CATALYTIC EFFECT ON THE CRYSTALLINE PRE-ORDER DURING
GRAFIITIZATION OF SIMPLE AROMATIC ORGANIC COMPOUNDS

BY

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CATALYTIC EFFECT ON THE CRYSTALLINE PRE-ORDER DURING
GRAPHITIZATION OF SIMPLE AROMATIC ORGANIC COMPOUNDS

BY

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Abstract:

Pyrolysis of some simple aromatic organic compounds in presence of AlCl₃ in the temperature range of 350°C to 600°C has been carried out to examine catalytic effect on the crystalline precursor during graphitization. IR spectroscopic analysis, DTA, TGA, X-ray diffractometry and micrographic investigation using reflected polarized-light technique have been carried out on the pyrolysed composite samples to see whether the graphitizability of the sample is accelerated in presence of the catalyst.

With the continued addition of AlCl₃ with anthracene and phenanthrene in different mole ratios, the heat of fusion and hence the activation energy increases indicating the catalytic effect on graphitization. TGA is measured to see the dynamic weight loss of the samples. The interlayer distance is found to decrease as the amount of AlCl₃ is increased showing another indication of increasing degree of graphitizability. The aromatization is increased with the increase of the catalyst indicating that the order of graphitization is enhanced. The polarized-light photomicrographs indicate the appearance of the mosaic texture and flow pattern of mesophase formation. Possible magnetic anisotropy of the samples in static magnetic fields is investigated using a torque magnetometer which showed a two-fold magneto-crystalline anisotropy.

The main findings of this research are increasing graphitization of anthracene and phenanthrene with increasing amount of AlCl₃ used as catalyst and a two-fold magneto-crystalline anisotropy in the hexagonally ordered carbon materials.
# Contents

## Chapter-1

<table>
<thead>
<tr>
<th>Introduction</th>
<th>Reference</th>
</tr>
</thead>
</table>

## Chapter-2 Carbonization and Graphitization

<table>
<thead>
<tr>
<th>2.1 General aspects</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2 Different forms of Carbon and Crystallographic Models</td>
<td>13</td>
</tr>
<tr>
<td>2.3 Structure of Carbons as determined by X-ray</td>
<td>16</td>
</tr>
<tr>
<td>2.4 Carbonization process</td>
<td>18</td>
</tr>
<tr>
<td>2.5 Mesophase</td>
<td>24</td>
</tr>
<tr>
<td>2.6 Liquid Crystals</td>
<td>25</td>
</tr>
<tr>
<td>2.7 Pressure effect on carbonization and Graphitization</td>
<td>26</td>
</tr>
<tr>
<td>2.8 Different types of Mesophase Spherules</td>
<td>27</td>
</tr>
<tr>
<td>2.9 Mathematical Model for Carbonization Process</td>
<td>28</td>
</tr>
</tbody>
</table>

## Chapter-3 Pyrolysis of Aromatic Hydrocarbon

<table>
<thead>
<tr>
<th>3.1 Mechanism</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 Polycyclic aromatic hydrocarbons</td>
<td>51</td>
</tr>
<tr>
<td>3.2.1 Investigated samples</td>
<td>53</td>
</tr>
<tr>
<td>3.2.2 Anthracene</td>
<td>53</td>
</tr>
<tr>
<td>3.2.3 Phenanthrene</td>
<td>54</td>
</tr>
<tr>
<td>3.3 Pyrolysis of Anthracene</td>
<td>55</td>
</tr>
<tr>
<td>3.4 Pyrolysis of Phenanthrene</td>
<td>56</td>
</tr>
<tr>
<td>3.5 Catalytic hydrogenation and dehydrogenation</td>
<td>57</td>
</tr>
</tbody>
</table>

## Chapter-4 Experimental

<table>
<thead>
<tr>
<th>4.1 Introduction</th>
<th>66</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 Working Principle of DTA &amp; TGA</td>
<td>68</td>
</tr>
<tr>
<td>4.2.1 Historical background</td>
<td>70</td>
</tr>
<tr>
<td>4.2.2 DTA apparatus</td>
<td>70</td>
</tr>
<tr>
<td>4.2.3 Thermogravimetric analysis(TGA)</td>
<td>72</td>
</tr>
<tr>
<td>4.2.4 Thermogravimetric Investigations</td>
<td>72</td>
</tr>
<tr>
<td>4.3 Polarized-Light Technique</td>
<td>73</td>
</tr>
<tr>
<td>4.3.1 Description of apparatus and working principle</td>
<td>74</td>
</tr>
<tr>
<td>4.4 Infrared Spectroscopy(IR)</td>
<td>77</td>
</tr>
<tr>
<td>4.4.1 Techniques used in IR spectroscopy</td>
<td>78</td>
</tr>
<tr>
<td>4.4.2 Working Principle</td>
<td>78</td>
</tr>
<tr>
<td>4.5 X-ray Diffraction</td>
<td>79</td>
</tr>
</tbody>
</table>
Chapter - 1

Introduction
Progress in the development of new carbon materials and the improvement of old carbon materials is still going on. Under special conditions of temperature and pressure, carbon atoms arrange themselves in parallel arrays to form graphite. Graphite has a laminar crystalline structure and is the anisotropic form of carbon consisting of soft, shiny and flat crystals.

X-ray analysis shows that the carbon-atoms are arranged in layers. Each layer is a continuous network of planar, hexagonal rings and carbon atoms within a layer are held by 1.415 Å long strong, covalent bonds. The different layers 3.354 Å apart are held to one another by weak forces of Vander Waals’ type. Lubricating properties of graphite i.e. the slipping of layers over one another is due to this weak forces. The tendency of graphite materials to fracture along planes is also due to this weak forces.

There are many uses of graphite in our every day life and in other fields like chemical, electrical, metallurgical and nuclear engineering. Graphite is used as a solid lubricant for dry bearings in many electric motors and in door locks. It is also used in motor-oil additives. The “lead” in lead pencils is compressed graphite. Graphite is used as electrodes in dry cells as it is a good conductor of electricity and has little tendency to react chemically. Carbon black is used as the pigment in printing press. As carbon can be produced by the low temperature charring of organic compounds, graphitization of organic compounds particularly those which
exist in coal or coal-tar pitch is a subject of considerable practical importance in carbon and graphite technology.

The study of carbon as a graphite is of interest for two main reasons, the first one is the need for extending our knowledge of the solid state in the field of anisotropic crystal and the second one is the importance of precise information concerning the effect of heat on elementary carbon in connection with the technological processes of carbonization and coking.

The manufacture of synthetic graphite is based on the initial formation of carbon during carbonization of an organic substance. It has been pointed out in many papers [1-11], that the formation of carbon structure and its ability to become graphite at high temperature is to be looked for in the initial carbonization stages.

The techniques of optical micrography applied to commercial organic materials at various stages of carbonization and graphitization have been fruitful in recent years in shedding light on the mechanisms involved in making a material graphitizable [1-14]. Although the chemical reactions involved in liquid-phase pyrolysis are complex [15-18], the problems of understanding the formation of the morphology have been simplified originally by Brooks and Taylor[3,4]. They recognized the significant role of the mesophase transformation which takes place in graphitizable organic materials during pyrolysis in the temperature range of 350° - 600°. This transformation is a liquid-state structural transition in which the large polymerizing aromatic molecules become aligned in a parallel array to form an anisotropic liquid
or plastic crystal, the life time of which is very short before it is hardened to a semi-
cake.

Most carbons which are formed from the liquid phase by solidification in the
temperature range of 350°C to 600°C an irregular mosaic texture composed of
optically anisotropic units exhibit in a polished section under the microscope. Such
carbons graphitize on heating to high temperatures and the compounds which do
not pass through fused state have isotropic structures and do not graphitize readily.
In the initial stages of nucleation and growth the mesophase appears as spherules
with the simple structure as demonstrated by Brooks and Taylor [3] (fig. 1.1) and
is called the Taylor model which is the most stable at the first heat stage. The
mesophase spherules are stacked perpendicular to a polar diameter and curve to
meet the interface with the isotropic phase normally. The structural sketch indicates
the orientation of the mesophase layers relative to the plane of section. The sketch
is prepared from a series of polarized light micrographs recorded at increasing
angles of stage of rotation. When these spherules are observed with crossed-
polarizers the extinction contours are found to be rather simple and define the loci
of points when the layers are either parallel or perpendicular to the plane of
polarization of the incident light [20].

Formation of anisotropic mesophase is a function of heat-treatment temperature
and duration of heat-treatment. As carbonization progresses with increasing
temperature and duration of heat-treatment, the growing mesophase spherules
become more dense than isotropic parent phase and sink to the bottom of the
container. When spherules meet each other, coalescence occurs to produce larger
droplets leading to bulk mesophase as shown in fig. 1.2. When viewed microscopically with cross-polarizers, the bulk mesophase developed by the pyrolysis of the graphitizable organic compounds, complex ensemble of extinction contours are usually displayed. The polarized-light extinction contours display nodes and maltese crosses when observed with cross-polarizers.

A parallel plate of gypsum which is called the first order red plate or tint plate, is inserted at 45° between crossed polars. By the use of this so called Sensitive-tint method, changes in pleochroism and in extinction contours for coalesced and deformed mesophase are observed. This method permits distinguishing between crosses and nodes and enables identify four types of linear defects in the stacking of the aromatic mesophase layer planes which is described in chapter 2.

The processes of the formation, coalescence and deformation of the plastic mesophase establish the basic elements of the graphitic structures, namely the parallel alignment of the aromatic layer planes and the rearrangement of the complex folds in the fibrous regions. Linear stacking discontinuities analogous to dislocations in solid crystals in the nodal and cross structures are essential features of the coalesced mesophase. The nodal structures are found to persist in their basic form upto the graphitization temperatures.

