

Thermal degradation of polyacrylonitrile fibres

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POLYACRYLONITRILE (PAN) fibres have so far proved to be one of the most successful precursors for producing carbon fibres, mainly because of their structure which gives high carbon yield and highly oriented carbon backbone when pyrolysed. In order to obtain high-performance carbon fibres from PAN, it is essential to first make the structure stable enough to undertake high-heat treatment temperatures (HTT 1000°C), so that no damage is caused to the oriented carbon backbone. PAN has initially an open chain structure which, when heated to 180°C and above, undergoes thermal degradation to form a ladder polymer. The process is known as low-temperature thermal stabilization, since it is generally carried out around 250–300°C. A thorough understanding of the process is required to convert PAN into a thermally stable structure, which could later on lead to high-performance carbon fibres.

Stabilization of PAN involves lengthy isothermal treatment in air at temperatures ranging from 200 to 300°C for periods 100–300 min^{1–5}. The extended length of time required for the stabilization step represents a limitation to the production of stabilized fibres on a high output industrial scale. However, at the same time, it provides motivation for many investigators to study the nature of the thermally induced transformations that occur during stabilization. One of the characteristic features of these chemical transformations is the evolution of considerable heat (Figure 1). Indeed, conditions must be chosen which moderate the rate of release of this heat, otherwise the reacting fibres can suffer physical damage. As stabilization proceeds, the reactants responsible for this heat generation are diminished. In general, it is at some point of diminished heat release that the thermally treated polymer fibre approaches the condition of being stabilized.

Process description

As shown in Figure 1, PAN initially possesses an open-chain structure, wherein acrylonitrile molecule is derived from ethylene by substituting one hydrogen atom for a nitrile group. The nitrile group has a highly polar character. The polymer is largely stable, short lengths of syndiotactic or isotactic structure may exist. The polarity of the nitrile group sets up strong

intermolecular dipole–dipole forces which act as cross-links and imparts strength to the fibre.

Since nitrile groups are unsaturated, there is a possibility of an additional polymerization reaction through them. This reaction is induced by simply heating the polymer, which results in a thermally stable cyclized structure and is often referred to as ladder polymer⁶. Ladder polymers tend to be thermally stable because they may be heated to greater temperatures before both the sides of the ladder break at the same ring. A linear polymer, on the other hand, requires only one bond to break the chain. The development of a structure which does not allow molecular disorientation and loss in molecular weight, when heated, is very important for completely stabilized material. The necessary step to achieve this is to heat-treat it isothermally at certain temperature which may cause maximum cyclization without damaging the structure. Such polymerization of PAN through nitrile group is not a simple reaction and is influenced by at least the following factors: (i) heating rate; (ii) temperature of stabilization/oxidation; (iii) treatment time; (iv) environment during heating; (v) stretch ratio during the process.

Heating rate

Since the conversion of PAN into a cyclized structure is an exothermic reaction, it is obvious to heat it at a very slow rate. Thus before going ahead with the stabilization of PAN, it is necessary to first look into its complete thermal behaviour, as it gives an indication for the processing parameters. A typical DSC/DTA curve for PAN is shown in Figure 2. If the heating rate is high, not only does the peak temperature of exotherm shift to higher temperatures but it is very steep as well, causing severe damage to the molecular chains. A heating rate of 5°C min⁻¹ up to 180°C and slower (2°C min⁻¹) thereafter is recommended. Area under the DSC curve gives the value of total heat flow, which is usually in the range 1200–1300 J/G.

The cyclization reaction is initiated around 180°C,

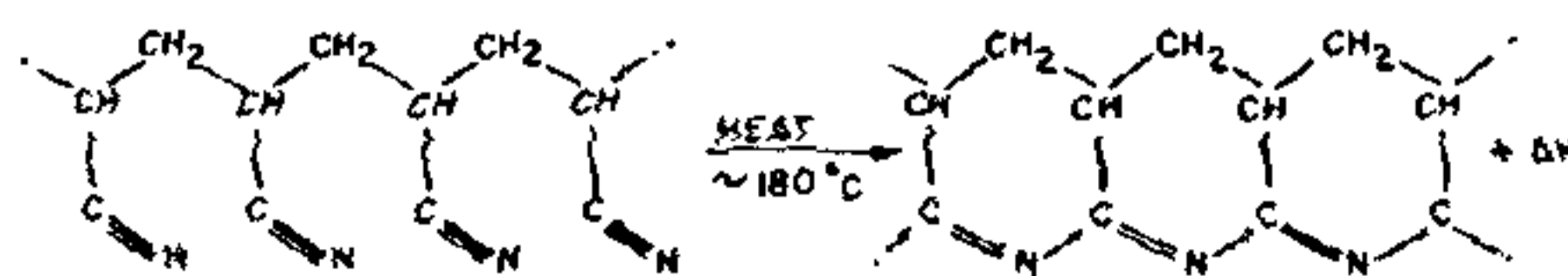


Figure 1. Cyclization reaction in polyacrylonitrile.

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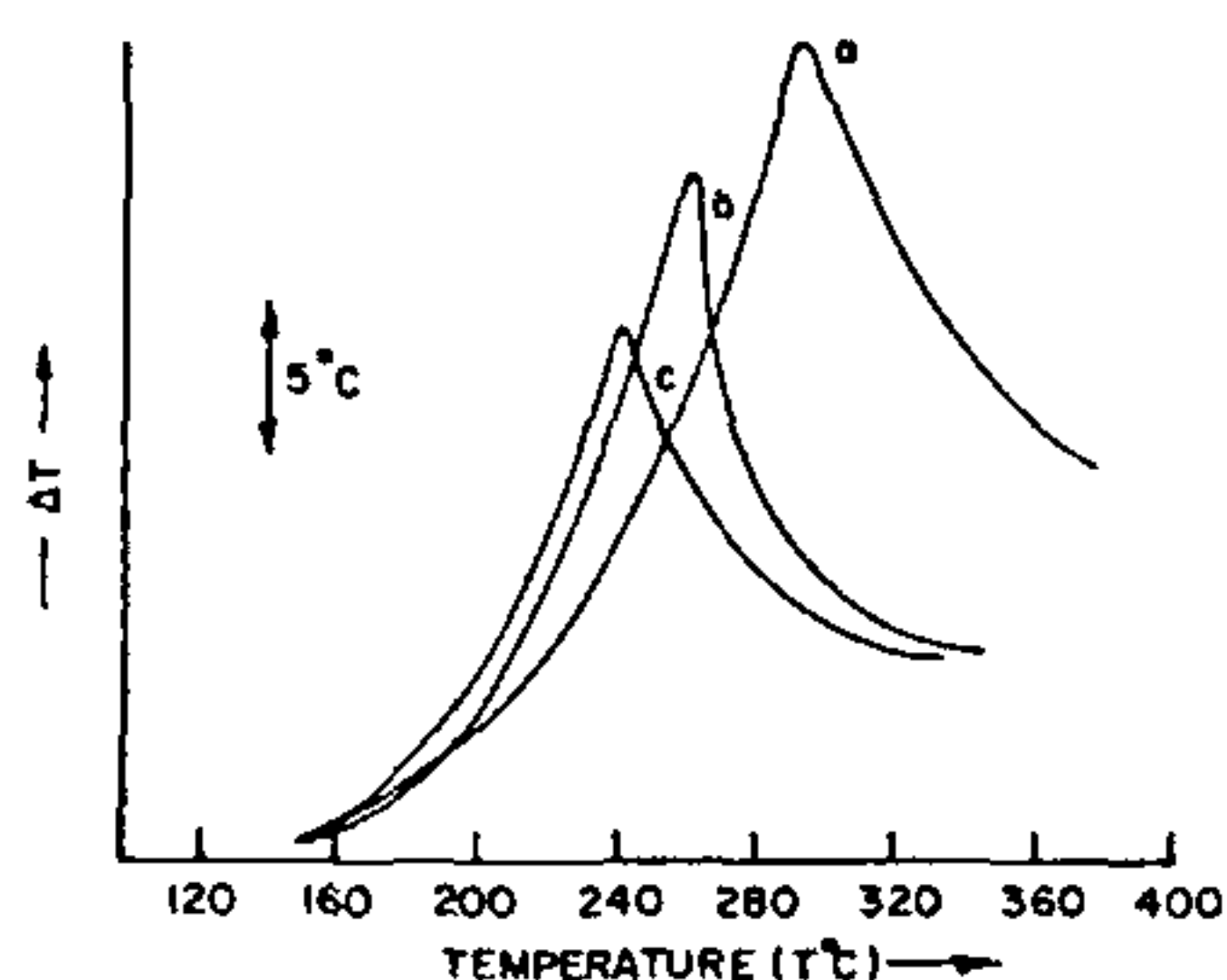


Figure 2. DTA curves of polyacrylonitrile fibres in presence of nitrogen at different heating rates (a) at $10^{\circ}\text{C min}^{-1}$, (b) at $5^{\circ}\text{C min}^{-1}$, and (c) at $3^{\circ}\text{C min}^{-1}$.

either by ionic species or comonomers present in the structure. It has been suggested that acids are particularly active. The polymer PAN has a largely atactic structure so that cyclization proceeds through isotactic sequences or when rotation about the carbon single bonds brings a nitrile group into the vicinity of the 'active chain end'. If there are large number of active sites in the initial structure, the rate of cyclization reaction can be extremely fast and it would be impossible to contain the exotherm. An optimum amount of comonomer content in the PAN fibre is therefore necessary.

