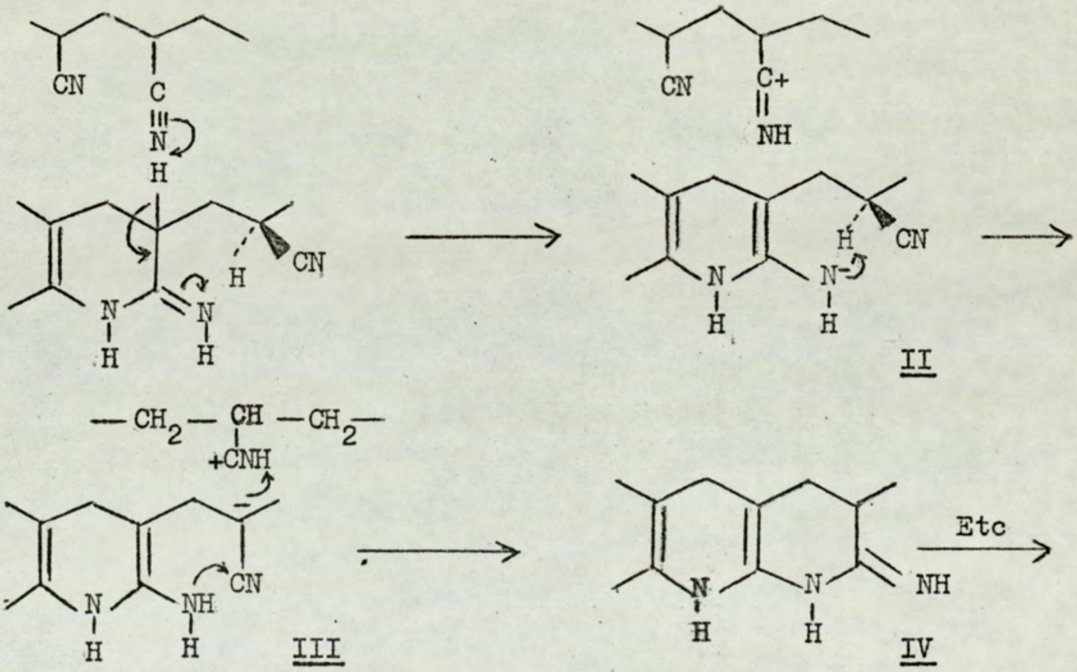
It is also possible that the tautomerism is brought about by local melting of the acridine, especially when it is subjected to mechanical force such as stirring[55].

In the case of PAN several schemes can be devised to allow for a tautomeric rearrangement of the propogating ketimine to an enamine group. If reaction occurs through free anionic species scheme XXI may apply :



SCHEME XXI

An alternative scheme (XXII) relying on the interaction between adjacent chains in the molecule to bring about proton transfer could apply:



SCHEME XXII

Scheme XXII would be facilitated by the presence of free bases, ester groups, or carboxylic acids in the polymer. The abstraction of the α-hydrogen by the free anion should be faster than cyclisation by attack on the nitrile group on steric grounds. Since stereospecificity within the molecule is destroyed before cyclisation and a planar ring is formed the steric problems associated with the formation of a hydrogenated naphthyridine in an atactic material are removed.

Rearrangements of this nature require some relative motion of the polymer molecules and are only likely to occur at or near the melting point of the polymer. Certainly melting could greatly enhance the formation of enamines from the ketimine species and an increase in the rate of cyclisation would occur. At temperatures considerably below the melting point such rearrangements as required for ketimine, enamine tautomerism would be prohibited. On the other hand cyclisation by a Grassie type mechanism to form a hydrogenated naphthyridine could occur above the glass transition temperature, provided the sequence lengths of cyclised units formed are short. Two distinct reactions are therefore possible depending on the temperature of the polymer relative to its glass transition temperature and melting point.

Many determinations have been made of the glass transition temperature for PAN by both dielectric measurements[56] and DTA[57]. Values in the range 56° - 96° have been obtained. There is evidence that two transition temperatures exist; one in the region 80-110° and a higher one in the range 142° - 176°, depending on polymer composition and molecular weight[24]. Copolymerisation and low molecular weights reduce the transition temperatures to the lower values in the ranges quoted. In the presence of initiating species, such as amines, discolouration of PAN begins at 100°C and is quite extensive at 150°C. This is probably due to formation of a hydrogenated naphthyridine structure; chemical investigations by Peebles and Brandrup[19] do support such structures being formed at 150°C.

As reported in the introduction, there is evidence that the reaction exotherm observed by DTA is associated with the melting point of the polymer, although actual melting is not observed because of the chemical changes occurring. Excellent correlation between the decay of nitrile groups and the extent of the exotherm has been obtained[24], suggesting the same reaction is responsible for both. It has always been assumed that this reaction is the formation of a hydrogenated naphthyridine structure although there is no direct evidence for this. Alternatively the formation of a condensed 1,4-dihydropyridine could be responsible for the exothermic loss of nitrile and the following evidence is presented:

1. Although discolouration occurs on heating PMAN and the changes in polymer structure are compatible with the formation of a hydrogenated naphthyridine structure no exotherm is observed.

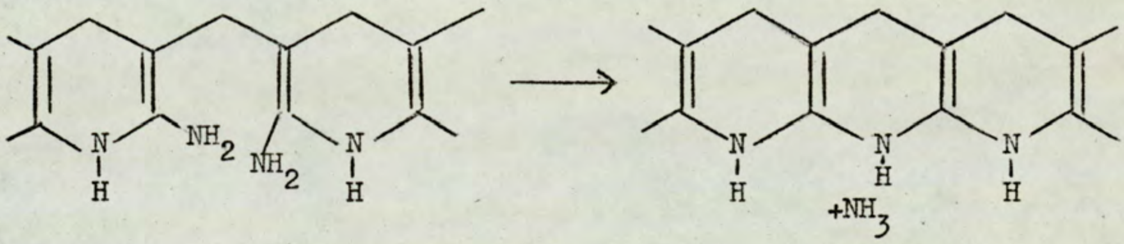
2. Rose[24] has demonstrated that up to 40% of the nitrile content of PAN in a programmed thermal treatment is lost without heat evolution below the exotherm temperature. Above this temperature nitrile is still lost but with considerable heat evolution. Obviously major changes in the reaction or reactions responsible for nitrile loss must occur at this temperature. The presence or absence of oxygen has little effect on these observations.

3. Vosburgh[26] reports that different products are obtained by heating PAN in air. Above 250°C (exotherm temperature) a black nonflammable material is formed with considerable heat evolution. Below this temperature a black flammable material forms without heat evolution.

It can be concluded that at or near the theoretical melting point of the polymer sufficient molecular motion occurs to allow the propogating ketimine structures in the cyclisation reaction to rearrange into the enamine tautomer, resulting in the formation of a condensed 1,4-dihydropyridine structure of the type formed in the PAN,cyanide reaction. Associated with the formation of the dihydropyridine structure is a liberation of heat and a dramatic increase in the sensitivity of the material to oxygen. In its presence immediate oxidation to a fully aromatic Houtz structure occurs, together with some 4-pyridone formation.

Rearrangement of the ketimines will produce a considerable increase in the concentration of carbanions of type II Scheme XXI, and III Scheme XXII. It has earlier been supposed (Chapter 4, Section ii) that such carbanions are responsible for the chain scission reaction. Therefore considerable molecular weight reduction and volatile formation should be associated with the production of a condensed 1,4-dihydropyridine structure. Experimentally this is found to be so: during the exothermic discolouration weight losses of 31% have been recorded[8], together with extensive chain scission[24]. Below the exotherm temperature weight losses are minimal[17].

Hay[47] has associated ammonia liberation with the exothermic loss of nitrile. This could be due to side reactions involving the formation of a condensed 1,4-dihydropyridine structure, for example the interaction of two prop~~o~~agating species:



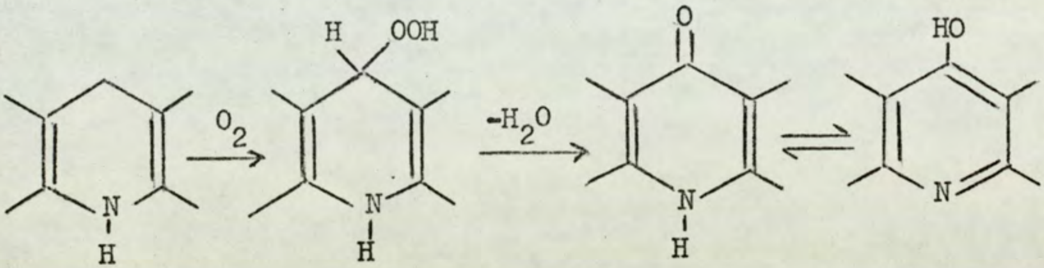
The effect of copolymerisation on the temperature at which the exothermic reaction occurs and the shape of the DTA trace can now be understood. Comonomers, such as carboxylic acids (itaconic and acrylic acids) and esters (acrylates), can facilitate the tautomeric rearrangement of the propogating ketimine groups over a wider range leading to a broadening of the DTA trace. The presence of comonomer will also lower the 'melting point' of the polymer and therefore the temperature at which the exotherm occurs. It had previously been supposed that comonomers simply acted as initiators[15] but this should in fact lead to a sharpening of the exotherm for copolymers since the overall rate of formation of the cyclic structure would be faster with higher initiator concentrations.

As already explained (Chapter 1, Section (v)) when a sample of PAN is maintained just below the temperature at which exotherm occurs it exhibits an isothermal induction period. During this induction period it is likely that fairly extensive chain scission is occurring together with the formation of hydrogenated naphthyridine structures of short sequence lengths. As a result of this chain scission molecular mobility will steadily increase until it is sufficient for the formation of a condensed 1,4-dihydropyridine system and heat will be liberated. Although oxidation of the material prior to measuring the isothermal induction period will increase the concentration of initiating species it will also cause the formation of polar groups, resulting in a decrease in the molecular mobility and an increase in the induction period. The fact that this is observed experimentally clearly demonstrates the importance of relaxation processes in determining the induction period.

(iii) CHANGES IN MECHANICAL PROPERTIES DURING OXIDATION

The changes in mechanical properties occurring during the oxidation of PAN fibre have previously been described (Chapter 1, Section (vi)). Above 260° - 280°C there is a marked divergence between the properties of fibres degraded under oxidative and inert conditions. Watt[58] has shown that oxidised PAN can not be crosslinked to any marked extent since after an initial elastic period in the stress, strain curve for the oxidised fibre there is a region of viscous flow. The increase in mechanical properties observed on oxidising the fibre must therefore be caused by some other phenomenon besides crosslinking.

One alternative is the formation of polar groups within the polymer causing increased intermolecular forces and improvement in the physical properties of the fibre. There is evidence of strong hydrogen bonding in oxidised PAN, for example the swelling and solubility of oxidised fibre in mineral acids reported by Rose[24] and the hygroscopic nature of the material[26,27,28,29]. Hydrogen bonding could arise out of the formation of ketonic species during the oxidation of a condensed 1,4-dihydropyridine structure. The methylene group in this structure is activated by two double bonds and should therefore be readily oxidised via hydroperoxide intermediates to form 4-pyridone units:



Therefore oxidation of the condensed 1,4-dihydropyridine will yield a mixture of condensed pyridine and 4-pyridone rings. Strong intermolecular hydrogen bonding through the 4-pyridone units will cause an increase in mechanical properties and preserve the fibre structure and orientation into the carbonisation stage.

This explains the similar behaviour of PAN fibres heated under inert and oxidative conditions below 260° - 280°C. Identical chemical rearrangements are occurring resulting in the formation of the condensed 1,4-dihydropyridine structure. Under inert conditions however further heating may still cause aromatisation by dehydrogenation but no polar groups capable of hydrogen bonding will be formed. Turner and Johnson[59] report the liberation of hydrogen under inert conditions at about 500°C. This is probably due to the dihydropyridine losing hydrogen and becoming aromatic. Preoxidation prevents hydrogen formation at this temperature. Although a stable aromatic system is still formed lack of strong intermolecular forces gives rise to poor mechanical properties and the fibre orientation is lost. Carbonisation without prior oxidation therefore leads to carbon fibre with inferior mechanical properties.