It is known that the heteroatom decreases the size of the anisotropic domains as well as the graphitizability [21,22]. The amount of the catalyst has an important effect on the properties of cokes obtained from some organic compounds[23-27]. Because the carbonization process includes steps of condensation, cracking,
dehydrogenation and increasing viscosity, it should influence the properties of cokes. Also it is established that the catalytic carbons are very reactive between 350°C and 600°C, where unecatalyzed carbons are inert[28]. The amount of catalyst is shown to have a significant influence on the properties of cokes. Some of the heterocyclic organic compounds give graphitizable needle cokes in presence of a suitable amount of the catalyst. Some aromatic organic compounds give graphitizable mosaic coke and some others give non-graphitizable isotropic cokes. The additive might bring about a change in the crystalline pre-order and will enhance graphitizability.

Very little information is available in literature about the chemical means of improving the crystalline pre-arrangement. In the present investigation, pyrolysis of some composite polynuclear aromatic compounds will be carried out to see if well ordered soft carbons can be produced as a raw material for the manufacture of artificial graphite and an attempt will be taken to see whether the magnitude of graphitizability is accelerated or decelerated by introducing limited proportion of catalytic agent with the polynuclear aromatic compounds.

Along with various criteria of the carbonization process, degree of graphitizability and the preferred orientation of microcrystallites are studied in the present investigation. The purpose of these studies is to investigate optical, thermal and magnetic properties of an oriented liquid crystal carbonaceous mesophase obtained from the composite samples. The amount of the catalyst has such an important contribution to the carbonization rate that it's influences on the properties of carbonization and graphitization have also been studied.
The present work has been done to get the catalytic effect of AlCl₃ on graphitization and confirm the findings by IR spectroscopy, DTA, TGA, X-ray diffraction pattern and Polarized-light microscopy.

Differential thermal analysis (DTA) has been found to be an effective tool in detecting carbonaceous mesophase and also in determining the temperature interval of mesophase formation[29,30]. DTA provides some knowledge about the heat of fusion and the activation energy of the carbons obtained from the composite samples. In graphitizable materials initial endothermal processes of transformation are typical with the values of the effective activation energy over 252 KJ/mol. For non-graphitizable materials initial exothermal processes of transformation are observed at low values of activation energy of about 84 KJ/mol[31]. In the present investigation, DTA of some aromatic samples with AlCl₃ as additive is carried out to see if the initial endothermic peaks grow in size with increasing amount of AlCl₃. Widening of the initial endotherm indicates the increase in the heat of fusion and so activation energy with increasing amount of the catalyst. With increased AlCl₃ it is expected that the mesophase interval will become significantly shorter indicating increasing degree of graphitization.

Infra-red spectroscopy has become a potential tool for investigating the structural information of organic substances and also in locating some important properties like stretching and bending of bonds which have wide application in the manufacture of graphite.
Chapter 1  

Introduction

The mesophase formation or liquid crystal formation of optical anisotropy as well as the degree of graphitization of the composite samples will be observed by the sensitive tint technique of reflected polarized light microscopy.

X-ray diffractometry is to be undertaken in order to assess their relevance for the graphitizability and the orientation of microcrystallites of the composite samples. Interlayer spacing i.e., d-spacing, miller indices, relative intensity and widths of the diffraction lines are to be calculated. The interlayer spacing is expected to be found decreased with the increase of catalyst, indicating increasing degree of graphitizability.
Fig. 1.1. Mesophase sphere with section including polar diameter.

Fig. 1.2. Rearrangements which appear to occur when two spheres coalesce.

Type of complex internal structure formed when composite of two or more spheres contracts to one large sphere.

Before contact

Just after contact

Short time after contact
Reference:

17. Marsh, H. and Evans, S., ibid 42.
Chapter 1

Chapter - 2

Carbonization and Graphitization
2.1 General aspects.
The unique atomic structure of carbon with electronic configuration \(1s^22s^22p^2\) results in its ability to react chemically with most other elements, as well as to bond with itself. Thus numerous compounds containing the carbon elements are known until today.

Carbon exists in nature in 'amorphous' forms such as in coal, lignite and gilsonite. In more limited quantities it occurs in its two allotropic crystalline forms such as in natural graphites and diamonds. The arrangement of the electrons in the outermost level of covalently bonded carbon is not the same as in carbon in the atomic state. The electron configuration of carbon in the atomic state is \(1s^22s^22p^1\). From this configuration, it would be expected that carbon would form bonds due to overlapping of the two partially filled \(p\)-orbitals with \(s\) or \(p\) atomic orbitals of other atoms.

Carbon uses \(sp^2\) hybridized orbitals when it forms bonds with four other atoms. However, organic compounds do not contain carbons with \(sp^2\) hybridized orbital only. In addition, carbons with \(sp^2\) and \(sp\) hybridized orbitals are possible.

The combination of one \(s\)-orbital and two \(p\)-orbitals forms three \(sp^2\) hybrid orbitals. The hybridization process results in the following change in the electron configuration,

\[
1s^22s^22p^1 \xrightarrow{\text{hybridization}} 1s^22\{sp^2\}2p^1
\]

Atomic State of carbon \(sp^2\) hybridized state of carbon.

The three \(sp^2\) orbitals are coplanar, and the angles between them are 120°. Each orbital contains one electron. The remaining \(p\)-orbital contains one electron and lies
Chapter 2  Carbonization and Graphitization

perpendicular to the plane of the \( SP^2 \) orbitals. The \( SP^2 \) orbitals with the lobes of the 
\( P \)-orbital above and below the plane are shown in Fig. 2.1.

Carbon uses \( SP^2 \) hybrid orbitals when it is bonded to three other atoms. The
combination of one \( S \)-orbital and one \( P \)-orbital produces two \( SP \) hybrid orbitals.
The hybridization process results in the following change in the electron configuration:

\[
1S^2 2S^2 2P^1 (2P^1 \text{ hybridization}) \rightarrow 1S^2 (2P^1 (2P^1 \text{ hybridization}) 2P^1 2P^1)
\]

Atomic State of carbon  SP hybridized state of carbon.

The two \( SP \) orbitals are 180° apart and lie along the same line. Each orbital contains
one electron. The remaining two \( P \)-orbitals, each contains one electron and are
perpendicular to one another. The \( SP \) orbitals with the lobes of one \( P \)-orbital above
and below the plane of the line joining the two \( SP \) orbitals and the other \( P \)-orbital in
front of and behind the line joining the two \( SP \) orbitals are shown in Fig 2.2.

Thus, Carbon uses \( SP^3 \) hybrid orbitals when it forms bonds with four other atoms,
as in methane; \( SP^2 \) hybrid orbitals when it forms bonds with three other atoms, as in
ethane; and \( SP \) hybrid orbitals when it is attached to two other atoms, as in
acetylene. The greatest overlap occurs in the neighbourhood of \( SP \) hybridization.

This suggests that \( SP \) bonds should be stronger than either \( SP^2 \) or \( SP^3 \). Carbon in a
graphite layer (Fig 2.3) apparently forms three identical localized bonds, at 120°
with one another and the trigonal set is appropriate. But carbon in Benzene
molecule (Fig - 2.4) is also quite well described using the trigonal set, though the
\( C-H \) bond differs somewhat from that of the other two \( C-C \) bonds. Trigonal
hybridization is characteristic of carbon in aromatic hydrocarbons. Finally, when
carbon occurs in a linear molecule such as \( O-C-O \) or \( H-C-N \), we may anticipate that
it forms bonds with digonal or roughly digonal hybrids, the remaining \( 2P \) electrons
Chapter 2  Carbonization and Graphitization

accounting for any remaining \( \pi \)-bonding. Both physical and chemical processes are involved in the carbonization of organic materials and in general carbonization is a complex phenomenon.

The process by which the non-carbon atoms such as oxygen, hydrogen, nitrogen, sulphur etc. are removed from the carbon-containing materials when pyrolyzed to high temperatures, is known as 'carbonization'. This process is followed by a rearrangement of order within the remaining carbon atoms giving rise to a greater degree of order within the carbon produced which may develop a three dimensional order. Such development of a three dimensional order gives rise to a structure very close to the well-defined structure of pure graphite which is termed as 'graphitization'. In fact, graphitization does not occur in 'graphitizable carbons' until they are annealed above 2500°C and the bonds break down above 3000°C. The temperature range from 2500°C to 3000°C is called 'graphitization temperature range'. The graphitization temperature has been found to differ from material to material and is dependent on the parent material.

2.2 Different Forms of Carbon and Crystallographic Models

There are only two allotropic crystalline forms of carbon: (i) graphite and (ii) diamond. Graphite and diamond resist oxidation even at high temperatures. Both exist in nature and can be produced artificially from carbon containing materials. The main difference in properties between these two allotropic forms is determined by the forces lying within and between crystallites.

Graphite is a laminar structure and this structure is the anisotropic allotropic form of carbon. Each layer consists of a very large number of carbon atoms covalently linked to form what may be considered to be a huge polynuclear aromatic macromolecule. Each layer is planar or very nearly so. The accepted ideal crystal
structure which was first established by Bernal[1] (1924) is illustrated in Fig 2.5.

Graphitizing carbons are generally relatively soft and are of high apparent density. It has a stable hexagonal lattice, where the basal planes or layer planes consist of open hexagons with inter-atomic C-C distance of 1.415 Å. These planes are stacked in an alternating sequence, the interplanar distance being 3.354 Å.

The graphite is converted into diamond under high temperatures and pressures and also by the assistance of catalysts. Though the structure of diamond (Fig 2.6) is not hexagonal, Ergun and Leroy[2] have shown that a hexagonal structure for diamond is possible. Again at ordinary pressure diamond changes spontaneously to graphite at above 1500°C[3]. Thermodynamically at atmospheric pressure the graphite is more stable form of the carbon.

Crystallographically perfect graphite has a density of 2.266 gm/cc, while for diamond the density is 3.53 gm/cc. Diamond is usually formed deep in the earth under great pressure and temperature. Presently 30% of the diamond used industrially are produced synthetically. In the graphite structure only three of the four valence electrons of carbon form regular covalent bonds with adjacent carbon atoms. The fourth electron is free and it resonates between the valence bond structures. The weak Vander Waals' forces exist between planes while the strong chemical bonding forces exist in the basal planes. The bonding energy between planes is only about 2% of that within the planes[4,5].