Temperature of stabilization/oxidation

The DSC/DTA curves shown in Figure 2 gives information regarding maximum heat treatment temperature, which should generally be lower than the peak exotherm temperature, i.e. 270°C in this case, to be given during stabilization process. In order to prevent molecular disorientation, isothermal heating at a relatively much lower temperature is carried out. However, heating at lower temperatures takes a very long time for completion of the cyclization reaction and hence increasing temperature in steps is generally preferred, e. g. isothermal heating of PAN at 200°C for several hours stabilizes it enough to withstand higher temperature, say 220°C , without damaging the structure. Not only is the resulting exotherm much less but the rate of diffusion of oxygen and cyclization is also much faster at higher temperatures. By doing so, the total isothermal heating time may be reduced to just half, which is vital for commercial production of thermally stable PAN fibres. An example is described below:

Effect of stepwise pre-oxidation on cyclization reactions

Figure 3 represents the heat flow behaviour of PAN fibre sample after it has been oxidized for 100 min at

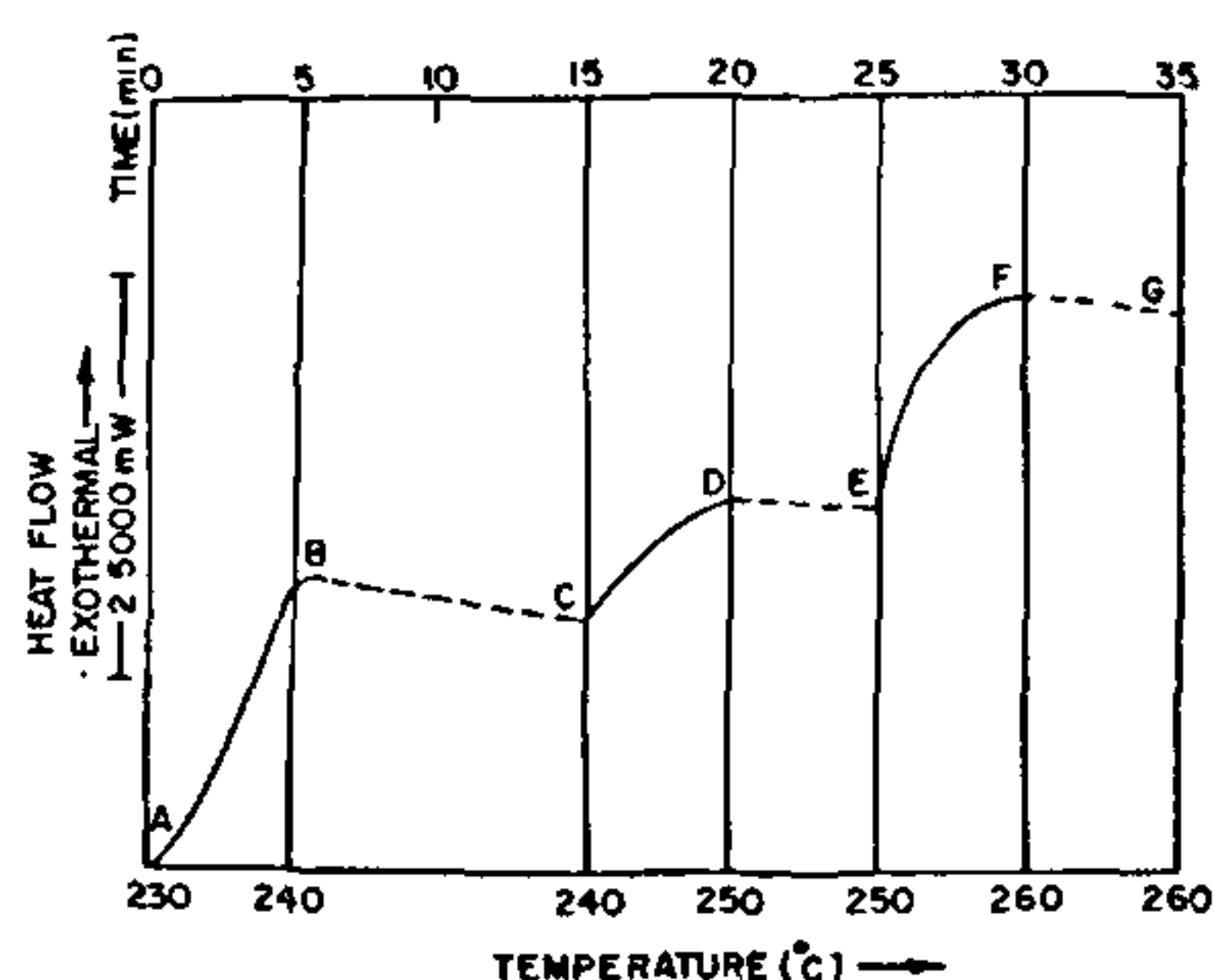


Figure 3. Effect of stepwise heating on the differential thermal analysis behaviour of PAN fibres stabilized for 100 min at 230°C .

230°C (ref. 7). Portion 'AB' in the curve represents the heat flow behaviour of this sample when the temperature is increased from 230°C to 240°C in five min. Isothermal treatment of this sample for 10 min at 240°C is shown by region 'BC'. As evident from the curve 'AB', sharp exotherm associated with the fibre between 230°C and 240°C shows the presence of uncyclized structure in sample at 'A'. Absence of the exotherm in region 'BC' suggests that the rate of cyclization is very slow at 240°C . However, if the temperature is further raised to 250°C in five min the exotherm again appears (region 'CD') though it is less severe compared to 'AB'. Isothermal heating at this temperature again does not show any peak at all (region 'DE'). Calculations of activation energy made at points 'C' and 'E' show an increase in the activation energy from 116.3 to 128.9 kJ mol^{-1} . Similar trend is followed in regions 'EF' and 'FG'.

In the case of PAN fibres with a certain average angle of orientation, it is clear that molecular chains possessing varying degree of orientation are present. At a given temperature, molecules with certain preferred orientations will react. For lesser oriented molecules, higher activation energy should be required, i.e. as the thermal stabilization of PAN fibres increases, higher activation energies would be required. Figure 3 shows that, although single low temperature, e.g. 240°C , is not sufficient to cyclize the whole structure, a single high temperature (say 260°C) may be more suitable. However, this is not practicable since a large exotherm associated with high temperature will destroy the structure of PAN. A choice of different temperatures in steps is therefore more suitable for the stabilization process.

Effect of oxidizing medium

As mentioned earlier, cyclization of PAN can be initiated by ionic initiators present in the form of

comonomers around 180°C. Some degree of nitrile polymerization can take place even in the presence of N₂ or inert atmosphere. However, in the presence of oxidizing agent the reaction rate is increased and the stabilization can be achieved in a much shorter duration. Various oxidizing media used so far are O₂, air, SO₂, NO₂, etc. (ref. 5).

Fast-reaction rates, on the other hand, cause large and sudden exothermic reaction. In order to avoid the sharp exotherm, oxygen in controlled amount has proved to be more useful. Use of air thus helps in catalysing the cyclization reaction and cause dehydrogenation by incorporating oxygen containing functional groups and keeping the exotherm in check as well, as shown in Figure 4. The dehydrogenation causes aromatization, thus making the structure of PAN thermally more stable. The colour of the fibres during stabilization changes from yellow or reddish brown to black. The rate of overall stabilization process is limited by the transport of oxygen to the interior of the fibre and is diffusion-controlled. The classic diffusion-limited kinetics vary with $t^{\frac{1}{2}}$.

During the initial period, the sheath or skin becomes stabilized and forms a barrier for further diffusion of oxygen. As such, for smaller durations of time the core remains relatively understabilized. This two-zone morphology of the cross-section of PAN can be viewed under optical microscope or scanning electron microscope.

Increasing temperature may cause further diffusion of oxygen, causing uniformity of the stabilization. For this reason the diameter and the denier of the fibre should be smaller. Moreover, for larger denier fibre it may require several hours for achieving complete cyclization, causing over-stabilization of sheath. Over-stabilization, on the other hand, causes more intermolecular cross-links, which inhibits linear movement of molecular chains and thus strain to failure of the fibre suffers. Under tensile loading the mismatch of linear motion of these chains relative to core and sheath may further cause stress

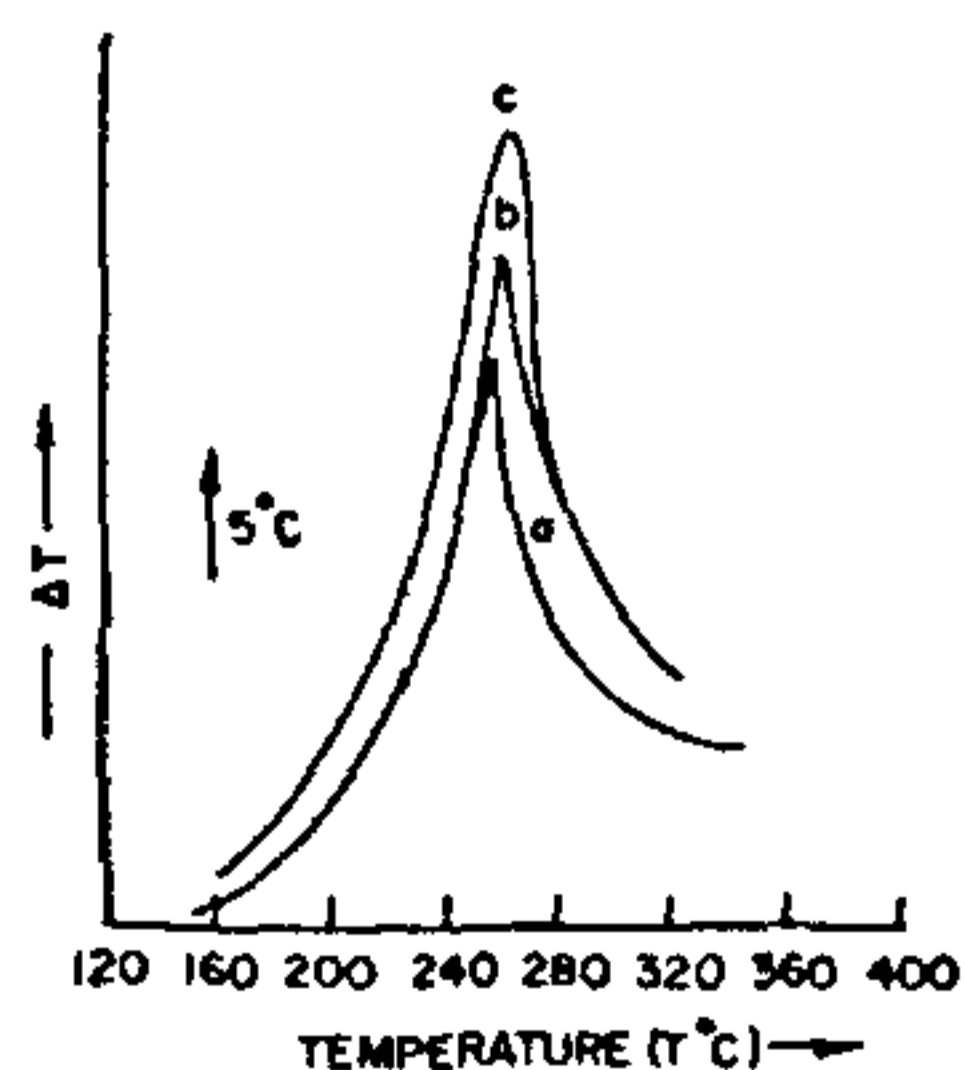


Figure 4. DTA curves of polyacrylonitrile fibre under different catalysts: (a) nitrogen, (b) air, (c) oxygen.

concentrations and hence lower the strength of the oxidized fibres. A typical curve for oxygen uptake of different denier PAN fibres with $t^{\frac{1}{2}}$ is shown in Figure 5. It also shows that smaller denier fibre has parabolic dependence whereas oxygen uptake of large denier fibre is much slower, increasing almost linearly.