Evidence that the formation of a dihydropyridine structure and its subsequent oxidation can be considered as two separate reactions is shown in the remarkable change in the stress, strain curves for a sample of Dralon T degraded under inert conditions before and after exposure to oxygen (Figure 22). This curve, produced by Rose[24], shows clearly how the inert pyrolysed material is a weak, brittle fibre but post-oxidation converts it into a fibre with similar properties to oxidised PAN.

It can be concluded that when PAN is degraded under oxidative conditions the role of oxygen is three-fold :

(1) Oxidative side products, such as β-ketonitriles, can act as ~~initiations~~ initiators for the cyclisation reaction.

(2) Oxygen causes the early conversion of the condensed 1,4-dihydropyridine system into a stable, fully aromatic structure.

(3) During the oxidation of the dihydropyridine structure some 4-pyridone formation occurs and it is the presence of these groups which leads to strong intermolecular hydrogen bonding, causing an improvement in the physical properties of the fibre and preserving the orientation and fibre structure into the carbonisation stage of carbon fibre manufacture.

(iv) EXPERIMENTAL EVIDENCE FOR THE FORMATION OF A CONDENSED 1,4-DIHYDROPYRIDINE DURING THERMAL TREATMENT OF PAN.

It has been proposed that below the temperature at which the exotherm occurs, a hydrogenated naphthyridine structure of the McCartney type is formed. Above this temperature the readily oxidisable condensed 1,4-dihydropyridine is formed. It should, as in the case of PAN treated with sodium cyanide at room temperature (Chapter 7, Section (iii)), be possible to convert the hydrogenated naphthyridine into the condensed 1,4-dihydropyridine type of structure by a short treatment in refluxing DMF. In an experiment to determine this 1g of PAN powder was heated at 200°C in a furnace under a nitrogen atmosphere for 72 hours. After treatment some of the sample, now a light brown, was dissolved in DMF (not all the sample dissolved) and refluxed for half an hour. After reflux the polymer was precipitated by adding excess ether, and dried at 80°C in an oven.

Figure 23 shows the IR spectra of the degraded material before and after treatment with DMF. It can be seen from the intensity of the nitrile band at $2240cm^{-1}$ that little further degradation has occurred on refluxing in DMF. However some loss of methylene absorption at $1450cm^{-1}$ has taken place and a new absorption at $1670cm^{-1}$ has developed. It is interesting that even with the sample heated at 200°C some loss of methylene has already occurred as shown by the diminution of the $1450cm^{-1}$ band relative to pure PAN. This must mean that even at this temperature some 1,4-dihydropyridine must be formed and the correct structure for the degraded polymer is a random mixture of hydrogenated naphthyridines and 1,4-dihydropyridines. The spectral changes on refluxing in DMF are compatable with the conversion of the hydrogenated naphthyridine units into 1,4-dihydropyridines and their subsequent oxidation.

FIGURE 23a: IR SPECTRUM DEGRADED PAN BEFORE AND AFTER REFLUXING IN DMF 4,000-1500 cm^{-1}

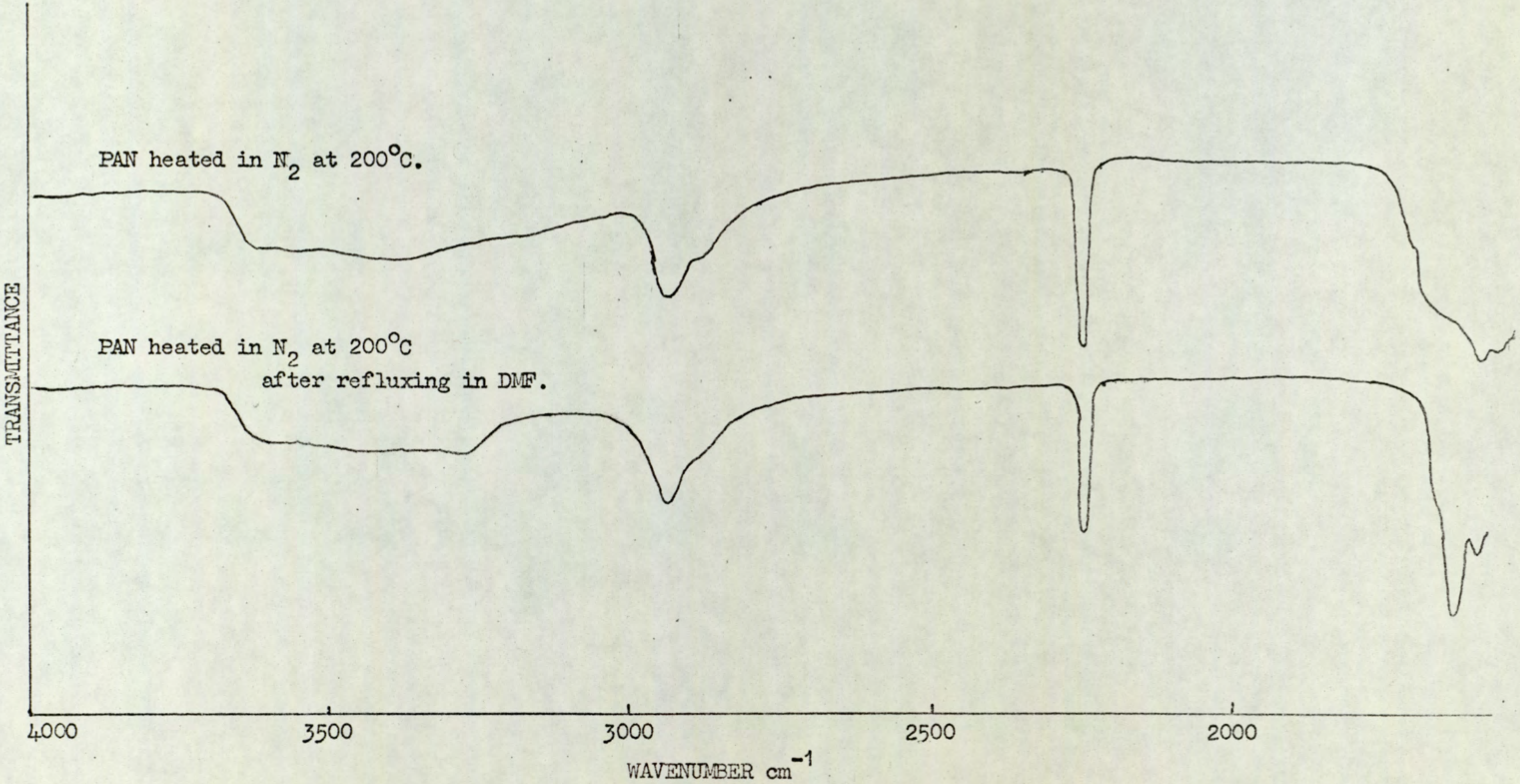
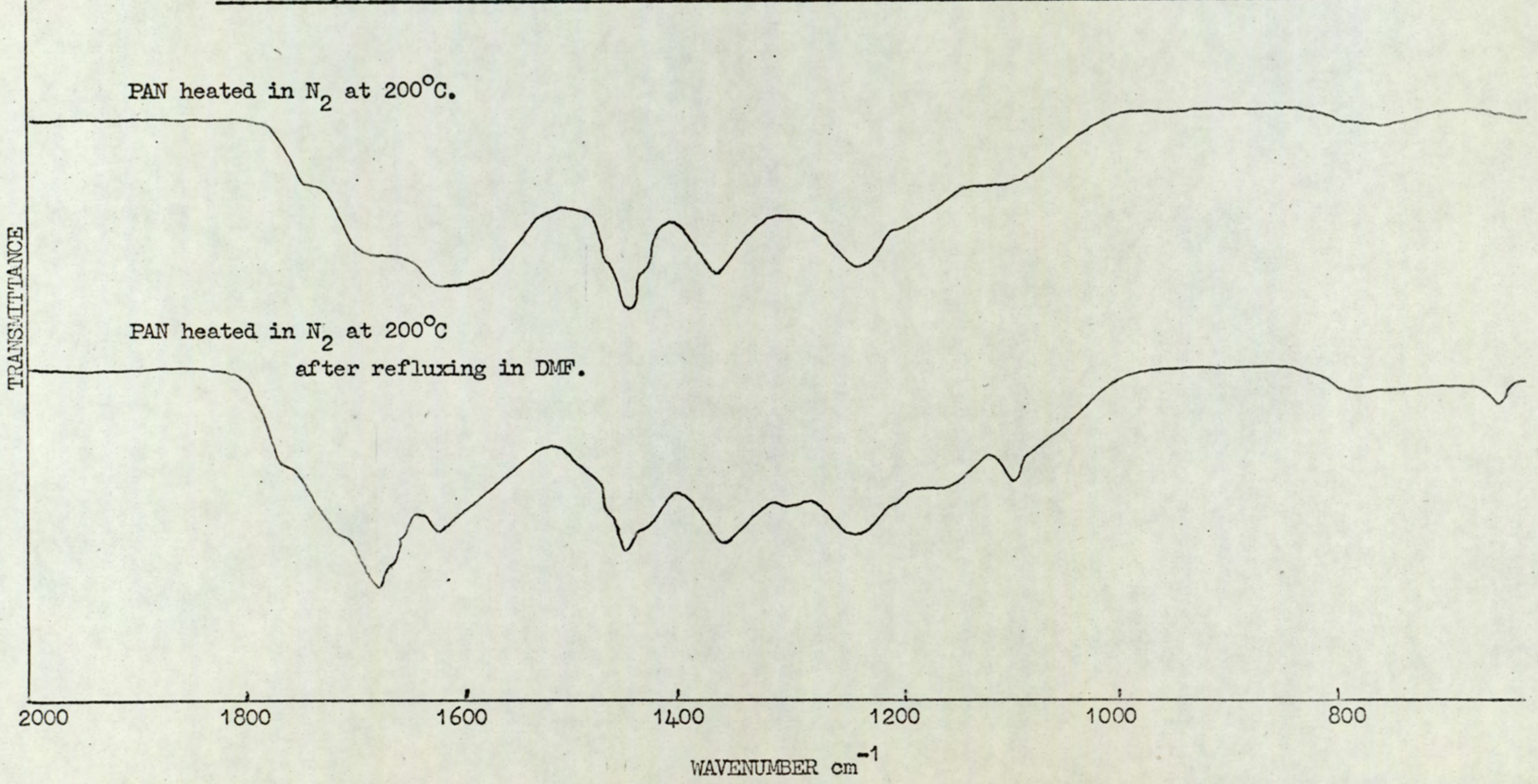


FIGURE 23b: IR SPECTRUM DEGRADED PAN BEFORE AND AFTER REFLUXING IN DMF 2000-800 cm^{-1}



9. INITIATION AND INHIBITION OF THE PAN DISCOLOURATION REACTION

(i) HYDROGEN CYANIDE

Following the observation that sodium cyanide is an excellent initiator for the degradation of PAN in solution experiments were conducted to see if hydrogen cyanide could behave as an initiator. This gas is known to be liberated in the thermal treatment of PAN and its presence could be responsible for the degradation. Negative results were obtained on passing hydrogen cyanide through a refluxing solution of PAN; the rate of discolouration was no greater than in the absence of any initiators. Similar results were found in the solid state. After passing the gas through PAN powder at 140°C no discolouration was observed. It is concluded that hydrogen cyanide does not act as an initiator for the thermal degradation of PAN.

(ii) SALTS OF WEAK ACID

The inhibition of the PAN, cyanide reaction by acids, even organic acids such as acetic acid, seemed contrary to the findings of Grassie and Hay[15] that acid groups can initiate the thermal degradation. However Grassie's experiments were conducted with copolymers of acrylonitrile and acrylic acid, and the carboxylic acid groups were actually bound into the polymer. It may be that acids can only act as initiators under these conditions.