In the case of hexagonal graphite structure the stacking sequence of the planes is AB AB as shown in Fig 2.5, so that the atoms in alternate planes are congruent. A rhombohedral structure has been found to exist in many graphites where the stacking sequence is ABC. ABC as shown in Fig 2.7. In 1942 Lipson and Stokes[6] were able to establish this rhombohedral lattice which was originally proposed by Debye and Scheirrer[7] in 1917 to account for the extra X-ray lines found in some
Chapter 2  Carbonization and Graphitization

powder photographs of graphites. The proportion of the rhombohedral form may be increased in graphites by grinding[8], the sample which indicates that the change arises from the movements of the layers of carbon networks with respect to one another.

Polycrystalline carbon is the most natural graphite. Perfect single crystals greater than 10 μm are quite rare, although they can be produced with difficulty. Most synthetic graphites prepared by high temperature calcination of pitch or coke blends are also polycrystalline. Single crystal of graphite of large dimension that occurs in some natural deposits can be obtained by pyrolytic deposition of carbon from carbonaceous vapours. Under suitable conditions the deposit of carbon can take the form of highly oriented layers. Subsequent treatment of this material can produce quite large single crystals of pure graphite which is known as 'Pyrolytic graphite'.

Another form of carbon is available in nature apart from diamond and graphite, which is known as 'amorphous carbon'. Coal, carbon blacks, charcoal, lamp blacks and similar products are primarily amorphous carbon. They lack in the crystalline structure of diamond and graphite and usually contain impurities. All amorphous carbons possess a short range order. This is actually a structureless form of carbon. The first application of X-ray diffraction method to amorphous carbons, however, led to the concept that they were also graphitic with their apparently amorphous character which arises from the very minute size of the crystallites. These amorphous carbons can be prepared by the combustion of hydrocarbons in an incomplete supply of air. Carbon blacks, charcoal and lamp-blacks belong to these forms.
2.3 Structure of Carbons as Determined by X-ray

There are two distinct and well-defined types of carbon: graphitizing and non-graphitizing. Graphitizing carbons may be defined as those which begin to develop a three-dimensional order on heating in a temperature near 1700°C. Such types of carbons are produced mainly by two processes: (a) the deposition from the vapour phase and (b) the solidification from the liquid or plastic state. Substances which produce graphitizing carbons from the liquid or plastic state include vitrinites of medium volatile coking coal, high temperature coal-tar pitch, petroleum bitumen, polymers such as PVC and polynuclear aromatic compounds. Carbons obtained by heating these substances are coke-like in appearance and they show complex patterns of optical anisotropy under the polarizing microscope.

'Non-graphitizing carbons' are defined as the carbons in which the graphite-like layers lie in parallel groups but are not oriented like the crystalline structure of graphite. Three-dimensional structure of crystalline graphite is not present in this type of carbons. On heating certain non-graphitic carbons to high temperature between 1700°C and 3000°C, graphite-like layers show a tendency of change from a 'random layer structure' towards an ordered structure of crystalline graphite, which can be experimentally shown by X-ray powder photography method. These intermediate type of structures in which the three-dimensional graphite structure is partly developed are called 'graphitic carbons'. Such formations have been observed by Franklin[9].

Carbons which on heating to temperatures between 1700°C and 3000°C show a continuous change from a non-graphitic to a graphitic structure are called 'graphitizing carbons' and carbons which on heating to 3000°C do not exhibit three-dimensional ordering are called 'non-graphitizing carbons'. These two types can be distinguished in terms of the relation between crystal height and crystal diameter on
Graphitizing carbons are generally relatively soft and are of high apparent density. Such carbons possess little microporosity and are relatively rich in hydrogen or low in oxygen, sulphur and nitrogen. They were termed as 'soft carbons' by Mrozowski [10]. During the early stages of the carbonisation process Franklin[11] considered that the crystallites in the graphitizing carbons are fairly mobile and that in the region of 1000°C, a high proportion of the crystallites lie nearly parallel to each other. Weak cross-linking is supposed to exist between the crystallites. A model (reproduced in Fig. 2.9) is put forward by Franklin for the structure of a graphitizing carbon. X-ray records confirm the movable nature of the whole layers or groups of layers with the rise of the heat-treatment temperature, but the most significant factor is that the neighbouring crystallites had to be nearly parallel. The layer planes are linked together for the crystallite growth.

Non-graphitizing carbons are generally hard carbons and are of low apparent density. Such type of carbons have a high microporosity and are relatively rich in oxygen, sulphur and nitrogen and low in hydrogen. They were correspondingly called 'hard carbons' by Mrozowski[10].

Again Franklin[11] put forward a model, which is shown in Fig. 2.10, to account for their structure. In this model the parallel layer groups were oriented at all angles and are joined together at their extremities which account for the microporosity. With the increase of the pyrolysis temperatures there is some growth in the basal plane direction by incorporation of disordered carbon atoms at the edges of the crystallites and the other carbon atoms act as linkages between crystallites.
2.4 Carbonization Process

Many workers have mentioned that the early stages of carbonization process that occur during the temperature range between 350°C and 600°C are most important in determining the ability to graphitize at higher temperature. Despite the complexity of carbonization it is essentially a polymerization process in which the common feature is the progressive elimination of non-carbon elements, and the aggregation of residual carbon atoms into solids comprising more or less highly dispersed graphitic structures.

At least three stages of carbonization process can be recognized: (i) a pre-carbonization stage, (ii) an intermediate stage involving active decomposition and (iii) a final stage in which residual traces of non-carbon elements are removed and some structural rearrangement in the solid product occurs. These stages are not sharply defined; they overlap and may vary according to the material concerned[12].

In the first stage, frequently in the temperature range of 200-350°C important molecular rearrangements and initial condensation reactions can occur.

In the second stage or the intermediate stage which extend to about 600°C, carbon formation generally occur due to condensation reactions. In one or both of these stages melting or formation of liquid or plastic material from the parent organic material may accompany the pyrolytic reactions. In such circumstances, the enhanced molecular mobility can profoundly affect the carbonization reactions. Resolidification of the product usually takes place at temperatures in the region of 600°C and it is accompanied by textural changes and pore formation in the carbonized products.
Chapter 2  

Carbonization And Graphitization

The optical anisotropy of coke was first described by Ramdohr[13] in 1928. Marshall[14] studied optical anisotropy in thin sections of natural coke. Similar observations were done by Stach[15] in polished surfaces of natural coke, Abramski and Mackowsky[16] in polished surfaces of manufactured coke. Others also have described the optical structures of various cokes and coke-like carbons. None of these workers appears to have recognized intermediate stages in the development of the characteristic anisotropic mosaic structure. Such stages were described by Taylor[17] and by Brooks and Taylor[18], who reported the appearance and growth of spherical bodies in the plastic carbonaceous material. The spheres were observed to grow at the expense of the plastic material until a three-dimensional mosaic structure was formed, which persisted in the solidified semi-coke. Stach[15] had observed spheres associated with carbonized coal and reported these spheres as "graphitic spherulites" which exhibited the so-called Brewster or stationary extinction cross. Abramski and Mackowsky[16] described that the spheres, which represent an intermediate stage in coke formation, have optical properties indicating a radial structure. Brooks and Taylor[19] first proposed "mesophase" as a technical term and since then the understanding of the carbonization process has improved substantially.

According to the studies of Winslow[20,21] and others[22,23], two competitive condensation processes play important parts in carbonization. They are aromatic condensation as in the development of highly condensed aromatic systems and condensation reactions leading to three-dimensional structure. If pyrolysis results in the formation of three-dimensional networks or cross linkages before or during the early stages of aromatic condensation, then the resulting carbon is hard having a highly disordered structure.
Chapter 2  Carbonization and Graphitization

Ruland[24] has utilized a novel theoretical approach to the analysis of the diffused X-ray pattern of the disordered layer systems formed in the early stages to carbonization of acenaphthylene and bifluorenyl.

Many studies concerning the formation of carbons and their properties from simple and polynuclear hydrocarbons have been reported[25-27]. They considered that the carbonization processes in aromatic hydrocarbons were influenced by several factors: physical, chemical and environmental.

Blayden et al[28] observed the liquid-like behaviour of short range ordering accompanied by the melting of coking coal.

Taylors and others'[29-31] investigations have shown that long-range structural organization may also occur with materials that pass through a liquid condition during carbonization. It is associated with optical anisotropy in the carbonized product.

Some of the properties of carbons made from polymers and polycyclic compounds (dibenzanthrone) were described by Kipling et al[32]. Mainly, the carbons could be divided into two groups; those which became graphitic at temperatures of 2700°C or above and those which remained non-graphitic. Kipling has investigated the relationship between fusion during carbonisation process and the ability of the resultant carbon to graphitize subsequently at a higher temperature. If the organic materials passed through a fusion stage under specific conditions, they could be formed into graphitic carbon[33,34]. The specific conditions were such that the pyrolytic aromatic structures formed in the residue during carbonisation readily oriented to form graphite. It was confirmed by using polarized-light microscopy[35].

A year after Taylor's presentation on mesophase, Otani[36] in Japan developed the first pitch-based carbon fiber using polyvinyl chloride pitch as the raw material in which he did not realize the presence of mesophase. In 1964-1965, the structure of
mesophase spherules was clearly characterized. Its first use in the production of needle cokes by KOA Petroleum Co[37] in Japan started in 1968. At the same time Nittetsu Chemical Co[38] in Japan started to manufacture pitch cokes using coal-tar pitches by a similar method to that of Petroleum cokes.

Using the Polarized-light micrography White et al[30] investigated the microstructure of the coalesced mesophase formed in the carbonization of coal-tar pitch. They noticed that the structural features of the coalesced mesophase are similar to those found in electron micrograph of graphitized materials. The prominent features in the polarized-light extinction contours are the nodes and crosses which do not move when the plane of polarization of the incident light is rotated. These nodal points are found to correspond to two types of linear defects in the stacking of the aromatic layer planes.