Most important are the very critical mass and heat transport problems during stabilization. The progress of stabilization under dehydrogenating effect of oxygen is diffusion-controlled. The increase in the temperature increases the diffusion rate which, however, is limited by heat transport. The overheating and melting of the precursor must be avoided. The major requirement is that the by-products must be allowed to evaporate without creating structural defects. Since PAN fibre is a bad conductor of heat, there is a definite limitation on heating rate due to heat transfer problems.

Shrinkage/elongation

It is well known that during thermal heating above 180°C, PAN fibres show characteristic shrinkage. The shrinkage is divided into two parts, i.e. physical and chemical. Stretching of the atactic noncrystalline PAN during its fabrication to fibres is accompanied by quasi-reversible decoiling of the molecular structure and in a subsequent thermal treatment above the glass transition temperature this decoiling reverses, thus leading to shrinkage. In other words, the stresses frozen during the spinning are released during heating, causing shrinkage in the molecular chains. This shrinkage is known as physical shrinkage. Shrinkage occurring as a result of cyclization of nitrile groups is called chemical shrinkage, leading to imperfect ladder polymer formation. For the formation of step ladder polymer, it is necessary that the cyclization reaction occurs between two different molecules which is possible only when the chains are close enough and the reactive nitrile groups oppose

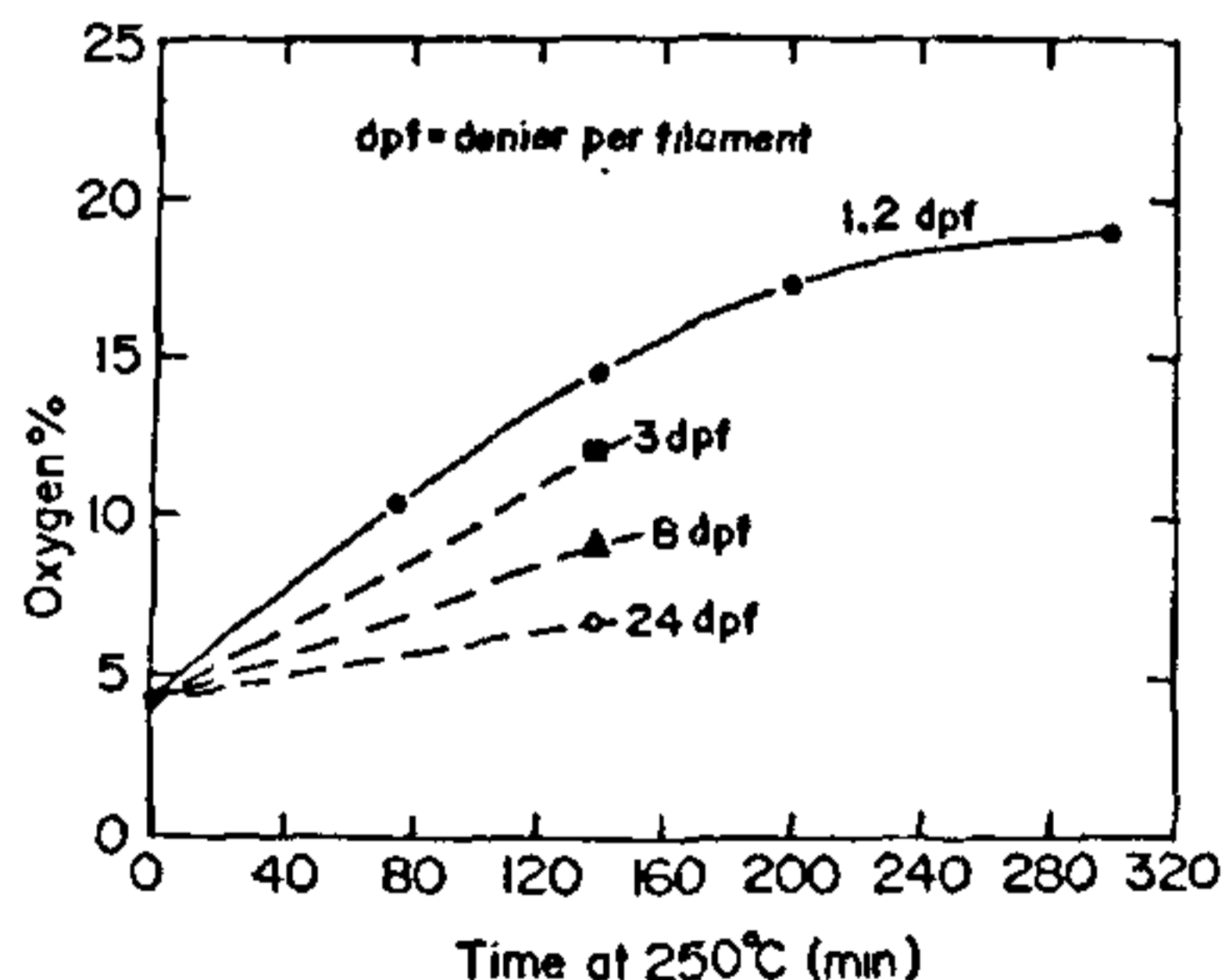


Figure 5. Oxygen uptake of various deniers of PAN fibres as a function of soaking time at 250°C.

each other. The extent of chemical shrinkage can also be controlled by applying load.

Tension/load on the fibre tow during stabilization process

As mentioned earlier, cyclization of PAN fibres causes shrinkage of the molecular chains and the amount of this shrinkage can be controlled by applying load to the fibre tow. The application of this load is essential to maintain the overall orientation of molecular chains along the fibre axis. However, excess of load may cause unwanted elongation in the fibre tow which may result in the breakage of the dense structure. The higher density may cause difficulty in the diffusion of O₂ in the fibre across the cross-section, which may result in a core-sheath structure. It is then difficult to achieve sufficient degree of stabilization of PAN. Once the core becomes dense and sheath becomes stabilized, no matter how much treatment time is increased, further diffusion of oxygen remains very much restricted. An optimum amount of load is therefore essential for better stabilization. Figure 6 shows a typical shrinkage vs load curve for PAN fibres. As shown in the figure, the behaviour and the amount of the shrinkage change with increase in the load per filament, so much so that for 1 kg load on fibre tow there is about 4% elongation in the fibre. It might be possible that overstretch may cause severe bond breakage in the molecules. For example, it is not necessary that an elongation of 60% achieved by applying a load of 2500 g should give good carbon fibre. Such a large elongation could be at the expense of bond breakages.

Chemistry of the process

Several mechanisms for thermal degradation may operate depending on what kind of initiators are present in PAN. When ionic species are present,