Although it has been assumed that acids act directly as initiators the possibility of salt formation during polymerisation and post treatments, such as fibre spinning, has not been considered. Tests showed that sodium acetate is a very good initiator for the discolouration of PAN in solution. Salts of acetic acid with weak bases, for example ammonium acetate and a complex formed from triethylamine and acetic acid, caused an initial fast rate of discolouration but after a time this ceased and no further change in colour was observed. A possible explanation of this effect is the loss of some base from the system by volatalisation or reaction with the polymer causing the formation of free acid and an inhibition of further discolouration. Therefore salt formation in copolymers containing acid groups, such as Courtelle which contains itaconic acid, prior or during thermal degradation may play an important role in initiating cyclisation.

(iii) OXYGEN

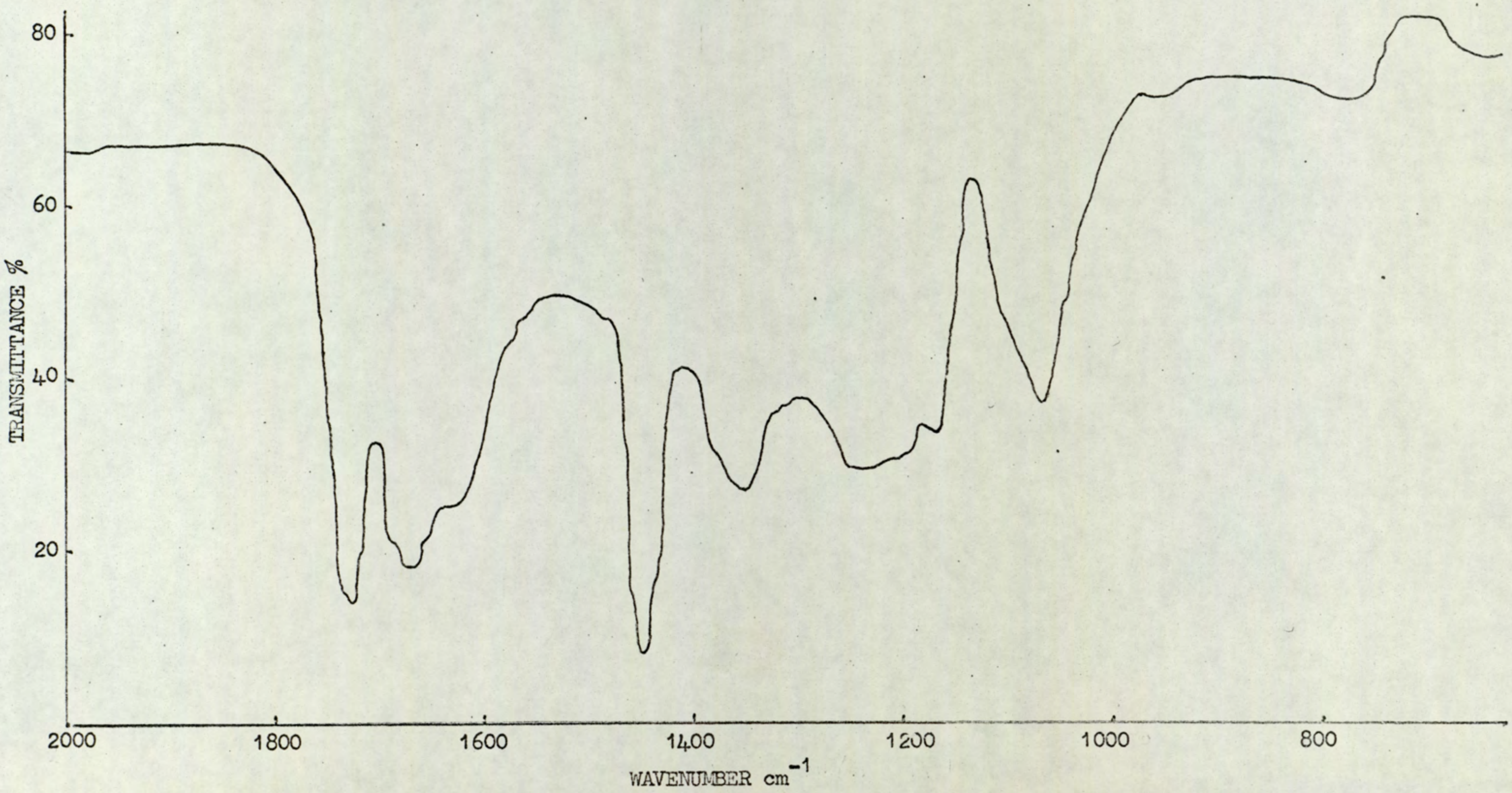
Heating PAN in oxygen is known to cause degradation at a lower temperature than heating in an inert atmosphere[5]. Peebles et al[17] attribute this to the formation of β-ketonitriles in the polymer and have demonstrated that model ketonitriles can initiate the thermal discolouration of PAN. Evidence for the formation of carbonyl groups is shown in the IR spectrum (Figure 24) of PAN partially oxidised by passing air through a refluxing DMF solution of the polymer. The fairly intense bands at 1730cm^{-1} and 1670cm^{-1} can be assigned to carbonyl.

As in the case of cyanide reaction, the oxidative degradation of PAN in solution can be inhibited by the addition of acids, particularly hydrochloric acid. This does not necessarily signify that the oxidative degradation of PAN is ionic in nature and not free radical since it has already been shown that possible intermediates, such as the hydrogenated naphthyridine or condensed 1,4-dihydropyridine structures, are hydrolysed under acidic conditions. It does show that even if the mechanism is free radical it must proceed through these intermediates and not directly to a fully aromatic Houtz type structure.

(iv) CONCLUSION

Although hydrogen cyanide is evolved during the thermal degradation of PAN there is no evidence that this can cause further degradation of

FIGURE 24: IR SPECTRUM OF PAN PARTIALLY OXIDISED IN DMF SOLUTION



the polymer as might be expected from the behaviour of cyanide salts. Initiation of the degradation reaction to give either a hydrogenated naphthyridine or condensed 1,4-dihydropyridine structure must be caused by impurities in the polymer such as acids, Lewis bases, β-ketonitriles and possibly salts formed by the interaction between bases and acidic groups within the polymer.

EXPERIMENTAL

HYDROGEN CYANIDE INITIATION IN SOLID STATE

Hydrogen cyanide, generated by adding sulphuric acid to a paste of sodium cyanide and water, was passed through a mixture of PAN powder and glass beads (mesh not known but probably 1-50). The glass beads were used to facilitate the flow of gas through the polymer. The mixture, contained in a glass tube, was heated to 140°C in an oil bath. After one hour no apparent discolouration of the polymer had occurred.

INITIATION BY SALTS OF WEAK ACIDS

In an attempt to prepare a salt from triethylamine and acetic acid excess of the amine was added to the acid and the mixture evaporated under vacuum. No solid salt formed but a viscous liquid was obtained which smelt of neither the acid nor the amine. A standard solution of PAN in DMF was placed in several tubes and heated in an oil bath to 120°C. Samples of the initiators under test were added to each tube and the rate of discolouration followed by eye.

TIME HOUR	PAN/DMF	PAN/DMF +SODIUM ACETATE	PAN/DMF +AMMONIUM ACETATE	PAN/DMF +TRIETHYLAMINE ACETIC ACID COMPLEX	PAN/DMF +TRIETHYLAMINE
0	Clear	Clear	Clear	Clear	Clear
1	Clear	Deep Yellow	Yellow	Light Yellow	Light Yellow
2	Light Yellow	Yellow/Brown	Yellow/Brown	Yellow	Yellow
3	Light Yellow	Mid Brown	Light Brown	Yellow	Yellow
4	Light Yellow	Dark Brown	Brown	Deep Yellow	Mid Yellow
5	Light Yellow	Deep Brown	Brown	Deep Yellow	Mid Yellow
6	Light Yellow	Black	Brown	Deep Yellow	Mid Yellow

It can be seen that sodium acetate is a good initiator. Although discolouration by ammonium acetate is at first rapid, it ceases once a brown colour is obtained. Similarly the amine complex causes an initial rate of discolouration which is faster than the free amine, but colouration stops at a deep yellow.

OXIDATION

1. OXIDATION IN SOLUTION

Air was passed through a refluxing 1% solution of PAN in DMF. After 14 hours a deep red colouration was produced and a brown polymer precipitated from the solution on the addition of excess ether. The IR spectrum of this compound is shown in Figure 24.

As much more rapid oxidation was brought about in ethylene glycol, the mixture becoming black in about 2 hours. The IR spectrum of PAN oxidised by this method was similar to that of PAN oxidised in the solid state.

2. INHIBITION BY ACID

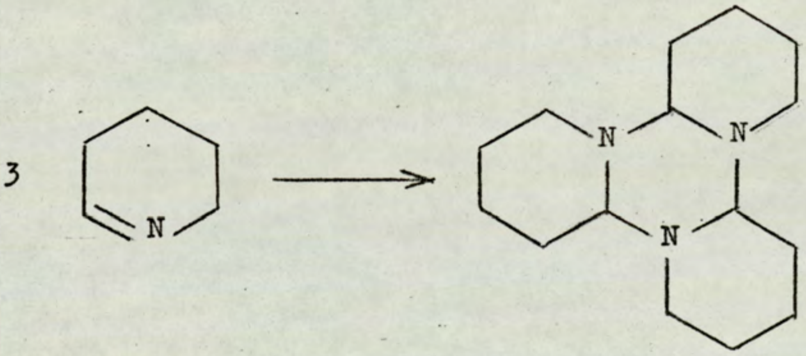
To 100ml solution of 1% PAN in DMF, 5ml of concentrated hydrochloric acid was added and the mixture refluxed gently. Air was continuously passed through the solution. After 24 hours no appreciable discolouration had occurred, the solution still being a bright yellow.

10. MODEL COMPOUNDS

(i) INTRODUCTION

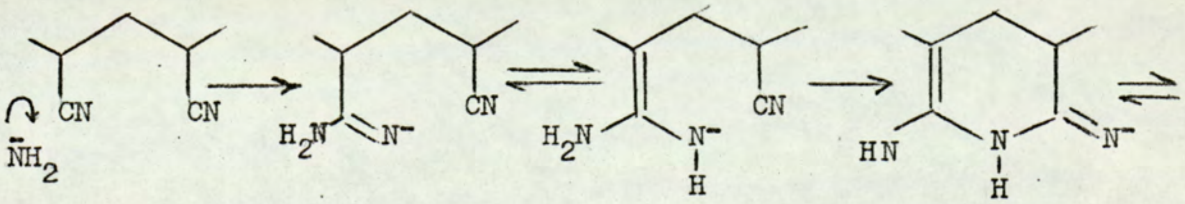
Studies on model compounds, apart from suggesting the instability of PAN towards sodium cyanide, have provided little information about the PAN, cyanide reaction. This is largely because compounds such as 2,4-dicyanopentane polymerise readily under basic conditions, probably before cyclisation occurs.

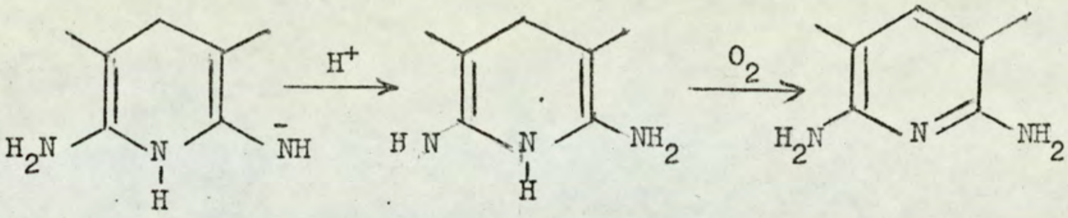
Originally it was hoped to isolate 3,4,5,6-tetrahydropyridines from model dimers as evidence of a Grassie type cyclisation reaction, but these compounds are highly reactive and unstable under normal conditions. For example 3,4,5,6-tetrahydropyridine instantly trimerises as shown below:



The isolation of tetrahydropyridines would therefore be quite impossible.

Later, model compounds were studied in an attempt to find evidence to support the formation of a condensed 1,4-dihydropyridine structure in PAN. Reacting model dimers, 2,4-dicyanopentane and glutaronitrile, with sodamide under oxidative conditions would, it was hoped, yield 2,6-diaminopyridines.