Later White and co-workers[39] extended their classification of defect structures in the stacking of the mesophase layer planes into four. These are: (a) co-rotating node, (b) counter-rotating node, (c) co-rotating cross and (d) counter-rotating cross.

These four classes of linear defects have been termed co- and counter-rotating nodes and crosses depending on whether extinction contours moved with or against the direction of rotation of the plane of polarization of the incident light. The four types of linear defects are represented schematically in Fig. 2.11.

White et al concluded that the processes of the formation, coalescence and deformation of the plastic mesophase established the basic elements of the graphite microstructure, i.e. the parallel alignment of the aromatic layer planes and the re-arrangement of the complex folds in the fibrous regions. The linear stacking discontinuities, namely the nodal and cross structures, are essential characteristics of the coalesced mesophase, and at least the nodal structures were found to persist in their basic form up to graphitization temperature. However, they did not appear to
be involved in shrinkage cracking, fold sharpening, the formation of mosaic blocks and kinks which occurred during pyrolysis. Later White et al.[40] extended their studies to include graphitizable materials such as coal-tar pitch and petroleum coke feedstocks and arrived at similar conclusions.

Honda and co-workers[41] supplemented the works of Brooks and Taylor by examining in much more detail the temperature effect and soaking times upon the growth and physical properties of the mesophase in pitches and also they found that temperature and duration of heat-treatment were essentially complementary factors. During the early stages of carbonization Honda et al.[42] used crossed polarizers with a gypsum plate in a polarized-light technique to investigate the microstructures of the carbonaceous mesophase developed in pitches. They observed the changes in pleochroism and in extinction contours for coalesced and for deformed mesophase by using the sensitive tint technique. Distinction between crosses and nodes, and four types of linear defects in the stacking of the aromatic layer planes were identified by this technique. These were similar to those seen by White et al.[39] and were termed as: (a) Y-type co-rotating nodes, (b) U-type counter-rotating nodes, (c) X-type co-rotating crosses and (d) O-type counter-rotating crosses. This notation is opposite to that of White[39] because of opposite direction of rotation of the plane of polarization of the incident light. Honda also explained schematically how the crosses and nodal structures were formed by the coalescence of two simple spherules and the deformation of such coalesced mesophase.

In 1970, Kureha Chemical Co.[43] of Japan built a commercial plant for producing carbon fibers from isotropic petroleum pitch. In 1971, a mesophase pitch based on carbon fiber, using tetrabenzophenazine pitch as the raw material was developed by Otani[43]. In 1975, Union Carbide Co.[43] announced a process to manufacture carbon fibers using certain types of petroleum mesophase pitch.
Taylor[17] carried out a detailed study of the microscopic changes exhibited by a vitrinite with the progress of carbonization using optical methods. Observations were made with samples of a thermally metamorphosed coal. The vitrinite, which in its unaltered state was anisotropic, became isotropic and this transition was followed under controlled conditions in the laboratory. The change from anisotropy to isotropy was observed to occur at a temperature slightly below that at which the plasticity became measurable. Later, the original structure was verified by Brooks and Taylor[19,44] using electron diffraction and optical microscopic techniques.

Brooks and Taylor showed that spheres growth occurs on heating bitumen, pitches, PVC, naphthene and dibenzanthrene, all of which produce graphitizing carbons. This two phase liquid state structural transformation is known as "carbonaceous mesophase" or "liquid crystal formation". Brooks and Taylor concluded that those materials which finally produce graphitizing carbons pass through a fluid state during the early stage of carbonization which generally occurs in the temperature range between 350°C and 600°C. In the final stages of this fluid phase a second phase having anisotropic structure is found to develop and this structure persists into the semi-coke and beyond. They concluded that any solid-surface has a preferred site for mesophase growth and nucleating effect of solids increases with available surface area. However, it is now thought that nucleation is not the principal mechanism in mesophase formation, but the growth of the anisotropic liquid crystals occurs at the expense of the isotropic liquid phase which was concluded by Walker[45].

Whittaker and Grindstaff[46] found that the rates of formation, growth and coalescence of the mesophase spheres varied from feedstock to feedstock and that the type of molecular structure in the original feedstocks and the type of structures developed on pyrolysis has significant influence on the resulting coke structure.
In 1979, Mitsubishi Chemical industry Ltd[47] and Nittetsu Chemical Co. [48] manufactured needle cokes using coal-tar pitch. During 1982-83, an attempt was made by the Union Carbide Co. to produce carbon fibers from mesophase pitches, but the spinning pitch was too viscous to spin carbon fibers. To overcome this viscosity problem, Otani developed a new method in 1982 in which the molten mesophase pitch was treated as dormant mesophase[49,50] which is easily spinnable. In 1983, the Government Industrial Research Institute, Kyushu[51] pointed out that hydrogenated coal-tar pitches are also easily spinnable. The pre-mesophase and the dormant mesophase pitches have good spinnability and good thermal stability. In 1983 Higuchi et al.[52] determined that the carbonaceous mesophase is optically a uniaxial negative liquid crystal.

As a pre-requisite to graphitization, carbonaceous mesophase formation and a liquid state structural transition of optical anisotropy in aromatic organic compounds, coals and pitches were also investigated by a number of workers like Graham[53], Chwastiak et al[54], Gasparoux et al[55], Weinberg and White[56], Hossain[57], Hossain and Dollimore[58], Honda et al[59].

The historical development of mesophase, the types of mesophase that can be produced and their structures and properties are studied by Huoda[60] in 1988.

### 2.5 Mesophase

Mesophase is an intermediate phase of graphite. An understanding of the conditions for the formation of carbonaceous mesophase is of considerable importance, because the mesophase predetermines the ultimate structures and properties of the resulting carbon. The initial stages of mesophase sphere formation can be envisaged as a
Chapter 2 Carbonization and Graphitization

nucleation step in which nuclei begin to appear homogeneously from the isotropic phase.

The first growth of spheres suggests that the formation of nuclei is more concerned with the matter of stability rather than the kinetics of growth, because it is found that the size, shape, and hardness of the spheres are developed within a very few minutes. One of the carbonization reactions leading to the production of mesophase spheres under hydrostatic pressure can be represented as,

\[
\text{(1)} \quad \text{Solid} \xrightarrow{\text{Polymerization and massive condensation}} \text{Polymeric products (IF)} \xrightarrow{\text{Polymerization and massive condensation}} \text{Polymeric products (MS)}
\]

where, IF denotes an isotropic fluid and MS a mesophase sphere.

Reaction step (1) is not expected to be influenced significantly by pressure levels because of the small value of \(dT/dP\).

Reaction (2) is affected through the influence of pressure on chemical kinetics and equilibrium. It is evident that the compositions of the polymeric products are remarkably different in reactions under pressure. However, reaction (3) is considered more important than the other steps in so far as nucleation of mesophase spheres is concerned.

2.6 Liquid Crystals

Liquid crystals are those materials which consist of a loose array of molecules. There are three main categories of liquid crystals viz. smectic, nematic and
Chapter 2  

Carbonization and Graphitization

cholesteric. Smectic liquid crystals consist of flat layers of cigar shaped molecules with their long axis oriented perpendicularly to the plane of the layer. The molecules within each layer can be ordered or random. At low temperatures these liquid crystals become crystalline. Heat-treatment weakens the forces between the layers and thus allows them to flow like liquids.

Nematic liquid crystals also have molecules that are oriented with their long axis parallel to the plane but they are not separated into layers and are free to move in any direction maintaining their orientation.

Cholesteric liquid crystals are formed in thin layers and within each layer the molecules are arranged with their long axis in the plane parallel to each other. The axis of alignment of each layer is rotated by a small angle with respect to the adjacent layers.

Certain organic substances when heated will melt first into the liquid crystal form and then into the true liquid state.

2.7 Pressure effect on Carbonization and Graphitization

Walker et al. [61,62] and Marsh et al. [63,64] performed the extensive studies on the carbonization of some organic compounds and coal-tar pitches under extremely high pressure (3 Kbar). But the use of low pressure seems to be more logical for producing high carbon residues by favoring the formation and escape of volatiles. Any conditions which would favor molecular rearrangement or increased molecular weight may also favor a high degree of carbon-carbon cross-linking or carbon-packing density. Pressure does control solubility, viscosity, density and phase separations within the system during polymerisation and carbonization, all of which may influence the kind and degree of cross-linking in the polymer and carry through
Chapter 2  Carbonization and Graphitization

pyrolysis and carbonization\[61\]. Carbonization of well-known organic compounds under moderate pressure has been reported by several investigators.

Fitzer and Terwiesch\[65\] studied the effect of gas pressures up to 100 bar on coke yield from conventional pitches. It was observed that up to 550°C the maximum coke yields are achieved at pressures of above 100 bar. Under pressures up to 200 bar, studies with conventional coal-tar and petroleum pitches\[66,67\] showed that increasing pressure not only increases the coke yield but also lowers the temperature at which pyrolysis is completed.

The structures of the solid products carbonized in a sealed tube surrounded by a hydrothermal pressure bomb, were characterized as anisotropic carbonaceous mesophase, whose morphologies changed from vesicular to spherical with increasing pressure. Pressure was also observed to prevent coalescence of the mesophase spheres and to enhance graphitizability. It was also observed that increasing pressure improves pre-order and graphitizability of the residues. Increasing pressure gives rise to a pronounced segregation of natural insolubles of conventional coal-tar pitches and of artificial insolubles like carbon-black. A highly ordered mesophase without insolubles is found to be deposited in the lower part, whereas, the separated insolubles accumulate in the upper part of the pyrolysis vessel. Fig 2.12 shows that the spherulite size of isotropic carbon formed under one set of carbonization conditions decreases steadily with increasing pressure of polymerization. It was also observed that the lower-pressure polymer could lead to the production of spherules which would coalesce in part\[66,67\].