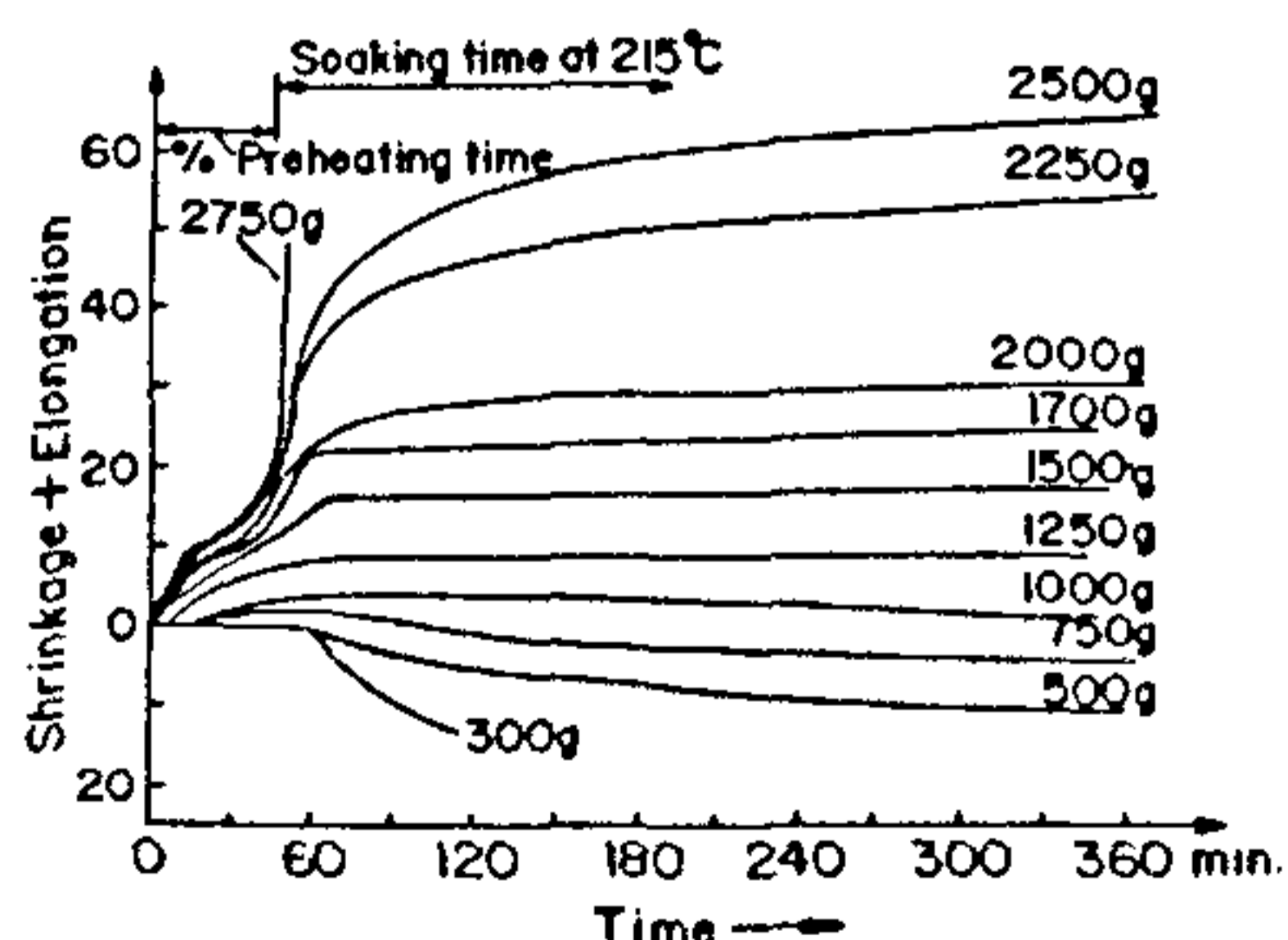
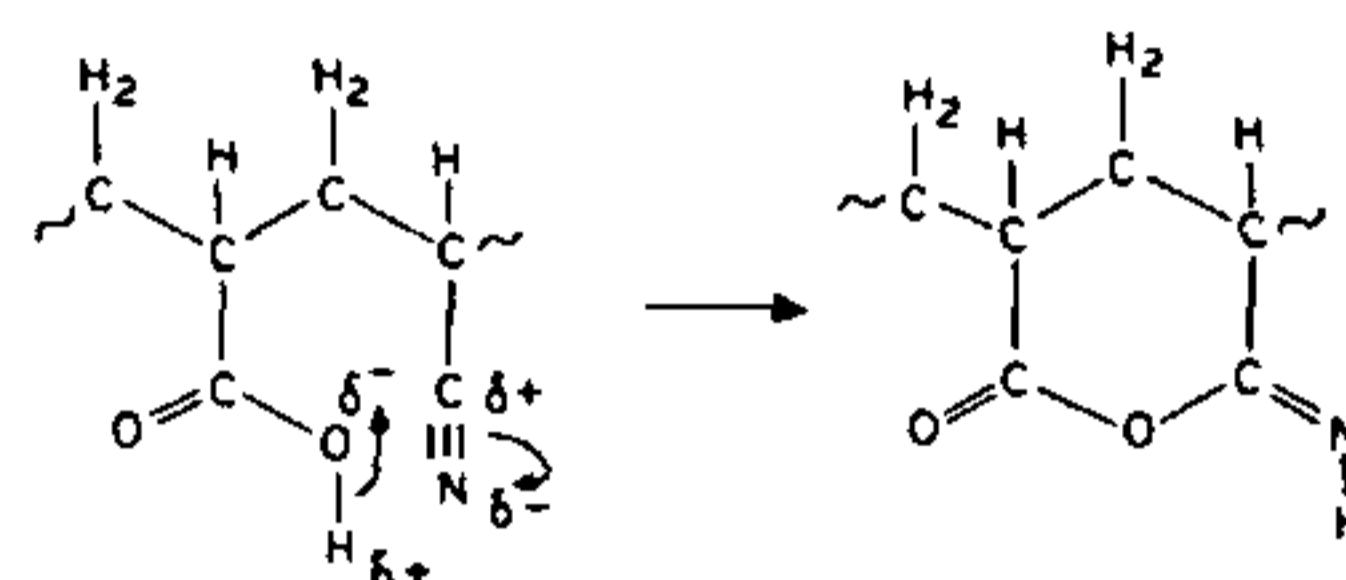
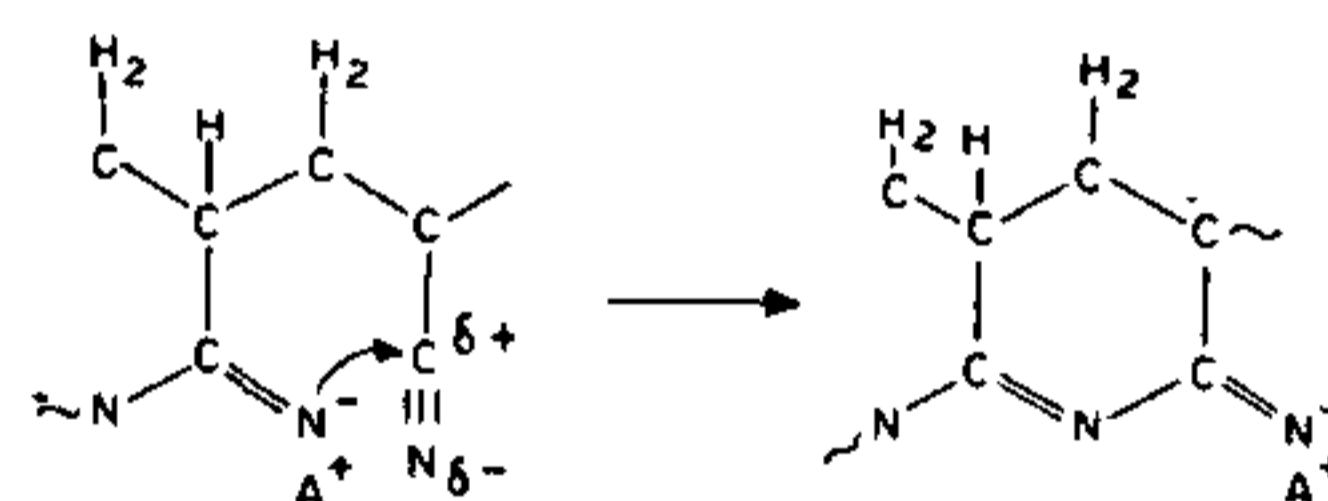


Figure 6. Shrinkage/elongation behaviour of PAN fibres under varying loads.

cyclization is likely to be initiated by them because in this, the initiation is a comparatively fast reaction. It has been estimated that 20% of the nitrile groups are used in initiation reactions. All commercial acrylic fibres are likely to contain ionic species because the polymer can be spun only from highly ionizing solvents, residual quantities of which remain in the fibre. The tertiary hydrogen atom may have a role in ionic initiation, but this is uncertain. It appears that comonomers can also initiate the cyclization. It has been shown that acids are particularly more active, and the following mechanism has been suggested.



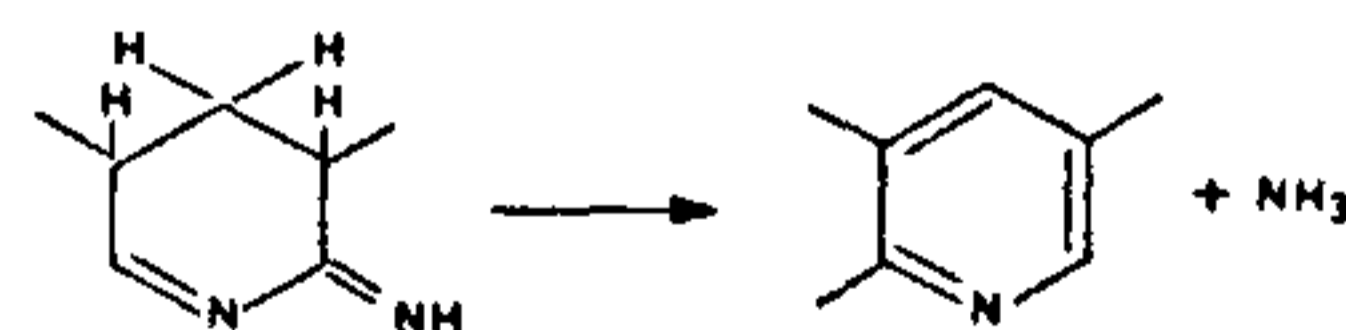
When ionic species are present they dominate the initiation and this is relevant to the catalysed cyclization reaction. However, in the absence of initiators the polymer which has a large atactic structure undergoes cyclization through short isotactic sequences or when rotation about the carbon single bonds brings a nitrile group into vicinity of the active chain end.



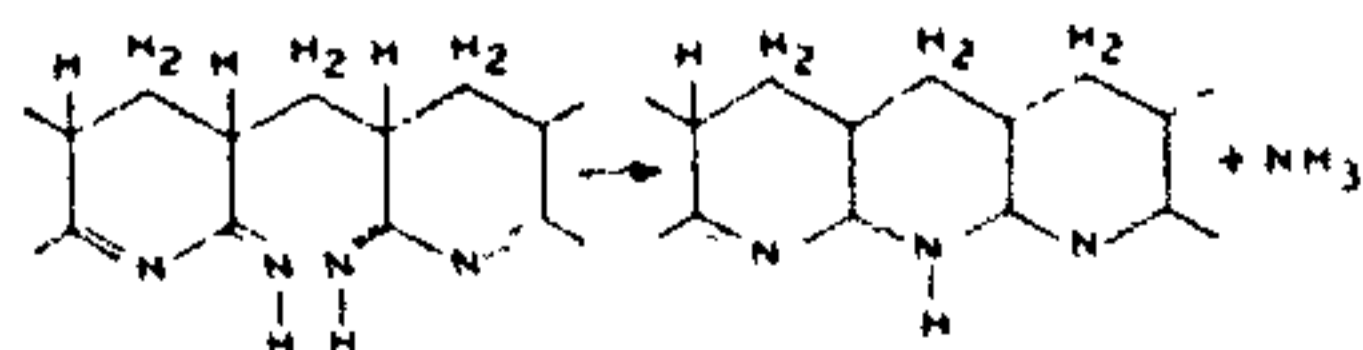
The main reaction products coming out during oxidative stabilization are ammonia, water and HCN.

The evolution of ammonia could be the result of two possible reactions:

i) Aromatization of the propagating colour unit, causing chain termination site.

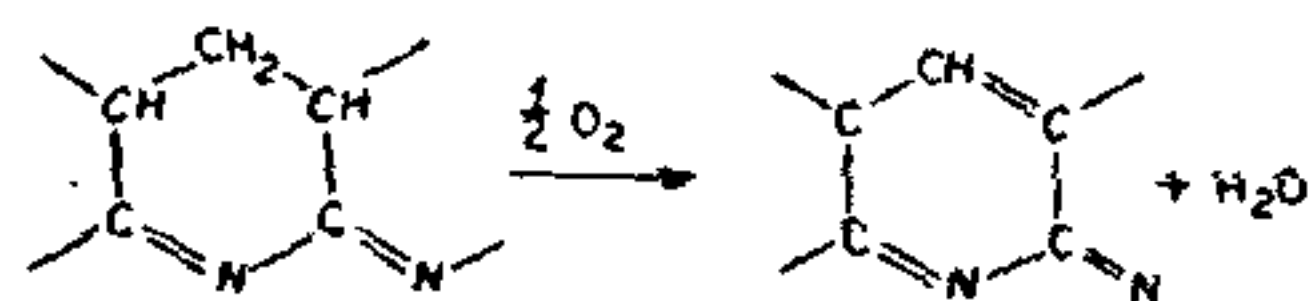


ii) The other possibility is derived from the chance interaction of two oppositely propagating units.