(ii) REACTION OF MODEL DIMERS OF PAN WITH SODAMIDE

Despite many attempts to detect 2,6-diaminopyridine formation in the reaction between glutaronitrile and sodamide by thin layer chromatography (TLC) negative results were obtained. A variety of solvents were used, together with dilute solutions in an attempt to reduce intermolecular reactions. Only traces of a compound with a similar retention time to the diaminopyridine were found and these were not in sufficient quantities for extraction. During the reaction between sodamide and glutaronitrile darkening of the solution occurred and it eventually became black and viscous.

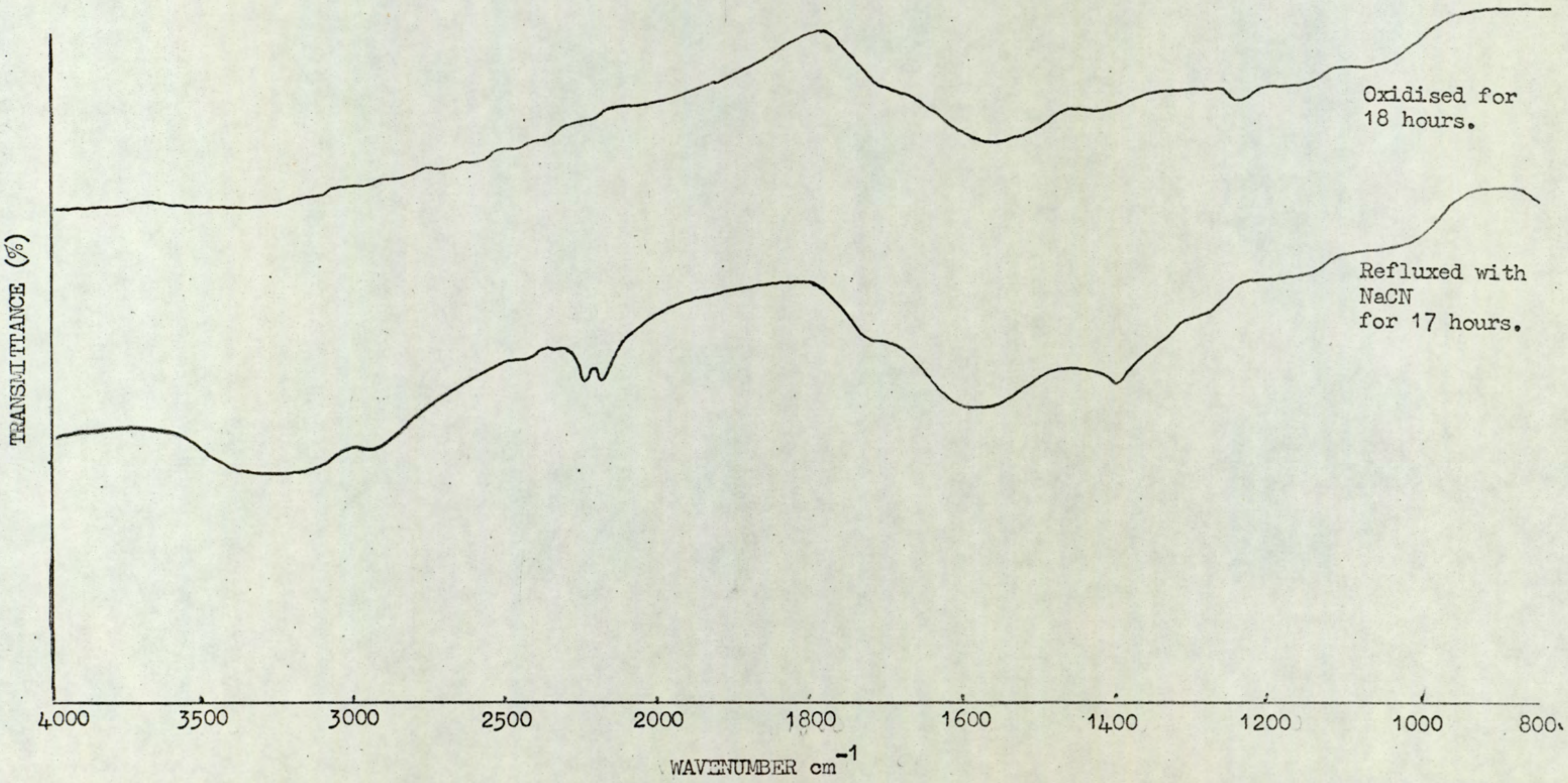
Similarly with 2,4-dicyanopentane no evidence of diaminopyridine formation was found and the reaction mixtures darkened and became viscous, suggesting polymerisation was occurring.

(iii) POLYMERISATION OF MODEL DIMERS

2,4-dicyanopentane synthesised by Clark's method was found to readily discolour when refluxed with sodium cyanide and eventually a black water soluble polymer could be obtained. Polymerisation also occurred under oxidative conditions but the product obtained was not water soluble, probably because of its increased molecular weight. Figure 25 shows the IR spectra of 2,4-dicyanopentane polymerised under basic and oxidative conditions. The lack of detail makes interpretation of these spectra impossible.

Glutaronitrile was found to polymerise under the same conditions as 2,4-dicyanopentane and, since it was more readily available than the latter compound, further investigations of the polymerisation mechanism were

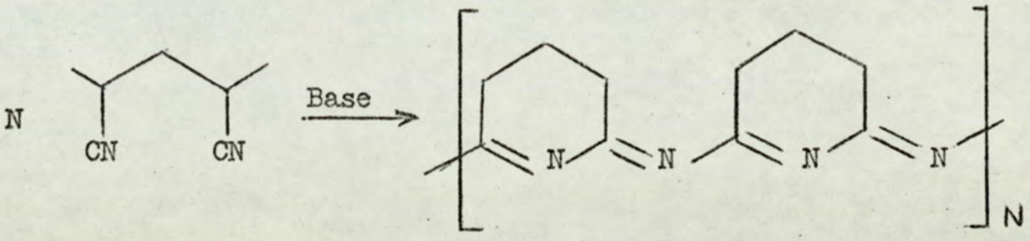
FIGURE 25: 2,4-DICYANOPENTANE POLYMERISED BY OXIDATION AND SODIUM CYANIDE.



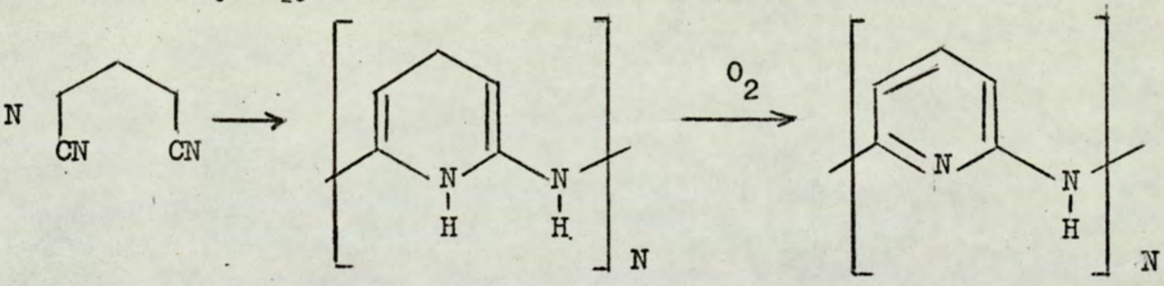
carried out with it.

There are two possible polymerisation schemes of relevance to the PAN degradation, both providing models of the cyclisation reactions thought to occur:

1. A Grassie type reaction:



2. A reaction similar to the one producing the dihydropyridine structure.



Attempts were made to isolate low molecular weight intermediates by column chromatography but it was found that most of the products stuck firmly to the column and separation was not possible. Figure 26 shows the IR spectrum of one intermediate isolated from a glutaronitrile, sodium hydride reaction by chromatography. It was shown to be fairly pure by TLC. Two nitrile bands are present at 2240cm^{-1} (small) and 2200cm^{-1} (intense). This latter band can be assigned to conjugated nitrile and its intensity suggests that there is a considerable concentration of these groups. Absorptions at 1630cm^{-1}, 1610cm^{-1} and 1570cm^{-1} are probably ν C=C and δNH with perhaps some ν C=N at 1700cm^{-1}. Very little change has occurred to the 1450cm^{-1} and 1420cm^{-1} bands.

These bands are also present in glutaronitrile and are methylene deformation absorptions. Since they are unchanged it suggests that this intermediate is not cyclic and is probably a condensation product.