2.8 Different types of Mesophase Spherules

The carbonaceous spherules of optical anisotropy was first reported by Brooks and Taylor\[19,44\]. A number of studies have been made on the nucleation, growth and
coalescence processes of mesophase spherules\cite{68-70}. Most of the studies confirmed the findings of Brooks and Taylor that in the individual mesophase spherule flat aromatic molecules lie parallel to each other in the interior and perpendicular to the surface of the spherule near the surface.

Most recently, mesophase spherules with structures other than that proposed by Brooks and Taylor have been reported and different types of structural sketches of sections and models are shown in Fig 2.13. A second-type mesophase spherules with different optical properties from those of the Brooks-Taylor was reported by Honda and Co-workers\cite{71} with structural model having the outer layers lying parallel to the spherule surface but a similar layer alignment to the Brooks-Taylor type spherule around the central region (Fig 2.13B). Similar mesophase spherules were also found by Kovac and Lewis\cite{72}, Imamura et al \cite{73}, Huttinger\cite{74} and by Imamura and Nakamizo\cite{75}. They reported the third-type of mesophase spherules with all the layers lying in concentric circles about the centre of the spherules (Fig 2.13C). The structure of a fourth-type spherule (Fig 2.13D) similar to that of the Brooks-Taylor type was reported by Imamura, Nakamizo and Honda\cite{76}, Hishiyama et al\cite{77}. It is now believed that the fourth-type spherule is a metastable phase of the Brooks-Taylor type. Novel anisotropic mesophase features having a flower-petaloid texture were reported by Mochida et al\cite{78}.

2.9 Mathematical Model for Carbonization Process\cite{79}.

The decomposition of graphitic materials may be distinguished into three successive reactions as shown in the following reactions:
Chapter 2 Carbonization and Graphitization

\[ k_1 \]
1. Sample \( \rightarrow \) Unstable intermediate phase (metaplast)

\[ k_2 \]
2. Metaplast \( \rightarrow \) Mesophase (R) + primary volatiles (G₁)

\[ k_3 \]
3. Mesophase \( \rightarrow \) Graphite (G) + secondary gas (G₂)

where \( k_1, k_2 \) and \( k_3 \) denote the respective reaction velocity constants.

The "metaplast theory" is based on the assumption that the carbonization process takes place in three successive reactions:

Reaction (1) is a depolymerization reaction in which an unstable "intermediate phase-metaplast" is formed which is responsible for the plastic behaviour of graphitizing organic compound.

Reaction (2) denotes a cracking process in which the samples (aromatic organic compounds) are vaporized and the reaction is attended by recondensation and formation of mesophase. Towards the end of the process the mass solidifies again.

Reaction (3) is a secondary degasification reaction in which the (semicoke) liquid formations are welded together through evolution of methane and especially at higher temperatures, of hydrogen, to yield the real carbon.

Depolymerisation and cracking reactions in general have frequently been shown to be first-order reactions [80,81], while several authors have advanced evidence that the primary decomposition of coal is also a first-order reaction [82]. Hence it is reasonable to assume that the reactions (1) and (2) are of the first order.

Reaction (3) is complicated, because its consists of composition of the gas and graphite in which graphite formation is gradual.
Supposing, for reasons of simplicity, that the third reaction is also a first-order reaction, the kinetics of the carbonization may be described by the following equations,

\[ -\frac{dP}{dt} = k_1 P \]  
\[ \frac{dM}{dt} = k_1 P - k_2 M \]  
\[ \frac{dG}{dt} = \frac{dG_1}{dt} + \frac{dG_2}{dt} = k_3 M + k_3 R \]

where, \( t \) denotes time and \( P, M, G \) and \( R \) are the amounts by weight of the reactant \( P \), the intermediate \( M \) and the reaction products \( G \) and \( R \).

The effect of reaction (3) does not become appreciable until reaction (2) has continued so far that the rate of devolatilisation reaches its maximum value.

For the time being we shall restrict ourselves, therefore, to a discussion of carbonization processes at low temperatures, i.e. below the temperature at which the devolatilisation rate reaches a maximum (\( T_{\text{m.d.}} \)). It may be assumed that under these conditions,

\[ \left( \frac{dG_1}{dt} \right)_{T < T_{\text{m.d.}}} \approx \circ \quad \text{or} \quad \left( k_3 \right)_{T < T_{\text{m.d.}}} \approx \circ \]

Equation (3) then becomes,

\[ \frac{dG}{dt} \approx \frac{dG_1}{dt} = k_2 M \]  

Chermin and Van Krevelen[83] have shown that the reaction rate constant \( k_1 \) and \( k_2 \) for coking carbon are approximately equal and,

\[ k_1 \approx k_2 \approx k \]  

To prove this, equations (1), (2) and (4) were numerically integrated. In doing so it was assumed that the temperature is a linear function of time. From experience we know that in the case of a linear temperature time programme, the temperature at
which the rate of degasification is maximum differs by about 10°-20°C from the
temperature of maximum plasticity (maximum value of $M$). It has been found that
such a difference can only exist if $k_1 \approx k_2$.

At constant temperature it is not difficult to express $PM$ and $G$ in terms of $P_0$, $k$ and
$\tau$ as (1) has the solution

$$P = P_0 e^{-kt}$$  \hfill (6)

From (2) and (6) it follows that,

$$\frac{dM}{dt} + M = P_0 k e^{-kt}$$  \hfill (7)

With reference to the initial condition $M=0$ if $t=0$, this differential equation has the
solution,

$$M = P_0 k t e^{-kt}$$  \hfill (8)

Up to a point slightly above the temperature at which the rate of devolatization is
maximum, $G$ is given by

$$G \approx G_f = P_0 - P - M$$

so that $G$ may, as a first approximation, be expressed by

$$G \approx P_0 [1 - (kt + 1)e^{-kt}]$$  \hfill (9)

At constant heating rate, when the temperature is given by $T = \nu t$, the problem can
not be solved by a simple analytical method.

The possibility of having graphitic carbon is determined by the following
temperature time equation,

$$e^{-2Tt/T} = bt$$  \hfill (10)

The above equation shows an inflection at $T_1$, which determines the value of the
constant $b$. The point of the inflection may be arbitrarily chosen.
Chapter 2  
Carbonization and Graphitization

Within a temperature range given by $0.8 \leq T/T_1 \leq 1.3$ equation (10) is a very close approximation of a linear temperature-time programme. Then, the equations (6), (8) and (9) retain their original forms, provided $k$ is replaced by the reduced reaction rate constant $k_r$, which is given by

$$k = \frac{k}{k/R_1 + 1}$$  \hspace{1cm} (11)

where, $E = \text{activation energy}$ defined by

$$k = k_o e^{-E/RT}.$$  \hspace{1cm} (12)

This may be derived as follows[83]. From $T = vt$ and equation (10) it follows,

$$b = \frac{2v}{e^T}$$  \hspace{1cm} (13)

With, $k_1 \approx k_2$, (1) and (12) give,

$$-\frac{dp}{dt} = Pk_o(bt)^{k/R_1}$$

Integration of this equation gives,

$$-\ln \frac{P}{P_0} = \frac{k_0}{b(2R_1-1)} \exp [-\left(\frac{E}{R} + 2T_1\right)]$$

which, after substitution of (10) becomes,

$$-\ln \frac{P}{P_0} = \frac{k_0}{b(2R_1-1)} e^{-E/RT}$$

or,

$$P = P_0 e^{-kt}$$  \hspace{1cm} (14)
By comparing this expression with (1), we get the important relationship,

$$\int \! k \, dt = \frac{1}{2}$$  \hspace{2cm} (15)$$

Substitution of (14) in (2) gives,

$$\frac{dM}{dt} + \lambda M = P_{o}k e^{-kt}$$  \hspace{2cm} (16)$$

Having the solution,

$$M = P_{o} \exp[-\int \! k \, dt] \left( \exp[\int \! \lambda \, dt] \right) e^{-kt} + \text{Const.} \exp[-\int \! k \, dt]$$  \hspace{2cm} (17)$$

Considering the initial condition $M = 0$ if $t = 0$ and using (15),

Equation can be transformed into,

$$M = P_{o} e^{-kt} \int_{0}^{t} e^{-kt} \, dt$$

At constant heating rate the amounts by weight of the products $P, M$ and $G$ are consequently given by

$$P = P_{o} e^{-kt}$$

$$M = P_{o} k t e^{-kt}$$  \hspace{2cm} (18)$$

$$G = P_{o} \{1-(kt+1)e^{-kt}\}$$  \hspace{2cm} (19)$$

Using this kinetic theory it has been found possible to give a satisfactory explanation of the phenomena occurring during the heating of coking carbon[83].
Chapter 2  
Carbonization and Graphitization

Heating at constant rate.

Experiments at constant heating rate are more valuable for the industrial carbonization of carbon than those conducted at constant temperature. The phenomena observed in these experiments may also be satisfactorily accounted for by the metaplast theory.

When the carbon is heated at a constant rate, the temperature will pass the point $T_{m,d}$, where, the rate of loss in weight is maximum. This rate is given by $\frac{dG}{dt}$ and becomes maximum when $\frac{d^2 G}{dt^2} = 0$.

A relationship can be derived between the rate of heating $v$ and the temperature of maximum degasification $T_{m,d}$.