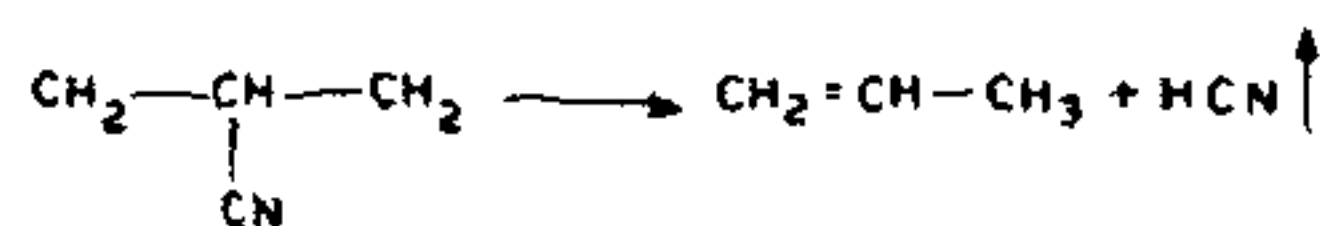


If reactions are carried out, both in presence of air as well as under nitrogen atmosphere, it is found that the

product prepared in air has comparatively higher density. The reaction under nitrogen yielded PAN with a density of 1.35 gm^{-3} , while under identical conditions in air, a density of 1.45 gm^{-3} resulted. The explanation for this is probably that some aromatization takes place in the presence of oxygen and this makes the density to shift towards the density of completely aromatic structure, which is 1.60 gm^{-3} . Water molecule is evolved as a result of attack of oxygen on the reactive CH_2 site as shown below.



The evolution of HCN has been suggested as a result of break-up of unsladdered part.



Characterization of stabilized fibres

Mechanical properties

Tensile strength (TS) and Young's modulus (YM) of PAN fibres decrease with increase in the degree of stabilization. As we know that thermal stabilization of PAN progresses by conversion of polar $\text{C}\equiv\text{N}$ groups to $\text{C}=\text{N}$ groups, this causes cyclization of the structure. The absence of polar forces between molecules is responsible for the decrease in the strength of the fibres. As shown in Figure 7 the strength at first decreases sharply and starts increasing slightly after prolonged heating. The increase in TS could be due to formation of intermolecular cross-links and the aromatization of the structure. This also results in the decrease of strain to failure. As the number of intermolecular cross-links increases by heating PAN for longer times or keeping higher treatment temperatures, the strain to failure

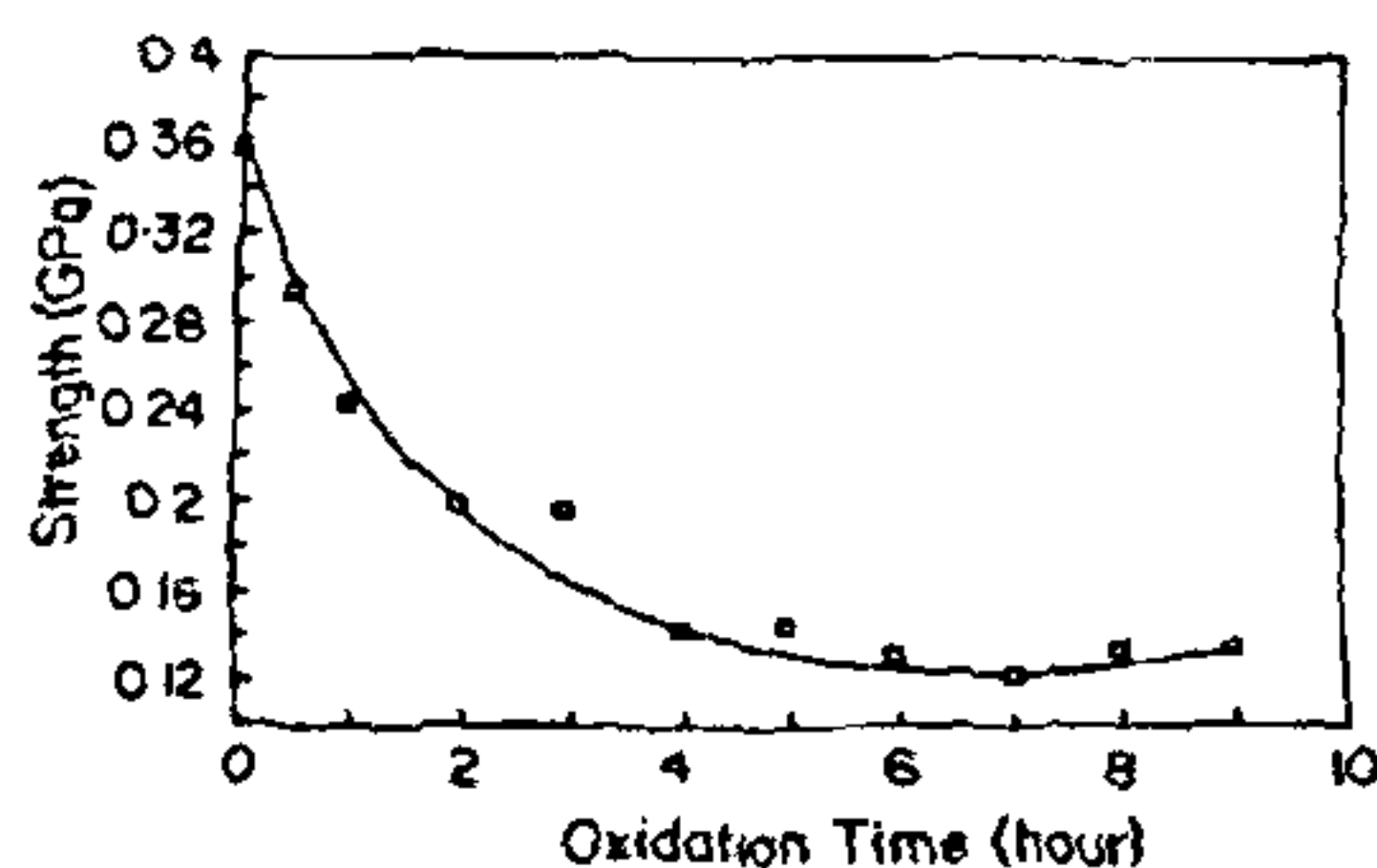


Figure 7. The tensile strength of oxidized fibres as a function of oxidation time. PAN fibres were heated in air at 230°C .

decreases from 25% for untreated PAN to only 5% for highly stabilized PAN. Care has to be taken to restrict the formation of intermolecular cross-links, while at the same time getting a stabilized material. This is made possible by not stretching the molecular chains too much during oxidation process and also keeping the maximum heat treatment temperature to around 250°C . Mechanical properties are measured on the Instron Tensile testing machine by following the standard techniques for fibres, i.e. ASTM No. 2101-79.

Density

Another criterion to judge the proper stabilization is the density, which should be 1.4 gm^{-3} for stabilized fibres. A typical density vs oxidation time curve for PAN fibres is given in Figure 8. For continued heating, the density may further rise beyond 1.5 gm^{-3} also, but strain to failure or the flexibility of fibres suffers. The theoretical density of the hundred per cent aromatized structure is 1.6 gm^{-3} . It is indeed possible to achieve this density, but is not conducive from carbon fibre point of view. A simple method to determine the density of fibres is sink-float method.

Degree of stabilization

A fairly good idea about the degree of stabilization is obtained by X-ray diffraction analysis of the powdered samples. As seen from Figure 9, PAN as such gives two characteristics diffraction maxima corresponding to (200) and (100) planes of orthorhombic structure at $2\theta = 17^\circ$ and 29° respectively, using CuK_α radiation as source. As the stabilization progresses, there is a transformation in the structure to naphthyridene-type structure because of the aromatization of the ring sequences. This results in the development of new broad peak at around $2\theta = 25.5^\circ$. This peak incidentally corresponds to (002) basal planes of graphite-like

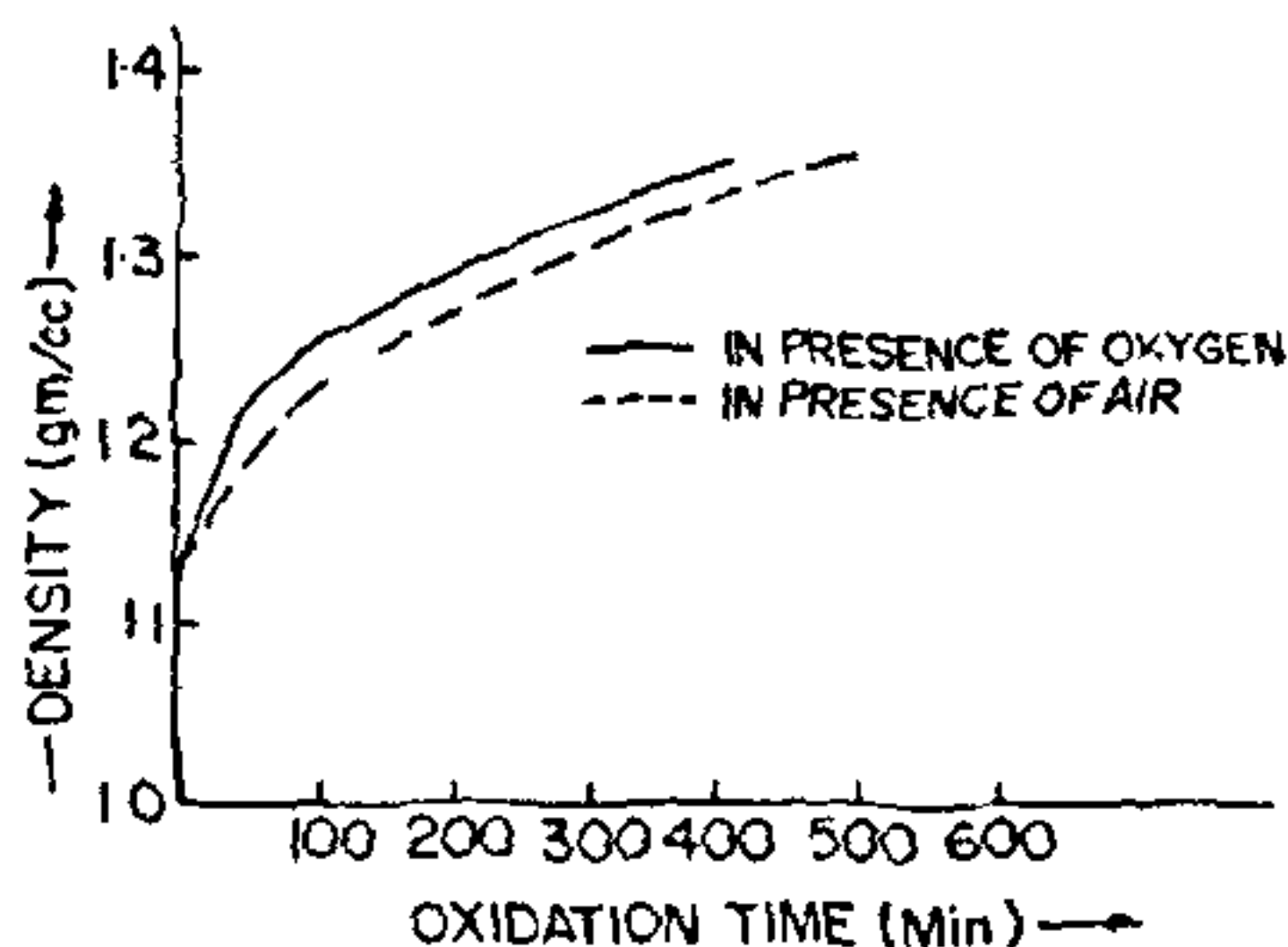


Figure 8. Variation in density of PAN fibre with oxidation time during oxidation under different atmosphere.