FIGURE 26a: IR SPECTRUM SECOND GLUTARONITRILE FRACTION 4000-1500 cm^{-1}

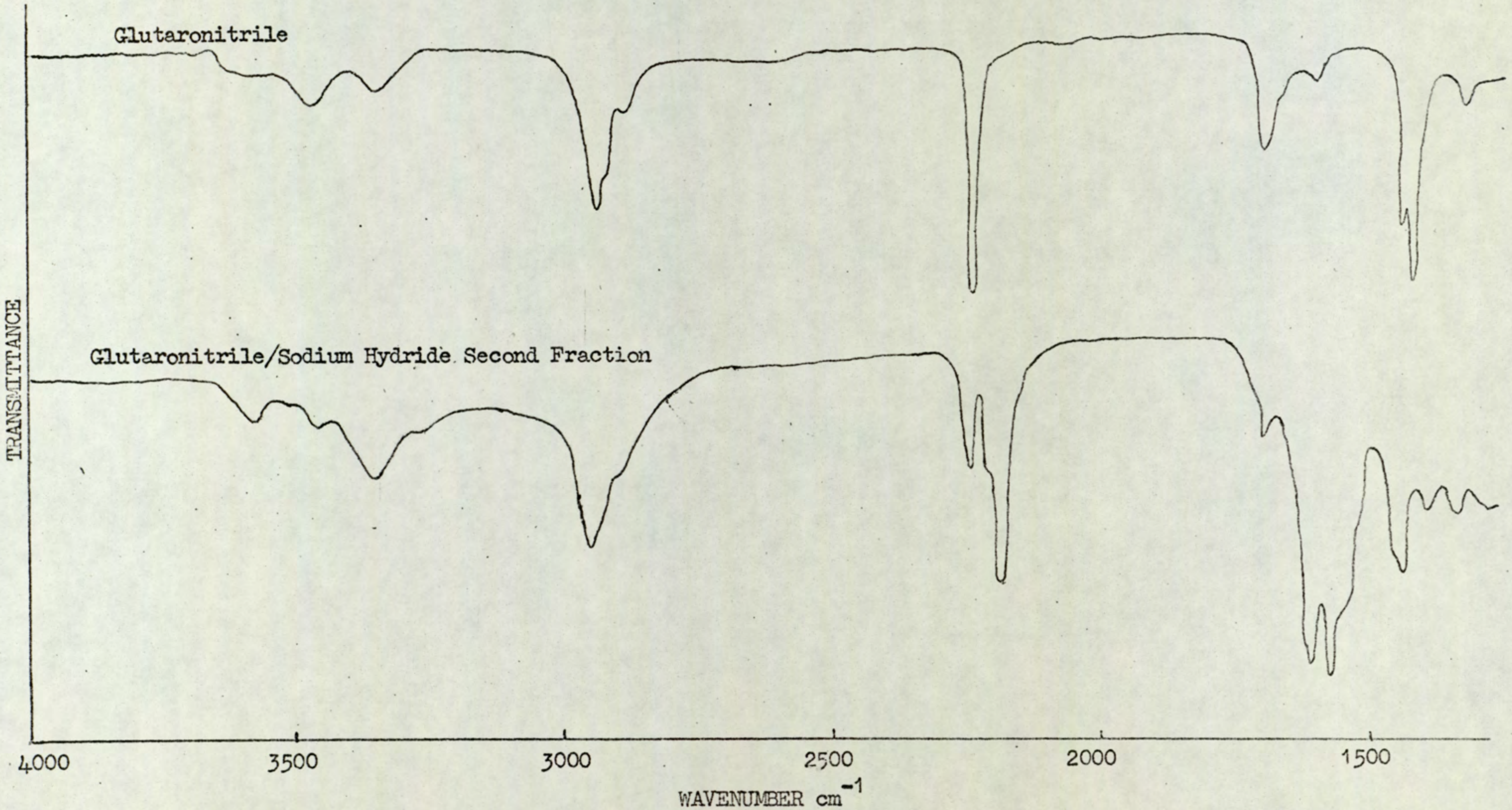
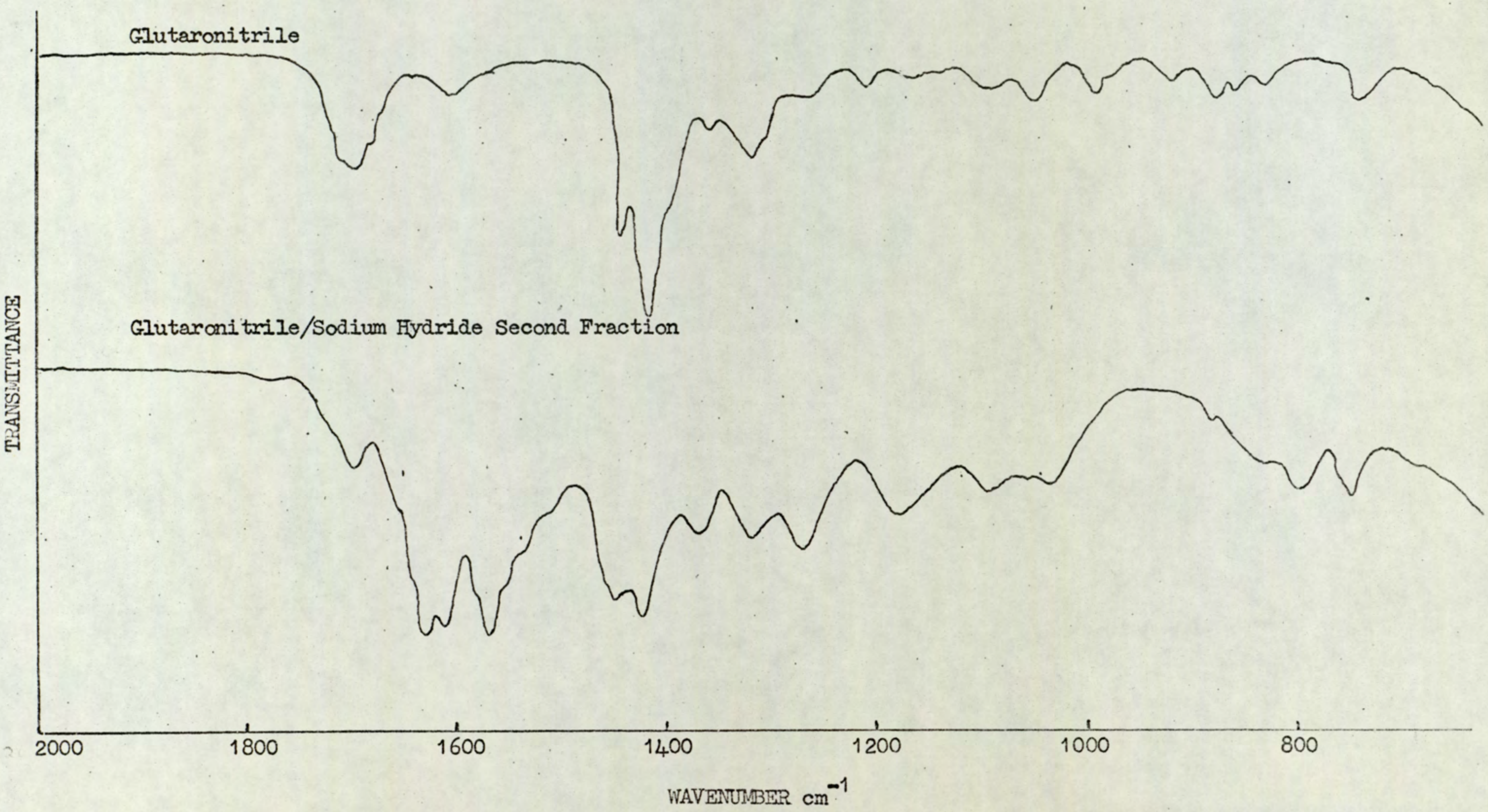


FIGURE 26b: IR SPECTRUM SECOND GLUTARONITRILE FRACTION 2000-800 cm^{-1}



(iv) POLYMERISATION OF OTHER DINITRILES

It was found that the series of dinitriles, malonitrile, succinonitrile, glutaronitrile and adiponitrile, all polymerised under the influence of strong bases or sodium cyanide. The chemistry of adiponitrile under basic conditions has been studied by other workers. It is known[32] to form a cyclic compound by intramolecular condensation and to dimerise[34] under more rigorous conditions. Because something was known of its chemistry it was decided to investigate its polymerisation further and determine the mechanism of this reaction.

A convenient method of polymerising adiponitrile is to heat it with sodium hydride. A vigorous exothermic reaction takes place, the mixture darkening and becoming viscous. Eventually the whole solution sets to a black, thermosoftening solid which can be crosslinked to an infusible mass by heating for c.a. 24 hours, just below its melting point. At intermediate stages an olive green thermosoftening material can be precipitated in ether. The IR spectrum of this compound (Figure 27) has broad bands at:3200 - 3300cm^{-1} and 3150cm^{-1} (νNH), 1650cm^{-1} (νC=C, or νC=N), 1580cm^{-1} (conjugated C=N, δNH), 1450cm^{-1} and 1400cm^{-1} (δ CH_2). There is a small sharp nitrile absorption at 2240cm^{-1}.

The reaction mixture obtained after treating adiponitrile with sodium hydride for a short time was separated into three fractions by column chromatography. TLC on these fractions demonstrated that the first and third were almost pure but the second was a mixture of the other two. Although the first fraction had an almost identical retention time on a silica gel plate as both adiponitrile and 1-amino-2-cyano-1,2-cyclopentene (the cyclic compound formed from adiponitrile) its IR spectrum (Figure 28) clearly shows it to be neither of these. There is a very unusual band at 2120cm^{-1}; this is very low for even a conjugated nitrile.

The second fraction was a yellow solid, melting at approximately 120°C. A molecular weight determination by Rast's method gave a value