By differentiating (18) twice with respect to $t$ and rearranging one obtains

$$1 + \frac{E}{2RT_1} \cdot \frac{1}{E/2RT_1 + 1} - \frac{k_{m,d}}{E/2RT_1 + 1} = 0$$

So that,

$$T_{m,d} = \frac{E / RT_1 + 1}{k}$$

(20)

Multiplication of (20) by $b$ and substitution of (10) and (12) in (20) gives,

$$\exp(-\frac{2I}{T_{m,d}}) = \frac{b}{k_o} \cdot \frac{E / RT_1 + 1}{\exp(-E / RT_{m,d})}$$

(21)

Combining equation (21) and (13) after rearrangement one gets,

$$-\log p = \log \frac{E / RT_1 + 1}{3.77k_o} + \frac{E + 2RT_1}{2.3 + RT_{m,d}}$$

(22)

This relationship between $p$ and $T_{m,d}$ may be written in the following form,

$$-\log p = M + \frac{E + 2RT_1}{2.3 + RT_{m,d}}$$

(23)
Chapter 2

Carbonization and Graphitization

where, \[ M = \log \frac{E / RT_1 + 1}{37T_1 k_o} \] (24)

It is probable that the activation energy of coal carbonization like activation energy of polymer pyrolysis be determined by the binding energy of C-C bonds.

According to (19) the rate of devolatization is given by

\[ \frac{dG}{dt} \approx P_0 k t e^{-kt} \] (25)

if the rate of devolatization is identified with the rate of change of reaction products.
Figure 2.1 An sp\(^2\) hybrid orbital. The P-orbital lies perpendicular to the plane of the sp\(^2\) orbital.

Figure 2.2 An sp hybrid orbital. The angle between the two P-orbitals is 90°.
Fig 2.3  Trigonal Hybrids: Carbon in a graphite layer showing appropriate SP² hybrids (each C-C bond formed from one over lapping pair).

Fig 2.4  Trigonal Hybrids: Carbon SP² Hybrids in Benzene
THE IDEAL GRAPHITE CRYSTAL STRUCTURE WITH THE HEXAGONAL UNIT CELL WITH CRYSTAL AXES AND LATTICE CO-ORDINATES.

DIAMOND STRUCTURE
Chapter 2  

Carbonization and Graphitization

Fig 2.7  THE RHOMBOHEDRAL STRUCTURE, SHOWING THE TRUE UNIT CELL AND THE ATOMIC CO-ORDINATES IN THE APPROXIMATE HEXAGONAL CELL SHOWN IN DOUBLE LINES.

Fig 2.8  RELATIONSHIP BETWEEN THE LAYER DIAMETER AND THE NUMBER OF LAYERS PER PARALLEL GROUP FOR GRAPHITIZING (X) AND NON-GRAFPHTIZING CARBONS (Δ).
Fig 2.9 SCHEMATIC REPRESENTATION OF THE STRUCTURE OF A GRAPHITIZING CARBON.

Fig 2.10 SCHEMATIC REPRESENTATION OF THE STRUCTURE OF A NON-GRAPHITIZING CARBON.
Fig 2.11 SCHEMATIC DIAGRAM OF THE FOUR TYPES OF MESOPHASE STACKING DEFECTS. EXTINCTION CONTOURS ARE SHOWN FOR THE CASE OF CROSSED POLARIZERS.

Fig 2.12 VARIATION IN DIAMETER OF ISOTROPIC CARBON SPHERULITES PRODUCED BY CARBONIZATION UNDER 0.69 KBAR PRESSURE AT 900°C AND 3h SOAK TIME FOLLOWING POLYMERIZATION OF DIVINYLBENZENE AT VARIOUS PressURES.
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Fig 2.13 Schematic structural sketches of sections and three-dimensional models for
(A) Brooks-Taylor type (B) 2nd type (C) 3rd type and (D) 4th type spherulites.
Chapter 2

Carbonization and Graphitization

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Chapter 2  
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Chapter - 3

Pyrolysis of Aromatic Hydrocarbon
3.1 Mechanism

The mechanism of condensation reactions leading to carbon formation appears to be largely specific on the material being carbonized. However, the formation and reaction of free radicals play important part in the processes concerned.

Both physical and chemical processes are involved in the carbonization of organic materials and in general carbonization is a complex phenomenon.

The present contribution is concerned primarily with complex pyrolytic carbonization in condensed phases.

Franklin, Kinney, Walker, Badger and others [1-4] have contributed significantly investigating the mechanism of the early stages of carbonization of aromatic hydrocarbons. They showed that the rate of heating and the temperature of decomposition are the two important parameters affecting the mechanism of carbonization of a given compound. At higher temperature such effect can cause simultaneous thermal rupture of several bonds of different reactivities. Complex competing reactions involving small molecular fragments would also be expected.

In the following discussion of the mechanism of the early stages of carbonization, only aromatic hydrocarbons in the liquid or solid phase will be considered. The initial chemical reactions of carbonization can be thought to occur in four main stages. Although these reactions may not proceed in distinct steps, for purposes of discussion, it will be assumed that they do so.

(i) Bond cleavage occurs at the most reactive molecular site to form a free radical.

(ii) Radicals rearrange into more stable molecular structures.

(iii) Radical units polymerize.

(iv) Hydrogen is eliminated from polymerized structures.
Most of the reactions occur in the liquid media where the molecules are mobile and can orient themselves properly for hydrogen transfer, rearrangement and subsequent polymerization reactions. The existence and importance of this liquid alignment and polymerization stage was pointed out by Brooks and Taylor[5], Ihnatowicz et al[6] and White et al[7]. At this stage, mobile aromatic molecules are converted to infusible aromatic polymers.

Excessive increase of degree of graphitization causes formation of solid graphite from liquid state. If adequate alignment is prevented by the premature reaction of highly unstable radical intermediates, disordered graphite structure results.

Organic compounds are the main and the most exclusive raw materials for the production of artificial carbons and graphite. By pyrolysis, these carbon compounds are converted to solid carbon as the main product and to different volatile compounds as by products. The pyrolysis is controlled by a few reaction parameters such as temperature, heating rate, heat-treatment duration and the total gas pressure etc. The low-temperature stage of pyrolysis below 700°C has the greatest influence on the carbon yield and carbon properties. In all such technical cases, the primary importance is to achieve a high carbon yield which is also determined by the mechanism of the pyrolysis.

Including the sealed tube method, there are five different methods which are adopted in the pyrolysis technique alternatively:

(i) Pyrolysis in a sealed tube, starting the heating under increasing pressure caused by the pyrolysis gases.

(ii) Pyrolysis in autoclaves, where the pressure can be regulated during the whole reaction time.
(iii) Liquid pyrolysis in an open crucible with continuous removal of the gaseous by-products; this is mostly used for reactions carried under normal pressure.

(iv) Gas cracking in a steady-state tubular flow reactor with relatively fast heating of the evaporated starting material and in most cases with quenching of the volatile products.

(v) The hot wire method as a special arrangement of the flow system.

In the first three cases mentioned above prolonged heat-treatment at low temperature is used, whereas, in the last two cases the shortest contact times and the highest temperatures are generally applied. Here, the influence of evaporation and physical condensation phenomena on these chemical reactions are also considered.

In the cases where the organic materials vaporizes on pyrolysis, it becomes necessary to heat the samples in sealed tubes in order to obtain appreciable carbon yields[8]. This is because increased gas pressures of evaporated hydrocarbons lead to high carbon yields. Again, as the vapour pressure of the compound being carbonized inside the sealed-tube is not known, it is always preferred to take a heavy-walled pyrex tube or quartz tube so that the tube can stand the increased pressure of the pyrolysis gases. Even then the tube may burst. So, some safety enclosure round the tube should be provided as a precautionary measure against any blow or blast.

Due to heavy pressure inside, it cannot be opened ordinarily by cutting with a diamond edge or by tungsten blade without adopting any safety measure against the blow or blast if any. It is, therefore, advised to open the tube inside a strong safety box. Alternately, the tube can be opened without the aid of a safety box provided it is immersed in a Dewar containing liquid nitrogen for at least an hour before opening. Since the second process involves a thermal shock, it should be avoided.
In the sealed tube technique of pyrolysis mentioned, heating of the sample is first carried out under normal pressure and then under increasing pressure caused by the pyrolysis of gases.

### 3.2 Polycyclic aromatic Hydrocarbons:

Any organic compound which undergoes substitution reactions of carbon-hydrogen (C-H) bonds is said to be aromatic. The word aromatic is derived from the Greek word "aroma" means "Sweet smell". Most of the aromatic organic compounds have a common property of possessing 'pleasant odour'.

Most aromatics are colourless solids or colourless liquids and are lighter than water. They are non-polar materials, immiscible with water, but readily soluble in non-polar solvents such as ether, petroleum ether and carbon tetrachloride.

With the advent of wave-mechanics a well known rule was put forward by W. Hückel[9] known as "Hückel's $4n+2$ rule". The rule refers to the properties of cyclic conjugate molecules in which there are $N$ electrons; these depend on the nature of the integer $N$. If $N$ is expressed in terms of a smaller integer $n$, the rule may be stated as follows,

\begin{align*}
\text{For, } N &= 4n + 2 \quad \rightarrow \text{the molecule is highly stable} \\
\text{For, } N &= 4n + 1 \quad \rightarrow \text{the molecule is a free radical} \\
\text{For, } N &= 4n \quad \rightarrow \text{the molecule has a triplet ground state and is highly unstable.}
\end{align*}

In dealing with any ring, we must remember of course that stability of molecule depends on the total energy, not that of the $\pi$-electrons alone, and that any departure from the 'natural' in-plane bond angles ($120^\circ$, corresponding to trigonal
hybridization) will raise the energy of the σ-bonded framework by an amount corresponding to the strain energy.

Hückel's rule stimulated a large amount of research on aromaticity and, thus no exception of the rule has been found. A further test for aromaticity is that such compounds sustain diamagnetic ring currents in the presence of magnetic fields. In general an aromatic organic compounds should fulfill the following requirements.

1. The "Hückel's (4n+2) rule" is obeyed (Fig. 3.1)
2. All the compounds undergo electrophilic substitution reactions (nitration, sulphonation etc.).
3. The compounds show delocalisation of the π-electrons by supporting a diamagnetic ring current.