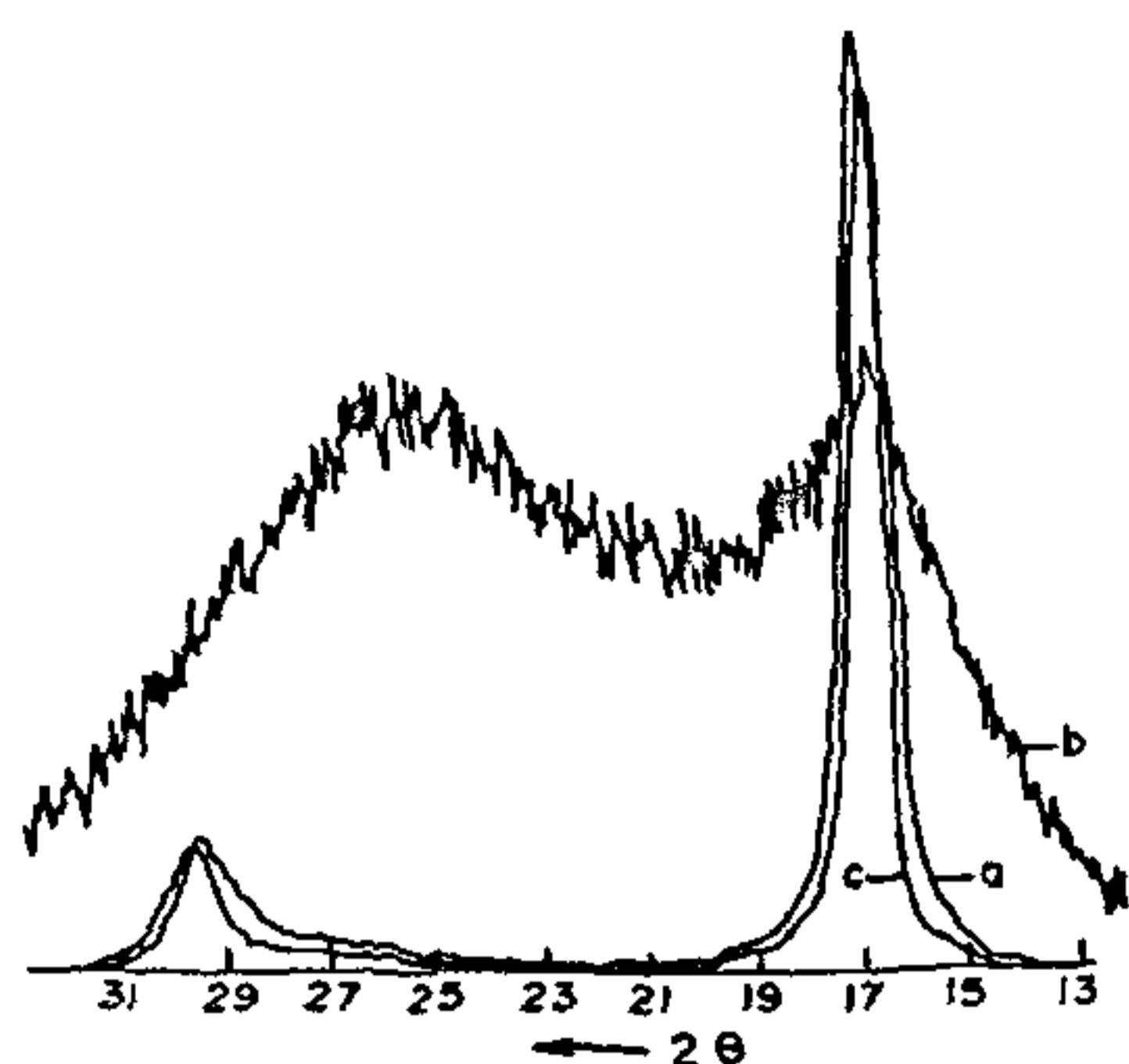


Figure 9. Wide-angle X-ray diffraction records of (a) precursor PAN, (b) oxidized in SO_2 for 15 min, (c) oxidized in air for 15 min.

structure. Figure 9 gives a typical example of catalytic role played by SO_2 gas in cyclizing the structure of PAN within just 15 min (curve b). The presence of air, on the other hand, does not show any transformation in the structure relative to precursor (curves a and c). It is in fact at this stage that the seed is sown for ultimate graphite structure to be developed during pyrolysis of PAN. As the aromatization of the structure increases the peak at 25.5° becomes stronger and sharper, whereas the other two peaks at $2\theta = 17^\circ$ and 29° corresponding to PAN structure start decreasing in intensity. A good measure of such conversions in the structure is denoted by the aromatization index (AI) (ref. 8).

$$\text{AI} = \frac{I_{25.5^\circ}}{I_{17^\circ} + I_{25.5^\circ}}$$

where I represents the total integrated area under the representative peaks. For a completely stabilized 'flame proof material, AI should be 100%. Figure 10 shows

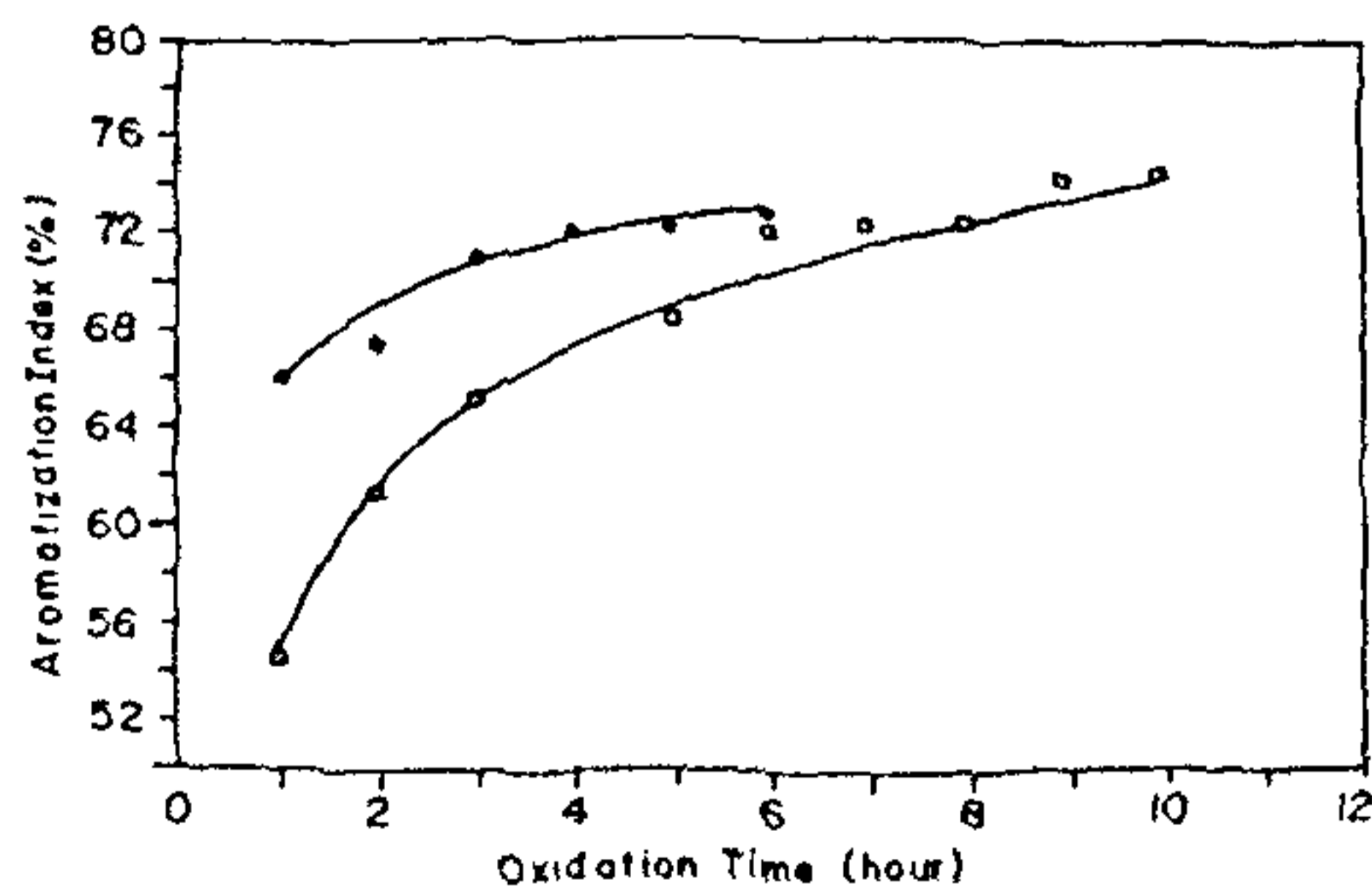


Figure 10. Aromatization index as a function of oxidation time: (○) PAN fibre heated at 230°C ; (◆) PAN fibre heated at 270°C .

variation of AI with oxidation time of the precursor PAN.