FIGURE 27a: IR SPECTRUM POLYADIPONITRILE AND ADIPONITRILE 4000-1500 cm^{-1}

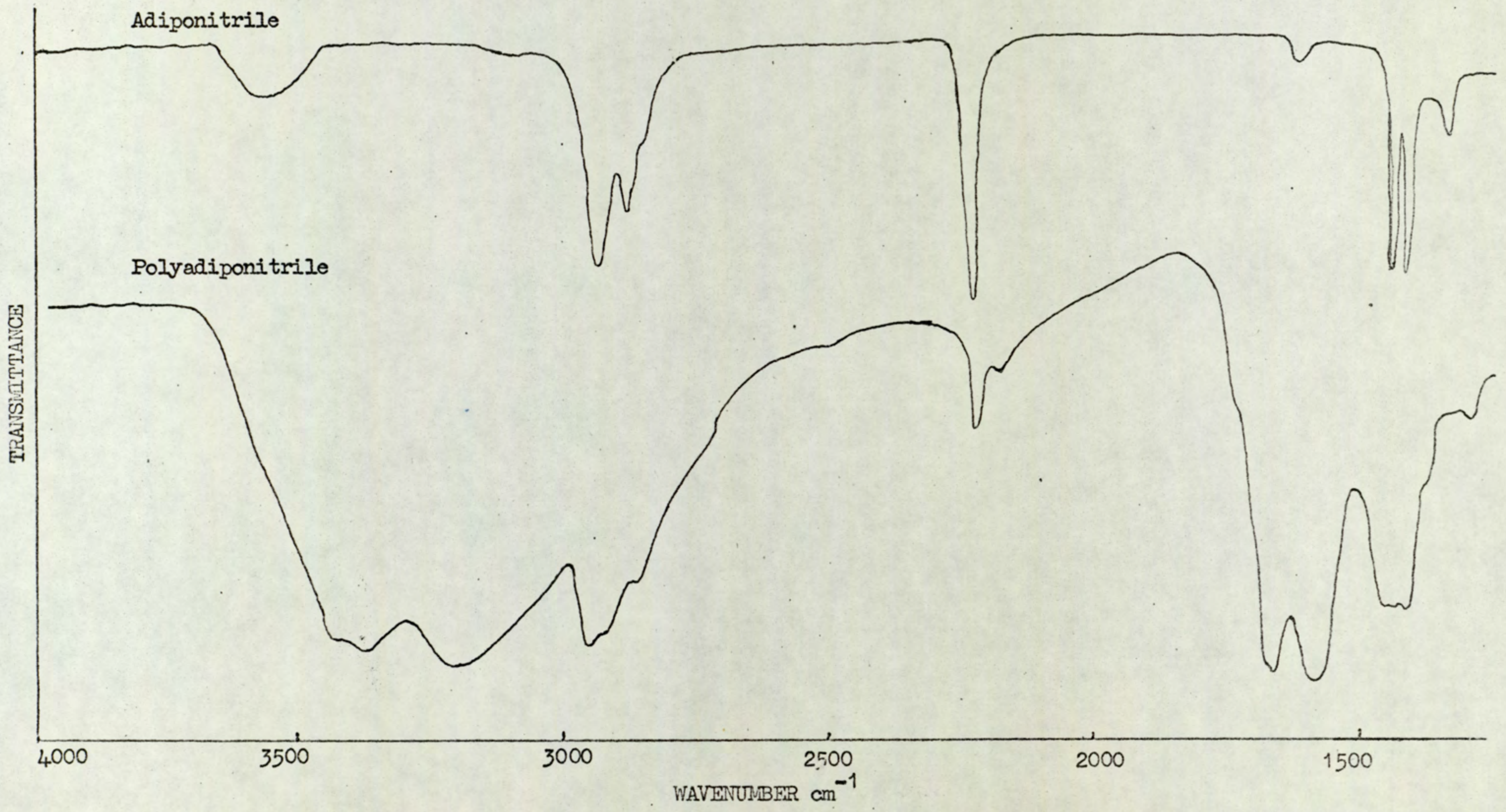


FIGURE 27b: IR SPECTRUM POLYADIPONITRILE AND ADIPONITRILE 2000-800 cm^{-1}

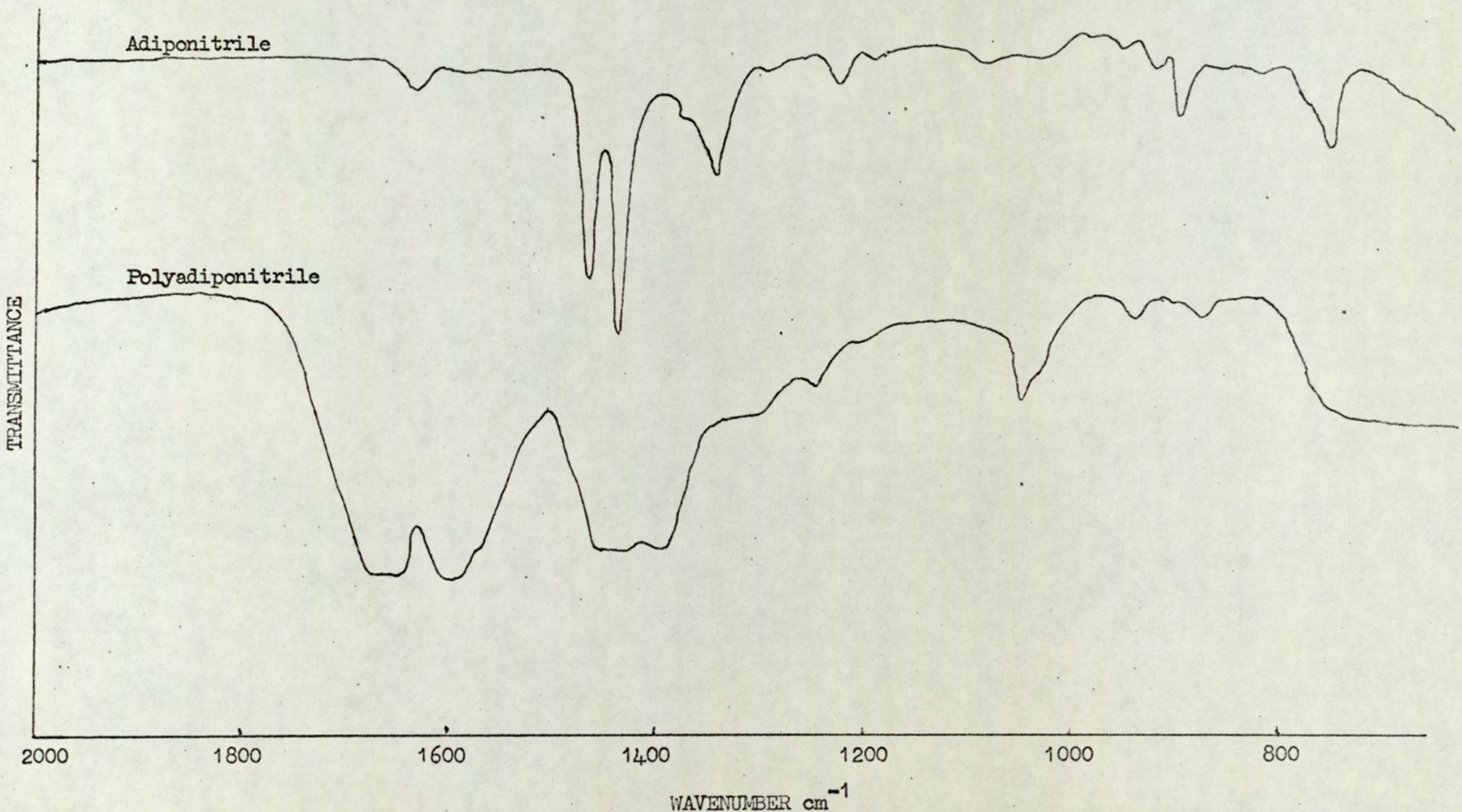


FIGURE 28a: IR SPECTRUM FIRST ADIPONITRILE FRACTION 4000-1500 cm^{-1}

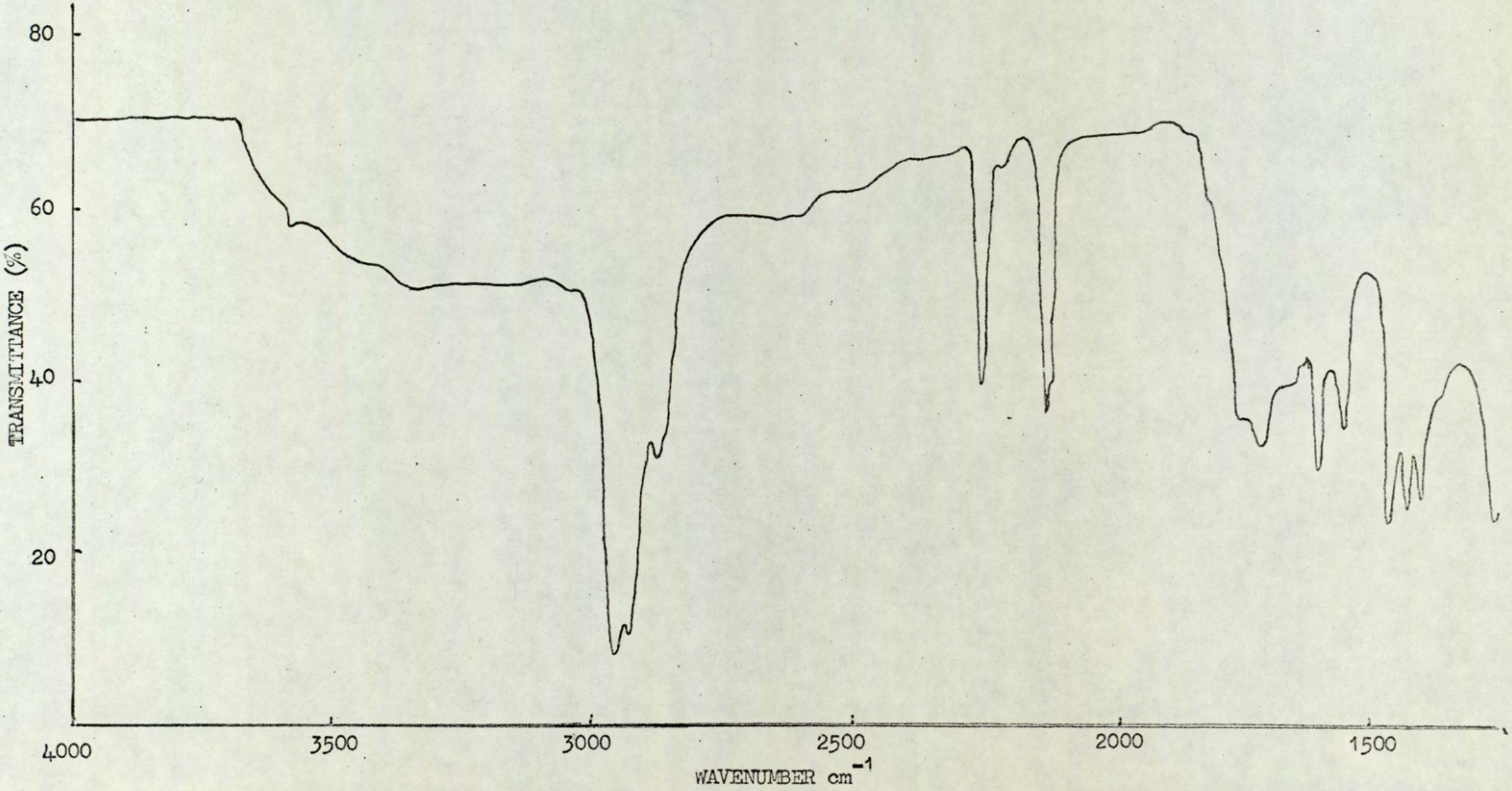
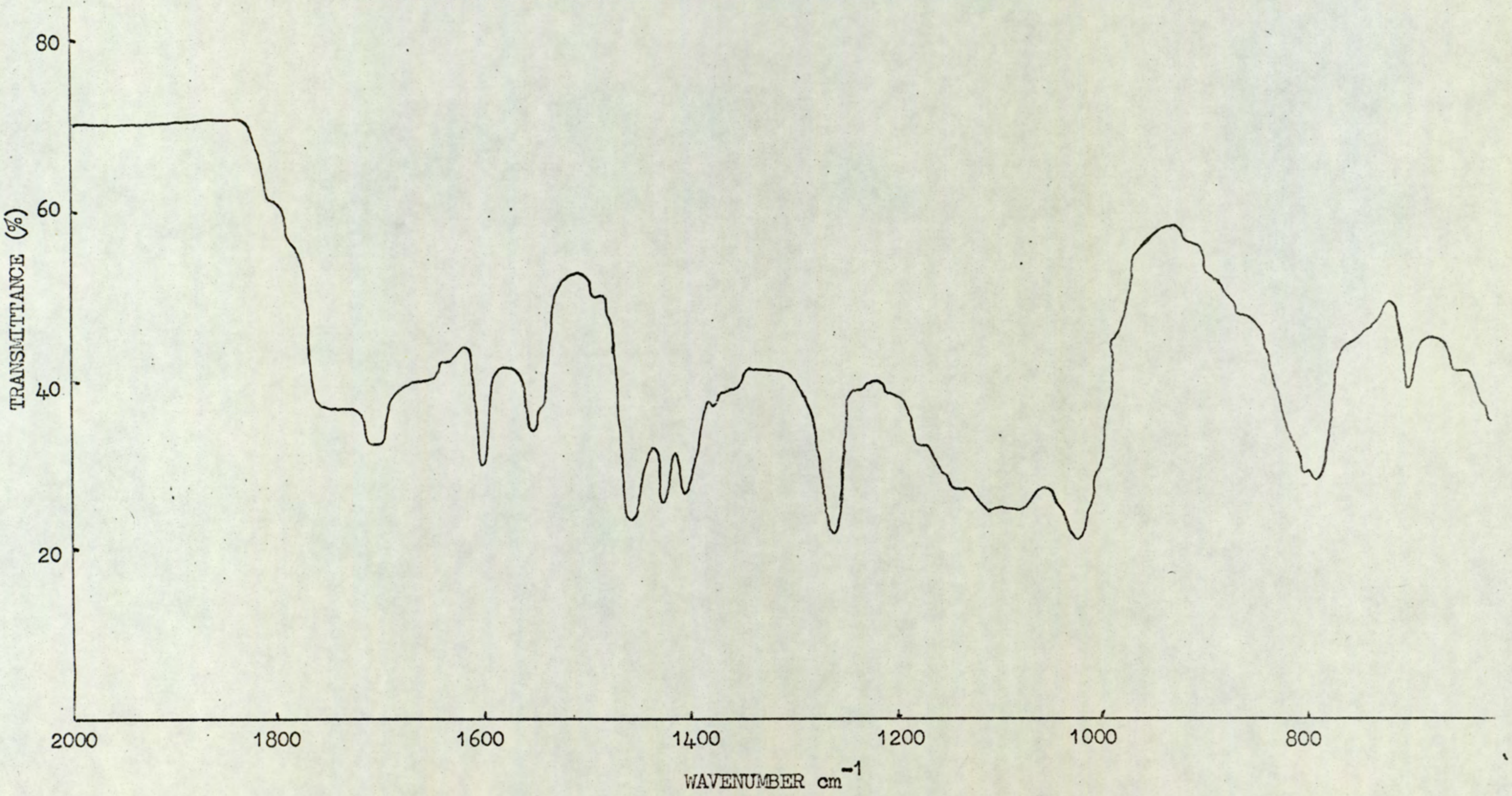
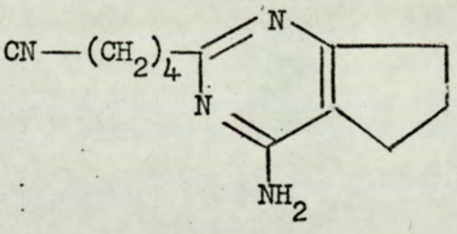


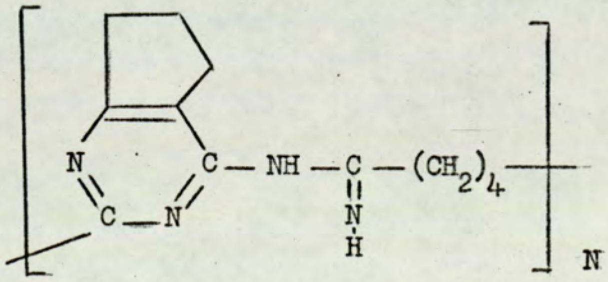
FIGURE 28b: IR SPECTRUM FIRST ADIPONITRILE FRACTION 2000-800 cm^{-1}



of 210 ± 30, indicating that the compound is a dimer (molecular weight dimer = 224) of adiponitrile. Its IR spectrum (Figure 29) is very similar to 1-amino-2-cyano-1,2-cyclopentene (Figure 30). However the nitrile absorption at 2240cm^{-1} shows there is no conjugation and there are significant differences in the region 1500cm^{-1} to 800cm^{-1}. With adiponitrile the methylene deformation absorptions appear at 1460cm^{-1} and 1430cm^{-1} whilst with 1-amino-2-cyano-1,2-cyclopentene there is a strong band at 1420cm^{-1} and smaller ones at 1430cm^{-1} and 1460cm^{-1}. Three strong bands in the IR spectrum of the fractionated compound at 1470cm^{-1}, 1440cm^{-1} and 1400cm^{-1} suggest that both cyclic and linear methylene chains are present. One possible structure which can be assigned to this compound is the pyrimidine reported by Thompson[34].



The IR spectrum of the adiponitrile polymer (Figure 27) is remarkably similar to the spectrum of this compound. All the bands are broader and less well defined, probably because of the polymer's higher molecular weight. Assuming that the fractionated compound is the above pyrimidine, a possible structure for the polymer is:



It can be concluded that the polymerisation of adiponitrile by bases probably involves intermolecular condensation via carbanion intermediates and not the formation of a polyimine.