The high stability of the aromatic organic compounds is due to resonance energy[10] which increases with the increasing molecular size of the ring system are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Resonance energy (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>36</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td>61</td>
</tr>
<tr>
<td>Anthracene</td>
<td>C₁₄H₁₀</td>
<td>84</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>C₁₄H₁₀</td>
<td>92</td>
</tr>
<tr>
<td>Chrysene</td>
<td>C₁₈H₁₂</td>
<td>117</td>
</tr>
</tbody>
</table>
3.2.1 Investigated samples

Generally, aromatic compounds are obtained by the distillation of coal-tar. Fused or condensed aromatic hydrocarbons contain more than one ring and have two carbons shared by two or three aromatic rings. The most important members of this class are naphthalene; anthracene and phenanthrene.

3.2.2 Anthracene

Anthracene occurs in coal-tar and is obtained from the green oil fraction. On cooling this fraction crude anthracene crystalizes out. It is a colourless solid. Its molecular formula is C\textsubscript{14}H\textsubscript{10}.

It melts at 216°C and boils at 340°C. Its molecular weight is 178.234. It is insoluble in water, but dissolves in benzene. It shows a strong blue fluorescence when exposed to ultraviolet light and very active in 9-10 positions.

Structure of Anthracene:

An anthracene molecule is planar and consists of three fused hexagonal benzene rings. All fourteen carbon atoms in anthracene are SP\textsuperscript{2} hybridized. The SP\textsuperscript{2} hybrid orbitals overlap with each other and with S-orbitals of the ten hydrogen atoms forming C-C and C-H σ-bonds. Since the bonds result from the overlap of trigonal SP\textsuperscript{2} orbitals, all carbon and hydrogen atoms in anthracene lie in the same plane. This has been confirmed by X-ray diffraction studies.

Also each carbon atom in anthracene possesses an unhybridized P-orbital containing one electron. These P-orbitals are perpendicular to the plane of the σ-bonds. The lateral overlap of these P-orbitals produces a π-molecular orbital containing fourteen electrons. One half of this π-molecular orbital lies above and the other half lies below the plane of the σ-bonds. Anthracene shows aromatic properties because
the resulting \( \pi \)-molecular orbital satisfies the Hückel's rule \( n = 3 \) in \( 4n^2 + 2 \).

A common shorthand representation of anthracene is three linearly fused hexagons with a circle inside each hexagon. The circles represent the \( \pi \)-molecular orbitals (Fig 3.2).

According to the resonance theory anthracene is considered to be a hybrid of four canonical forms (Fig 3.3).

The resonance energy of anthracene is 84 Kcal/mole. This averages to 28 Kcal/mole per ring, which is substantially lower than that of benzene (36 Kcal/mole). As a result, anthracene is much less aromatic than benzene and behaves more like an unsaturated aliphatic hydrocarbon, but far more reactive than benzene.

3.2.3 Phenanthrene:

Phenanthrene is an isomer of anthracene. It occurs along with anthracene from the green oil fraction of coal-tar and is separated from anthracene by means of solution in solvent naphtha. It is also a colourless solid. Its molecular formula is \( \text{C}_4\text{H}_{10} \). It melts at 100°C and boils at 338°C. Its molecular weight is 178.234. It is insoluble in water, but dissolves readily in ethanol, benzene and ether. It gives blue fluorescence in benzene solution and very active in 9-10 positions.

Structure of Phenanthrene:

Like anthracene, Phenanthrene is a planar molecule. All fourteen carbon atoms are \( \text{SP}^2 \) hybridized. The \( \text{SP}^2 \) orbitals overlap with each other and with \( \text{S}\)-orbitals of ten hydrogen atoms to form C-C and C-H \( \sigma \)-bonds. Each carbon atom also possesses a \( \text{P}\)-orbital and these are perpendicular to the plane containing the \( \sigma \)-bonds.
Chapter - 3  Pyrolysis of Aromatic Hydrocarbon

The lateral overlap of these $\pi$-orbitals produces a $\pi$-molecular orbital containing ten electrons. Phenanthrene shows aromatic properties because the resulting $\pi$-molecular orbital satisfies the Hückel’s rule ($n = 3$ in $4n + 2$).

A shorthand representation of phenanthrene is three hexagons fused in angular fashion with a circle inside each hexagon. The circles represent the $\pi$-molecular orbital (Fig 3.4).

Phenanthrene is considered to be a hybrid of live resonance forms (Fig 3.5).

The resonance energy of phenanthrene is 92 Kcal/mole. Of the two tricyclic aromatics anthracene and phenanthrene, phenanthrene is more thermally stable than the anthracene.

3.3 Pyrolysis of anthracene

The pyrolysis of anthracene has been investigated by a number of authors[9-16]. Six isomers of bianthryl (I-VI) as represented in Fig 3.6 are possible under the assumption of the radial mechanism.

Mayer and Hofmann[14] carried out hot wire pyrolysis of anthracene with quenching of the volatile products and then utilized molecular spectroscopy to study the resultant product. They have identified the product bianthryl. Lang and Buflleb[16] employed a flow tube method for pyrolysis of anthracene between 700-750°C and found the products VII, VIII and IX. Sharkey et al[13] undertook the fluid-phase pyrolysis of anthracene at 450°C for a residue time of 4 hours. They adopted the sealed tube technique and examined the residence of the fluid-phase pyrolysis with the help of mass spectroscopy.

Lewis and Singer[17] heat-treated 9,9-bianthryl at 500°C in a stable liquid and studied the beginning of pyrolysis by high resolution ESR. They found the formation of anthryl radicals at the first step and at the second step there is loss of a
hydrogen atom which leads to formation of bianthryl radical. By way of a hydrogen-transfer step, bianthryl eventually leads to anthracene reformation, as described by Conroy et al[15] and subsequently confirmed by Lewis and Edstrom[12].

The high temperature pyrolysis of anthracene in an open system giving a little amount of carbon residue adhering to the surface of the open crucible. This is due to the volatility of bianthryl and anthracene. In the range of 800°C to 1000°C, anthracene is rapidly decomposed to carbon if pyrolysed in a sealed tube.

3.4 The Pyrolysis of Phenanthrene

The pyrolysis of phenanthrene has been described by numerous investigators[11,12,15,18-20]. Lang et al[19] carried out gas phase pyrolysis of phenanthrene at 750°C and identified the main products as a mixture of isomers of the biphenanthryls I, II & III as shown in Figs 3.7. The IR spectrum revealed that biphenanthryl (I) is predominant. In addition, Lang found the two dibenzoperylenes IV and V which represent chemical condensation product of biphenanthrene in which the phenanthryl portions are connected in the 1, 4 and 9 positions. However, Lang could not identify biphenyl.

Sharkey et al[13], took phenanthrene in a sealed tube and pyrolysed in a liquid-phase at 400°C for a duration of 4 hours and then employed mass spectroscopy to examine the residue of the liquid-phase pyrolysis. Milliken[20] also investigated the liquid-phase pyrolysis of phenanthrene and assumed that during the initial stage of carbonization the 9,10 carbon-carbon bond is probably severed (Fig. 3.8). The resulting non-planar radical molecule is similar to biphenyl. Milliken, however, failed to identify this compound in the pyrolysis product.
Chapter 3

Pyrolysis of Aromatic Hydrocarbon

The rate of cracking of phenanthrene at 500°C is 370 times slower than that of anthracene, as measured by gas formation[21]. The cracking of phenanthrene at high temperatures in the region of 800°C to 1000°C has not been reported and so no comparison with anthracene can be made.

3.5 Catalytic Hydrogenation and Dehydrogenation

Of the many reactions available for the reduction of the organic compounds, the reaction of a compound with hydrogen in presence of a catalyst offers the advantage of wide spread applicability and experimental simplicity to a unique degree is known as catalytic hydrogenation.

Common dehydrogenation is the reverse of catalytic hydrogenation. The most common application of this reaction has been the removal of two hydrogen atoms from a cyclohexadiene derivative or the removal of four hydrogen atoms from a cyclohexene derivative to form the corresponding aromatic compound.

As a general rule, the reaction conditions required for dehydrogenation become milder the fewer the number of hydrogen atoms that must be removed or transferred to form an aromatic system.

The carbon skeleton of compounds to be dehydrogenated cannot be altered unless the ring system to be aromatized contains a quaternary carbon atom (e.g. the following reaction).

\[
\text{Heat treatment} \quad \xrightarrow{\text{CH}_3 \text{CH}_3} \quad \xrightarrow{\text{CH}_3} + \text{CH}_3
\]

In such cases aromatization can occur only if one of the alkyl groups is lost or migrates to a nearby-atom[22,23].

57
Since the tendency toward rearrangement is normally enhanced when relatively high temperatures are used to dehydrogenation, it is often desirable in synthetic work to introduce multiple unsaturation prior to dehydrogenation. By this means, the final reaction leading to aromatization can be performed under relatively mild conditions which minimise the possibility of rearrangement.

In the presence of catalyst (AlCl₃), anthracene is converted to its dianion which is protonated to give the dihydroproduct i.e. the analogous reduction of 9,10 dihydroanthracenes yields primarily trans-dihydroderivatives; where as the reduction of 9,10 dihydrophenanthrenes produces mainly cis-dihydro compounds[24-26].
Chapter 3

Pyrolysis of Aromatic Hydrocarbon

6π ELECTRONS = (4 × 1 + 2), AROMATIC

BENZENE, C₆H₆

10π ELECTRONS = (4 × 2 + 2), AROMATIC

NAPHTHALENE, C₁₀H₈

14π ELECTRONS = (4 × 3 + 2), AROMATIC

ANTHRACENE, C₁₄H₁₀

14π ELECTRONS = (4 × 3 + 2), AROMATIC

PHEMANTHRENE, C₁₆H₁₀

18π ELECTRONS = (4 × 4 + 2), AROMATIC

CHRYSENE, C₁₈H₁₂

Fig 3.1 SIMPLE AROMATIC ORGANIC COMPOUNDS OBEYING 'HUCKEL'S 14n + 2 RULE'
**Chapter 3**

Pyrolysis of Aromatic Hydrocarbons

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**Fig 3.2** MOLECULAR ORBITAL OF ANTHRACENE

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**Fig 3.3** MOLECULAR ORBITAL OF PHENANTHRENE
Chapter 3

Pyrolysis of Aromatic Hydrocarbon

FIVE RESONATING STRUCTURES OF PHENANTHRENE

Fig 3.5
Chapter 3

Pyrolysis of Aromatic Hydrocarbon

I 1,1'-BIANTHRYL

II 9,9'-BIANTHRYL

III 1,2-BIANTRYL

IV 2,2'-BIANTHRYL

V 1,2-BIANTRYL

VI 2,9-BIANTRYL

VII BIGANTRYLENE

VIII

IX

Fig 3.6 PYROLYSIS OF ANTHRACENE
Chapter 3

Pyrolysis of Aromatic Hydrocarbon

Fig 3.7 Pyrolysis of Phenanthrene

Fig 3.8 Expected rupture of 9,10 bond in Phenanthrene.
Chapter - 3  

Pyrolysis of Aromatic Hydrocarbon

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Chapter - 3

Pyrolysis of Aromatic Hydrocarbon

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Chapter - 4

Experimental
4.1 Introduction.