Infrared analysis

Room temperature absorbance IR spectra of undegraded PAN is shown in Figure 11. Of particular interest are the major IR bands characteristic of the acrylonitrile unit in the polymer chain at 2240 cm^{-1} corresponding to the $\text{C}\equiv\text{N}$ stretching frequency, and at 1451 cm^{-1} corresponding to CH_2 -bending frequency. Major IR bands characteristic of the comonomers present in the three different copolymers are as follows: (i) PAN/VAC- 1735 cm^{-1} $\text{C}=\text{O}$ stretching mode of the acetate group, (ii) PAN/AM- 1740 cm^{-1} mixed mode containing contributions of the $\text{C}=\text{O}$, (iii) $\text{C}=\text{N}$ 1685 cm^{-1} stretching and N-H bending modes of the acylamide PAN/MMA- 1735 cm^{-1} $\text{C}=\text{O}$ stretching of the acrylic group. When fibres are oxidized, the reduction in intensities of peaks at 2940 cm^{-1} indicates that the CH_2 and $\text{C}=\text{N}$ groups are reacting. Also, new absorption peaks are created at 1590 and 800 cm^{-1} and a shoulder forms at 2180 cm^{-1} . The absorption at 2180 cm^{-1} is probably caused by a nitrile group which is in electron resonance with another part of the molecule. The formation of $\text{C}=\text{N}$ groups is indicative of the development of heterocyclic structures. This is further confirmed by the fact that the polymer has a highly improved thermal stability.

The oxidation of polymer PAN also results in the formation of carbonyl ($\text{C}=\text{O}$) groups, but the spectrum of starting PAN itself contains a strong carbonyl absorption from the comonomer. It can be seen, however, from the spectra of oxidized PAN that during oxidation, carbonyl groups (1710 cm^{-1}) are formed. Apart from carbon-carbon unsaturation, shoulder at

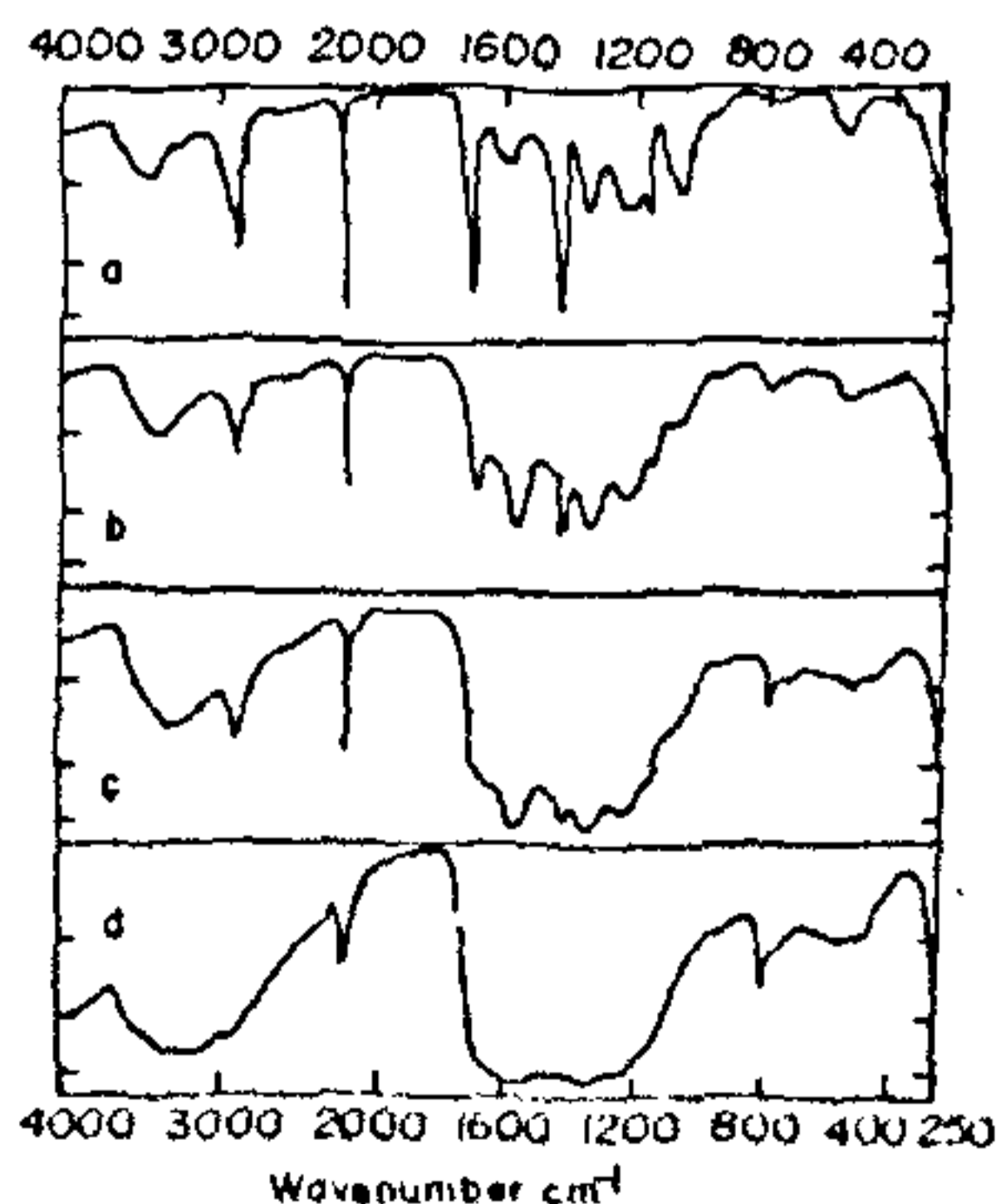


Figure 11. IR spectra of (a) untreated 'Cottelle' fibres and of those heated in air 225°C for (b) 0.25 h, (c) 1.25 h, (d) 5 h.

1650 cm^{-1} could be attributed to a carbonyl group in a β -diketene. Both these absorbances are absent in the spectrum of PAN heat treated in N_2 . The formation of OH and or NH groups (3330 to 3230 cm^{-1}) are prominent reactions and their concentration steadily increases during oxidation.

In conclusion, the results of the infrared analysis indicate that the chemical structure of the oxidized PAN fibres includes C=C, C=N, C-N, O-H, N-H, CH_2 and C=O groups. Although it is difficult to obtain accurate quantitative estimates, the quantitative indications are that the C=C, C=N, C-N, OH and NH groups are important constituents of the oxidized fibres, whereas the CH_2 , C=N and C=O groups are present in only small quantities. Furthermore, the appearance of strong absorption attributable to NH groups suggests that the number of rings cyclized in a sequence is small and probably variable. These basic conclusions have been used to draw Figure 12, which merely indicates the type of chemical bonds which must be accounted for, but which cannot be used to make structural inferences.

The KBr pellet method is the standard technique used for obtaining IR spectra of polymer fibres.

A new approach to thermal stabilization of PAN fibres

As has been discussed in previous sections, PAN fibres when heated to 180°C and above, undergo thermal degradation which causes cyclization of the structure. This cyclization reaction is exothermic in nature and has to be controlled to produce good quality carbon fibres from PAN. A number of studies on this aspect alone were therefore carried out by Grassie and co-workers^{9,10} to understand exothermic behaviour of PAN, using calorimetric techniques. Curve A in Figure 13 depicts a typical DSC curve of a particular variety of PAN fibres obtained by maintaining a heating rate of 5°C min^{-1} in air. One finds that sharp exotherm due to cyclization of PAN structure starts at about 200°C and the peak is formed around 265°C (maxima I). Several authors^{7,11} have taken recourse to such DSC curves for carrying out proper thermal stabilization of PAN fibres before carbonization, as it gives vital information regarding the total heat flow, energy of activation, cyclization initiation temperature, final temperature of oxidation, etc. A careful study of

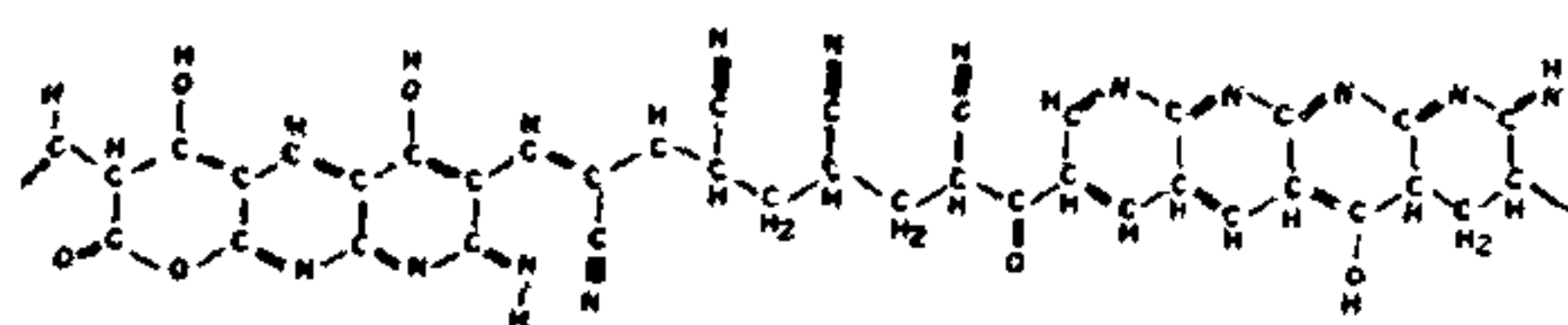


Figure 12. Structure of oxidized (thermally stabilized) PAN fibres.