(v) CONCLUSION

Work on model compounds has failed to produce any confirmation of

FIGURE 29a: IR SPECTRUM SECOND ADIPONITRILE FRACTION 4000-1500 cm^{-1}

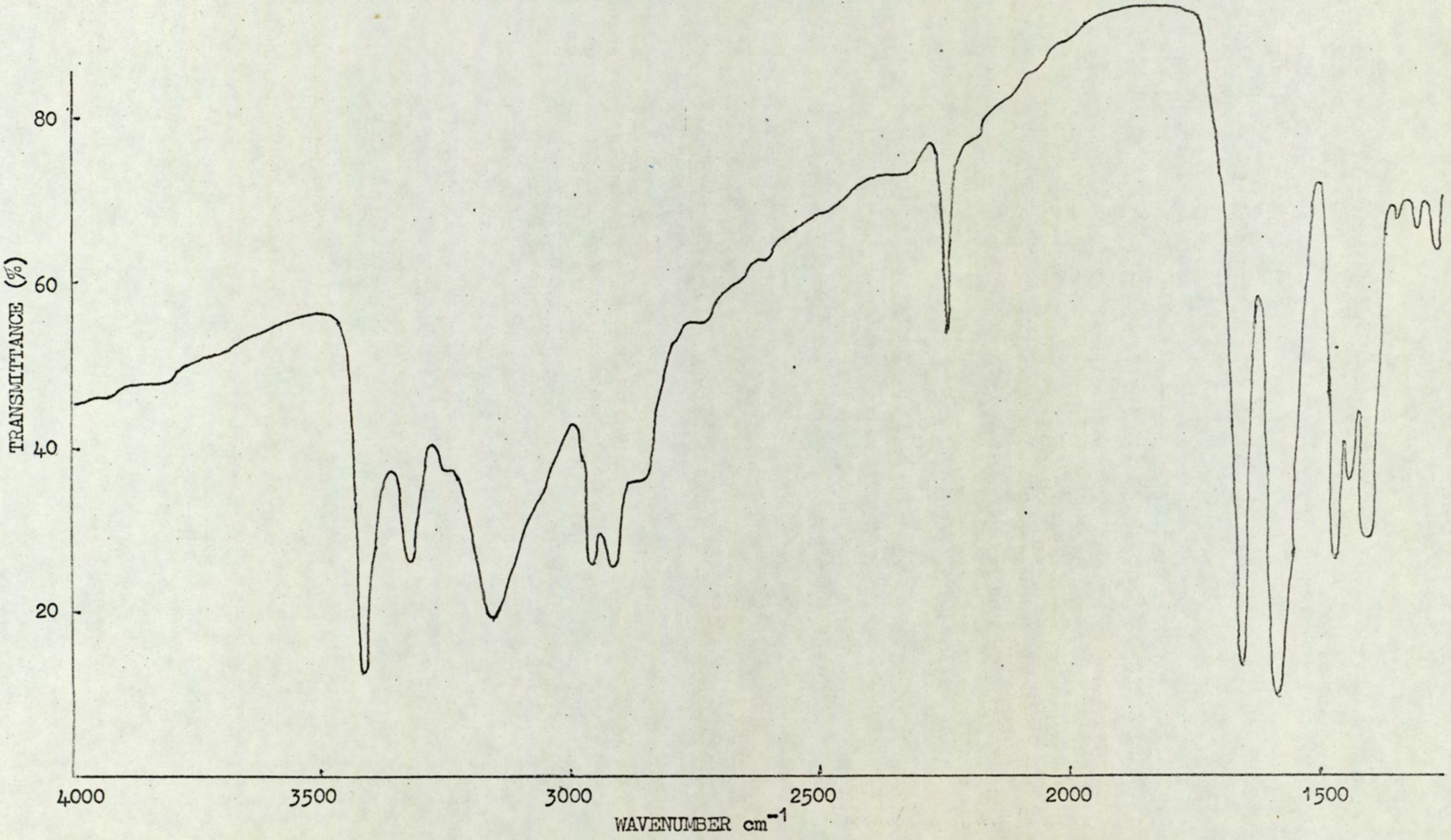


FIGURE 29b: IR SPECTRUM SECOND ADIPONITRILE FRACTION 2000-800 cm^{-1}

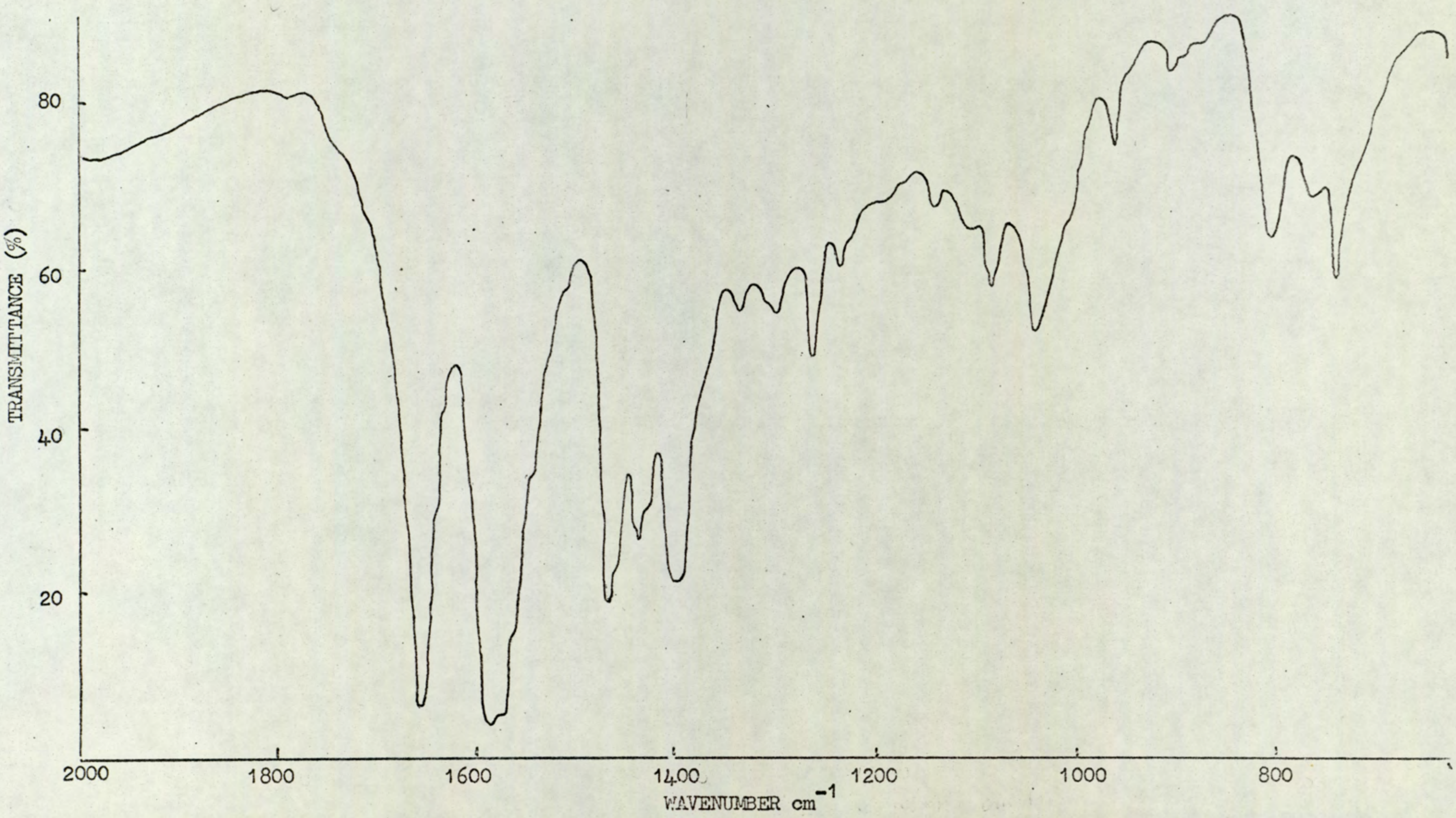


FIGURE 30a: IR SPECTRUM 1-AMINO-2-CYANO-1,2-CYCLOPENTENE 4000-1500 cm^{-1}

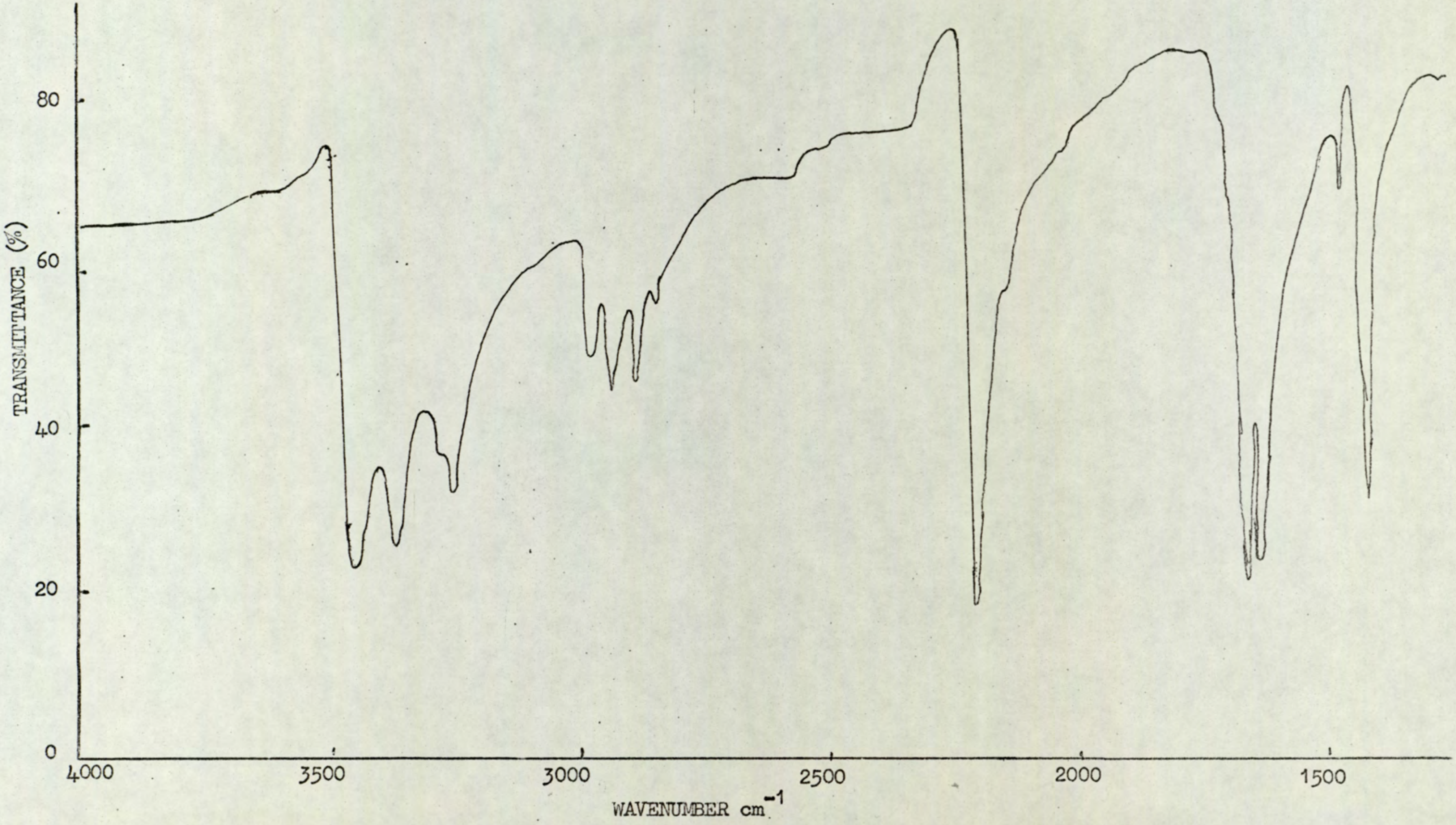
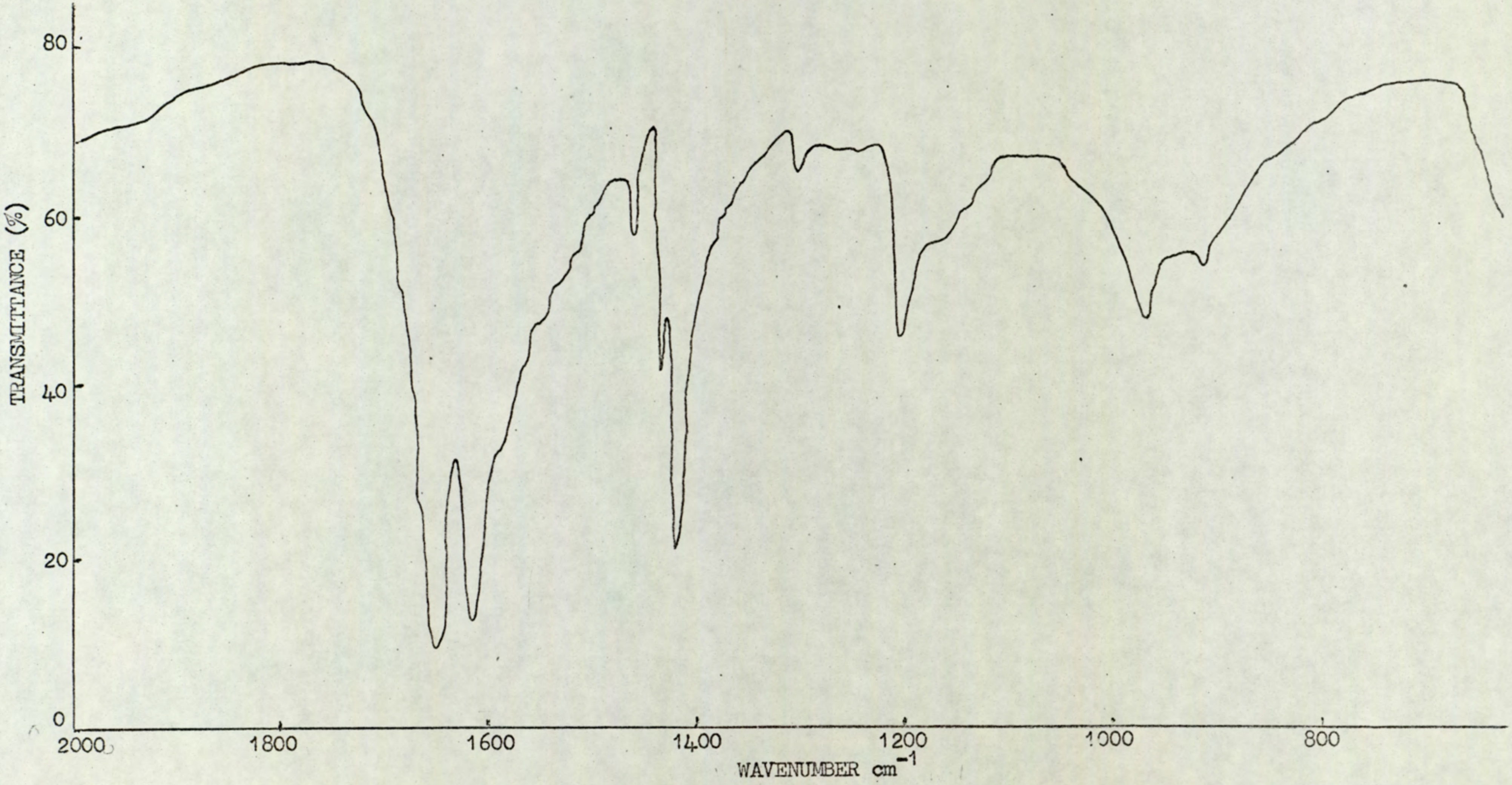
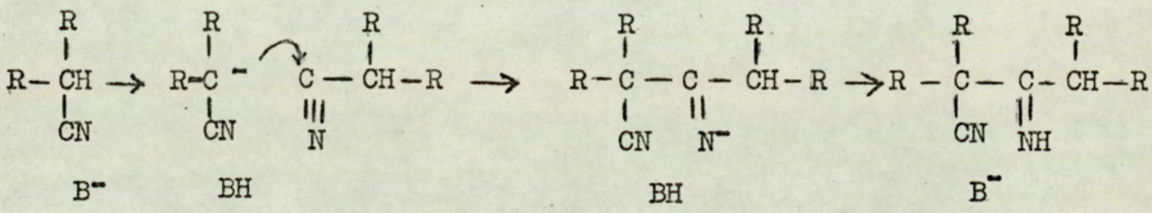


FIGURE 30b: IR SPECTRUM 1-AMINO-2-CYANO-1,2-CYCLOPENTENE 2000-800 cm^{-1}



1,4-dihydropyridine formation in support of the proposed degradation scheme for PAN. It has been demonstrated that under strongly basic conditions all dinitriles of general formula $CN-(CH_2)_n-CN$ for n = 1, 2, 3 and 4 polymerise, producing black, often intractable materials. An investigation of two of these compounds, glutaronitrile and adiponitrile, suggests that polymerisation is not by polyimine, $\left(C{=}N\right)_n$, formation but by a condensation reaction reminiscent of the aldol condensation :



Subsequent cyclisation, aromatisation and condensation may then occur.

EXPERIMENTAL

REACTION OF SODAMIDE WITH GLUTARONITRILE

In a typical reaction 4g of glutaronitrile and 2g of powdered sodamide, together with 50ml of solvent (DMF, dioxane or formamide) were reflux for thirty minutes with constant stirring. During reflux air was slowly bubbled through the mixture. Afterwards the reaction mixture was carefully diluted with a few ml of water to destroy any residual sodamide.

Thin layer chromatography was carried out on microscope slides coated with silica gel. The plates were developed in 50% ethanol, 50% chloroform and exposed to iodine vapour to render the spots visible. 2,6-diaminopyridine was used as a standard. In no cases was this compound observed in the reaction products, although very slight traces may have been present.

POLYMERISATION OF MODEL DIMERS.

1. 2,4-dicyanopentane

A mixture of 5ml 2,4-dicyanopentane and 0.05g of sodium cyanide were refluxed together. After a few minutes the solution began to darken and became black. The reaction was continued for 17 hours but no solid precipitate formed. A solid, water soluble black material was obtained by pouring the mixture into toluene.

Under similar conditions discolouration occurred in the absence of sodium cyanide when air was passed through the refluxing compound. After 17 hours a solid had precipitated. This was found to be water insoluble.

2. Glutaronitrile

Glutaronitrile behaved indentically to 2,4-dicyanopentane forming black polymers. An attempt to isolate intermediates was made as follows:

2ml of glutaronitrile was refluxed with 0.05g of sodium hydride for 5 minutes. Chloroform was added to the mixture and a solid precipitated. This was filtered off and the solution chromatographed on a column of silica gel, eluting with a mixture of chloroform (90%) and ethanol (10%). Two fractions were obtained but most of the mixture remained at the top of the column in a dark brown band.

The IR spectrum of the first fraction showed it to be unreacted glutaronitrile. The spectrum of the second fraction is shown in Figure 26.

3. Adiponitrile

In a typical polymerisation 1 ml of adiponitrile was heated with 0.05g of sodium hydride. A very vigorous reaction started with considerable heat being evolved and the liquid became a dark green and viscous. An olive green material was obtained by pouring this liquid into ether. On further heating the reaction mixture became progressively darker and more viscous until, on cooling, a black solid mass formed. This could be rendered infusible by heating in an oven at c.a. 100°C for 24 hours.

The product from one of these polymerisations was dissolved in chloroform and chromatographed on a silica gell column, eluting with 90% chloroform, 10% ethanol. Three fractions were obtained but, as in the case of glutaronitrile, most of the product remained at the top of the column. Thin layer chromatography on silica gel demonstrated that fractions one and three were fairly pure and fraction two was a mixture.

An approximate molecular weight for the third fraction was found by Rast's method. 0.0486g of the compound was placed in a tube with 0.5334g of camphor and melted very carefully in an oil bath at 180°C. The mixture was thoroughly mixed with a fine glass rod then allowed to cool and solidify. The melting points of several samples taken from the mixture were obtained to ensure adequate mixing. Molecular weight was calculated from the equation:

$$M = \frac{K \times w \times 1{,}000}{\Delta T \times W}$$

Where: K = Freezing point depression constant for camphor = 39.7

w = weight of compound = 0.0486g.

W = weight of camphor = 0.5334g.

ΔT = melting point camphor - melting point mixture

$= 172 - 155 \pm 2 = 17 \pm 2\ ^{\circ}C.$

$M = \underline{210 \pm 30}$

11. CONCLUSIONS

The cyanide ion is a very efficient initiator for the degradation of PAN in solution. A black nonflammable material is produced with very similar properties to oxidised PAN. Associated with the cyanide initiated reaction is an oxidative process and it has been shown that the degradation product is responsible for this. These findings are not compatable with the hydrogenated naphthyridine structure for degraded PAN previously proposed by other workers.

An alternative reaction with the propogating ketimine species undergoing rearrangement to the tautomeric enamine before cyclisation is proposed. The product from this reaction is a condensed 1,4-dihydropyridine which probably has a planar structure and some degree of resonance stabilisation. From the known chemistry of 1,4-dihydropyridines this compound should undergo a facile oxidation, particularly under basic conditions, with the formation of a stable fully aromatic pyrinoid system. Some 4-pyridone formation will also occur, the extent of which will depend upon the prevailing conditions, and this will cause strong hydrogen bonding within the degraded material. The deterioration in mechanical properties caused by chain scission will therefore be compensated by increased polar interactions between the molecules.

A similar theory applied to the thermal degradation can give an excellent account of the known facts about this reaction, particularly the post-oxidation of PAN pyrolysed under inert conditions at high temperatures. For the ketimine, enamine rearrangement to occur some molecular motion will probably be necessary so the formation of a condensed 1,4-dihydropyridine will be limited to temperatures near the melting point of the polymer. At lower temperatures, provided the glass transition temperature is exceeded, a hydrogenated naphthyridine structure will be formed, probably of limited sequence length.

This explains the fact that heating PAN to different temperatures can produce either a flammable or nonflammable product.

In the presence of oxygen the condensed 1,4-dihydropyridine structure produced will be immediately oxidised to a random mixture of pyrinoid and 4-pyridone sequences, as in the case of the cyanide initiated reaction. The oxidised fibre will consist of relatively low molecular weight, stable, 'ladder' polymer units strongly hydrogen bonded into a rigid structure. Fibre orientation and order will therefore be conserved until condensation of these units begins at higher temperatures.

Under inert conditions a fully aromatic pyrinoid system will still be formed by thermal dehydrogenation but this will probably not occur until higher temperatures and no polar species capable of 'bonding' the intermediate structure will be formed. Consequently, fibre orientation will be lost, mechanical properties will deteriorate and although a carbon fibre will still be produced it will have inferior properties.

Although sodium cyanide initiates the cyclisation reaction, hydrogen cyanide has no such effect. The liberation of this compound during the thermal treatment of PAN can not be responsible for initiating the further degradation of the polymer. Initiation of the cyclisation reaction must be by nucleophilic species in the fibre: amines, amides, carboxylic acids or their salts, and products from the oxidation of the methylene group such as -ketonitriles.

The role of oxygen in the preoxidation stage of carbon fibre manufacture is therefore threefold:

1. Oxidation of the methylene group by a radical chain mechanism forms active species, such as -ketonitriles, capable of initiating the cyclisation reaction of the nitrile groups.

2. Oxygen causes the dehydrogenation of the condensed 1,4-dihydropyridine intermediate to give a stable pyrinoid product.

3. Some 4-pyrinoid groups are formed which cause the preoxidised material to be strongly hydrogen bonded, preserving molecular orientation and fibre structure into the carbonisation stage.

The extensive chain scission occurring during the thermal degradation is probably essential, allowing the extensive chemical changes associated with the formation of a condensed ring system to take place without damage to the fibre structure.

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