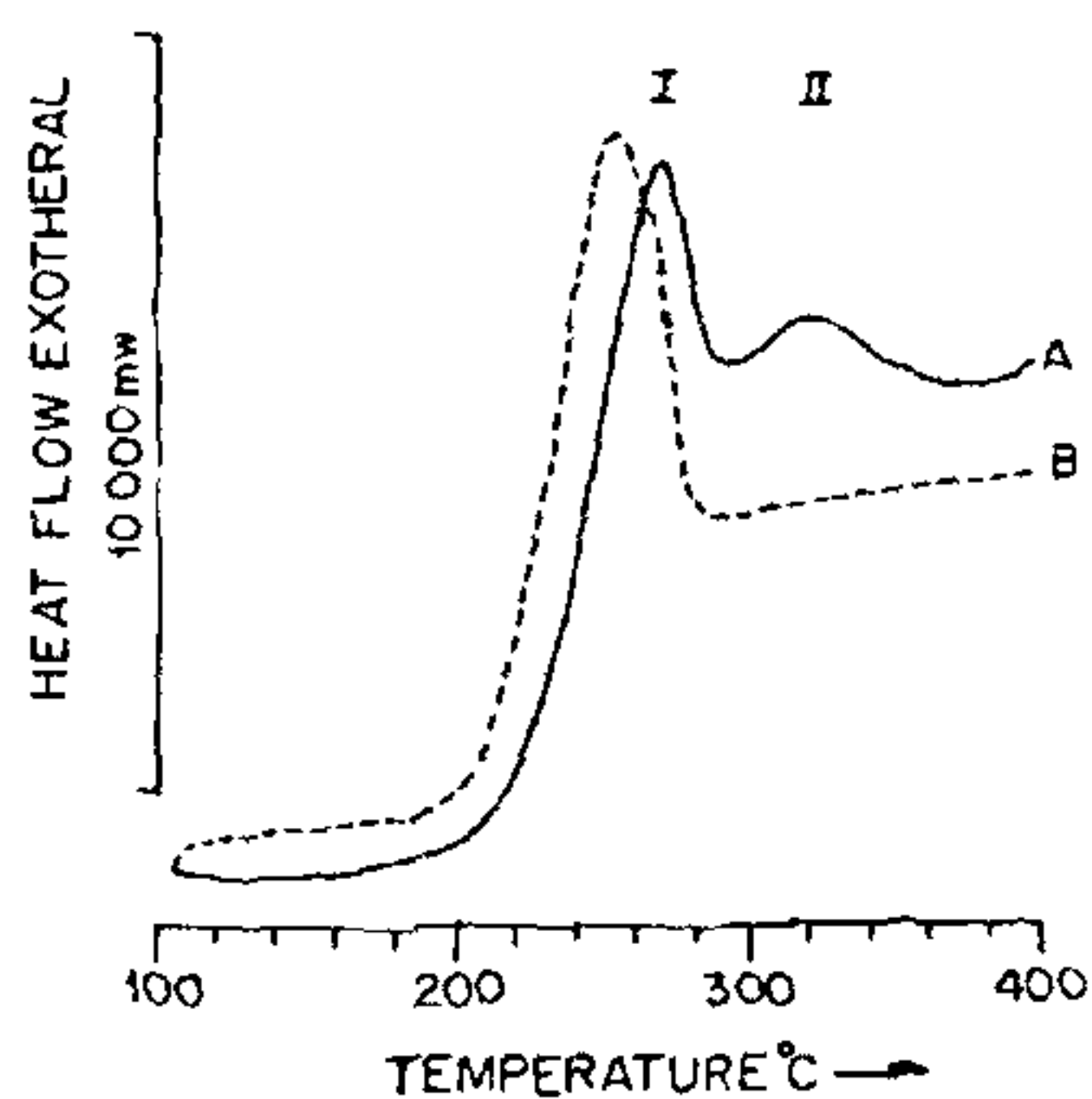
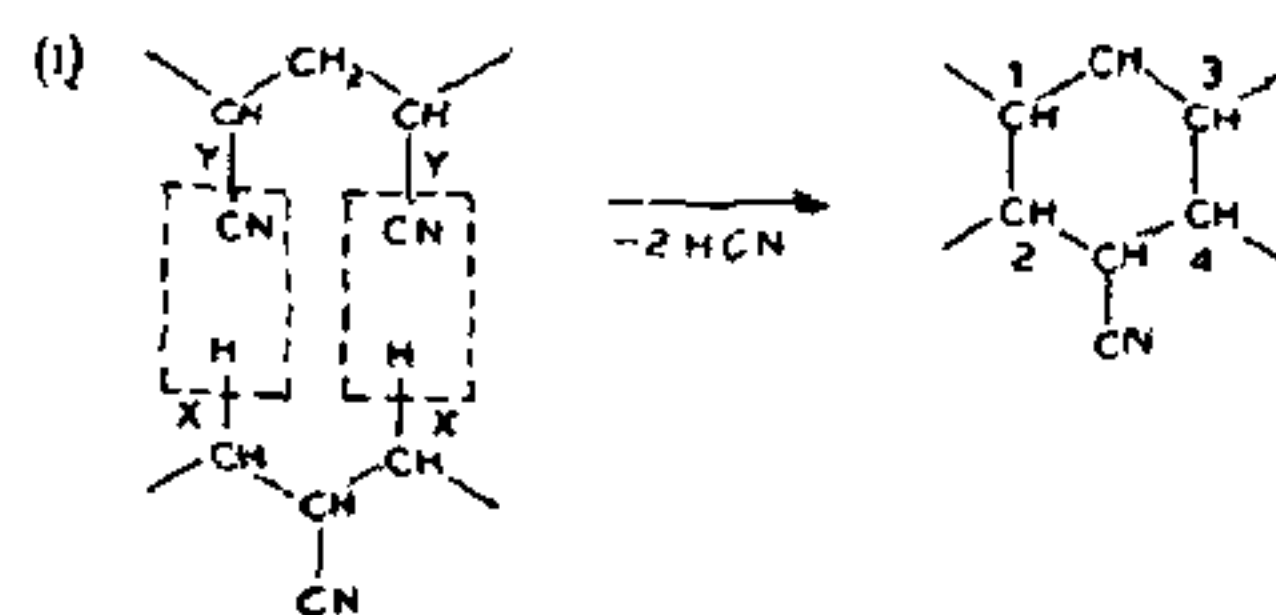


Figure 13. DSC curves of PAN fibres. A, In the presence of air. B, In the presence of nitrogen. Heating rate 5°C min^{-1} .

such DSC curves has revealed another small and relatively broad exotherm peak at about 325°C associated with prominent maxima I, centred around 265°C. Surprisingly no importance seems to have been given to this second maxima, most probably because thermal stabilization of PAN is usually carried out up to a maximum temperature of 270°C.

Physical, mechanical and thermal analyses have shown¹² that the following two reactions occur if the thermal stabilization of PAN fibres is carried out to higher temperatures, covering the second exothermic maxima:



Formation of bonds:

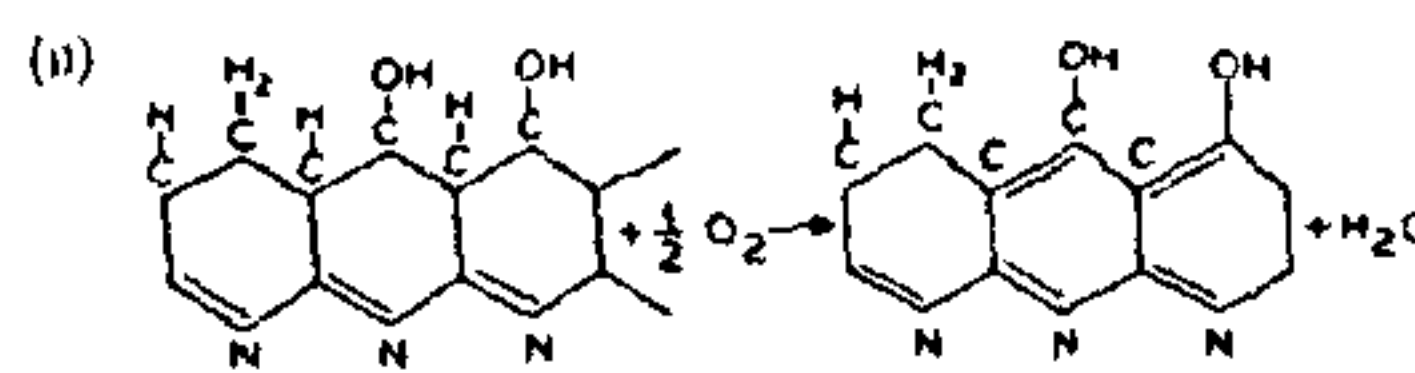
Two C-H bonds. (In formation of two molecules of HCN)

Two C-C bonds. (Cross-linking between atoms 1-2 & 3-4)

Cleavage of bonds:

Two C-H bonds (X-X)

Two C-C bonds (Y-Y)



Whereas reaction (i) causes intermolecular cross-linking of the adjacent molecular chains, the reaction (ii) results into further aromatization of the fibre structure. Both these reactions have additional influence on the structure of oxidized fibres which become rigid and rod-like as revealed by the density values, which is 1.5 g cm^{-3} for such fibre compared to 1.35 g cm^{-3} for normally stabilized fibres. As a result of evolution of HCN and H_2O there is more dehydrogenation of the backbone during initial stages itself. This may lead one to believe that these reactions may occur during carbonization of the oxidized fibres beyond 300°C under normal pyrolysis conditions and the second exothermic maxima is part of that only. In order to confirm this, the DSC run of PAN fibres was carried out in N_2 atmosphere also and, as shown in Figure 13, curve B, there is no second exothermic maxima observed here. This shows that there are certain reactions, described above, that are possible in presence of oxygen only and remains incomplete if the stabilization of PAN is restricted to low temperatures. Preliminary studies show that the carbon fibres prepared with fibres stabilized by following new approach possess superior mechanical properties, to those produced conventionally.

Mathur *et al.*¹³ carried out detailed studies on the

structural aspect of such fibres using wide-angle X-ray diffraction technique and found a new diffraction peak at $2\theta = 13^\circ$ in addition to the usual pregraphitic broad peak at $2\theta = 25.5^\circ$ observed for conventionally stabilized fibres. Based on these studies a model has been proposed¹³ for the structure of the fibres stabilized up to second exothermic maxima.

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REVIEW ARTICLES

Models for organic ferromagnetism

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Synthesis of a purely organic ferromagnet is an outstanding challenge in chemistry today. Theoretical formulation of models and their computational and experimental studies have engaged the attention of physicists, chemists and material scientists over the past several years. Various models have been suggested for ferromagnetism in organic systems. Experimental and computational studies have also dealt with this problem.

Quasi one-dimensional solid-state materials have attracted the attention of chemists, physicists and material scientists in the last few decades, owing to their unique physical properties and the theoretical insights gained from their study. These materials characterized by highly anisotropic electrical, magnetic and optical properties include a wide range of systems

like (i) linear chain metal salts and complexes, (ii) stacked metal complexes, (iii) inorganic and organic polymers, and (iv) stacked organic charge transfer or ion-radical complexes¹⁻¹³. The anisotropy of the physical properties results either from the linear polymeric structure or the one-dimensional packing of atomic or molecular units in the solid state, with strong interactions along the column direction and much weaker interactions in the orthogonal directions. This review will be concerned with purely organic systems only.

The discovery of semiconduction in the perylene-bromine complex¹⁴ and the development of tetracyanoquinodimethane salts¹⁵ led to the fabrication of numerous organic conductors^{4,6-8,10,12,16-18}. Suggestion of an excitonic model for organic superconductivity¹⁹ sparked off intense research efforts, and,