The different experimental techniques used to study the graphitization process of carbonization in the present work are Polarized-light technique, DTA, TGA, Infrared spectrometry, X-ray diffractometry and Torque magnetometer with PID compensation.

Graphitizable organic solid materials usually pass through a fusion stage during carbonization in the temperature range of 350°C-600°C. This is one but not the only necessary condition for the graphitizability of organic solid compounds. Many researchers have demonstrated the formation of carbonaceous mesophase as precursor to graphitization. This mesophase is a liquid or plastic state structural transition in which the large planar aromatic molecules formed by the reactions of thermal cracking and aromatic polymerization become aligned in a parallel array to form an optically anisotropic liquid crystal, the lifetime of which is limited by its hardening to a semi-cake.

A parallel plate of quartz or gypsum called the "first order-red plate", the thickness of which is adjusted to give a path difference between the two transmitted components equal to one wave-length of yellow light, is inserted at 45° between crossed polars. Between crossed polars it gives the violet-red interference colour at the end of the first order and if it suffers a very small subtractive effect there is a very marked change to orange or yellow. Whereas, if it suffers a very small additive effect, the red colour changes to indigo or blue. By the use of this Sensitive Tint Technique changes in pleochroism and in extinction contours for coalesced and for deformed mesophase forming mosaic texture are observed.

Additional information is necessary to supplement the polarized-light micrography and in this respect DTA has been found to be an important tool in ascertaining
whether a simple organic aromatic composite sample is graphitic or not. DTA as a technique to detect the graphitizing and non-graphitizing properties of organic compounds was adopted by many researchers[1-14]. Under heat-treatment a substance may undergo structural changes, physical as well as chemical changes. These changes occur due to dehydration, transition from one crystalline variety to another, destruction of crystalline lattice, oxidation, decomposition etc. In a physical change the chemical nature of the transformed material will be same as that of the starting material. In a chemical change the thermal heat-treatment may rupture the chemical bonds to form new compounds. The binding energy of the substance after a thermal change is different from that of the starting material. This difference may manifest itself as heat-energy. The change of heat is reflected in the corresponding change of temperature.

The actual temperature interval in which the mesophase develops in the carbonization of a particular compound may be a few degrees or it may be tens of degrees. This obviously causes practical difficulties in locating the exact temperature interval of mesophase formation of graphitizable organic samples. A combination of differential thermal analysis and polarized-light micrography [13-17] has proved a valuable approach to the determination of mesophase interval and temperature interval of mesophase formation. This combination is thus an effective method to study mesophase and mosaic formation, thereby characterizing graphitic carbons.

TGA has been used to locate quantitative analysis of the samples and it has been carried out to find the losses of volatile matters and to see the thermal behaviour of the sample.
Infrared spectroscopy is a potential tool for investigating the structures of the carbonized samples. Its application to organic systems has been in the areas of both quantitative and qualitative analysis.

X-ray diffraction gives the information about the spacing between the crystal planes. Miller indices, relative intensity and widths of the diffraction lines can be calculated from X-ray diffractograms.

The magnetic anisotropy of the sample in a static magnetic field is measured by a torque magnetometer which tends to align itself so as to minimize the energy. It is clear that by measuring the torque from a sample in a magnetic field we can gain information about the magnetic energy.

4.2. Working Principle of DTA & TGA.

When a sample and reference substance is heated or cooled at a constant rate under identical environment, its temperature differences are measured as a function of time or temperature (as shown by the curve in Fig. 4.1). The sample and reference cups are isolated from each other and are independent of the thermo-couples. This is why this arrangement facilitates weighing before and after heating, so that weight changes can be readily determined. Approximately, 0.1g anhydrous alumina is used in the reference cup and the sample weights varies over a range 0.05g to 0.125g, depending on their packed density. Normally, a heating rate is standardized at 10°C per minute.

The temperature of the reference substance, which is thermally inactive, rise uniformly when heated. The temperature of sample stops rising as endothermic reaction (e.g. fusion) occurs, because the heat supplied from outside is consumed by the reaction. As the reaction is over, the sample temperature is different from the
ambient, and it rises rapidly at first and then uniformly. The temperature difference $T$ is detected, amplified and recorded as a peak (Fig. 4.2).

The temperature in the sample holder is measured by a thermo-couple, the signal of which is compensated for the ambient temperature and fed to the temperature controller. The signal is compared with the program signal and the voltage impressed to the furnace is adjusted accordingly. Thus the sample and reference substances are heated or cooled at a desired rate. The temperature in the sample holder is digitally displayed on the TAS-100 and is also recorded on the recorder.

The temperature difference arises due to the phase transition or chemical reaction in the sample. Reaction attended by the absorption of heat are endothermic, while those that evolve heat are exothermic. The exothermic and the endothermic reactions are generally shown in the DTA traces as positive and negative deviations respectively from a base line. So, DTA gives a continuous thermal record of reactions occurring in a sample.

Experiments are carried out at atmospheric pressure in an inert gas environment, usually of argon, nitrogen or helium. Gases are normally entered into the furnace chamber at the lower end through a purification train in which oxygen and water are removed by heated copper wool and exhausted from the top into a condensate trap[18] for collecting the condensable volatile products.

The condensable volatile reaction products along with the unchanged starting material, if any, are thus swept by the flow of inert gas into a KBr-filled condensate trap placed in the exhaust end of the furnace. The non-condensable gases then pass through a sulphuric acid bubbler which seals the system and prevents back diffusion of air.

Normally, the DTA thermograms on carbonization are obtained by heating continuously to 750°C at which the residue is mostly carbon.
4.2.1 Historical background

The technique of Differential thermal analysis (DTA) was first proposed by Le Chatelier[19] in 1887. This method was successfully employed to investigate clays, ceramics and other minerals. The thermal reaction was invented by Roberts Austin in 1899 and is popularly known as Differential thermal analysis. The DTA technique was mainly used in the field of metallurgy until 1913. Since then DTA has become an invaluable tool in clay mineralogy. But in recent years this technique has been extensively applied to chemical problems. The study of thermal behavior of carbonizing materials by DTA was first reported at the Fourth Carbon Conference by Nakamura and Atlas[20], Smoother & Chiang[21] and Mackenzie[22]. They described elaborately the theoretical basis and applications of DTA.

The technique of Differential thermal analysis is a convenient tool of accurately recording the temperature difference between a thermocouple embedded in a sample being studied and a thermocouple in a standard inert material such as aluminium oxide while both are being heated at an uniform rate. The temperature difference arises due to the phase transformation or chemical reaction in the sample which may be endothermic or exothermic. This technique has recently attained considerable importance in determining the carbonizing and graphitizing properties of pure organic compounds, coals, pitches etc.

4.2.2 DTA Apparatus.

The basic design parameter of the DTA apparatus has been fully described by Lewis and Edstrom[23,24]. A sketch of sample holder and a block diagram of controlling, detecting, amplifying and recording systems of the DTA unit are shown.
Experimental

in Figs 4.3 and 4.4. The apparatus used in this program to detect and record these small temperature differences consists of three basic units[20].

(a) A DTA furnace and control system,
(b) An atmosphere control system and
(c) Electronic apparatus for amplifying and recording the temperature difference between the sample and the standard and for recording the actual temperature of the standard.

The apparatus of the DTA consists of a thin walled refractory specimen holder made of centered alumina with two adjacent cubical compartments of exactly the same size 1 cm in length, one for the reference material and the other for the test material, the compartments being separated by a wall of 1 mm thick. The specimen holder is placed in the cavity of the heating block, which is made from fine grained refractory cement. The block is operated in the centre of the cylindrical refractory tube of an electrical furnace which supplies heat at a uniform rate. The furnace is packed with calcined china clay. The controllable input current into the furnace is obtained from the secondary of a variable transformer. In the DTA apparatus the thermo-couple which is used within the assembly consists of two matched chromel-alumel thermo-couple which are supported in a porcelain tube held in position in a furnace combustion tube. The sample and the reference containers are both nickel cylinders with a thermocouple well extending into the centre of the cylinder from the bottom. With this arrangement, the thermo-couples are protected from the destructive action of the hydrocarbons during carbonization and so the thermocouple can be used repeatedly.
4.2.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis involves the determination of weight loss from a sample as a function of time or temperature while the sample is heated or cooled at a constant rate.

Generally, the technique of the thermogravimetric analysis is effective in quantitative analysis of the samples. When substances are gradually heated, change in weight of the samples are observed owing to the loss of water, evaporation of CO₂, hydrogen or other volatile components and the occurrence of chemical reactions. The results are directly comparable with those obtained by DTA which is inherently a dynamic method.

Dynamic weight loss curve shows the weight losses of the samples with temperature. Dynamic weight loss curves are used to determine the relative amounts in a mixture of two or more phases which undergo weight changes in different temperature ranges. It has often been assumed that points of inflexion or horizontal regions on the curve distinguish the weight losses due to the separate processes. The rate of decomposition varies with the heating rate. A higher decomposition rate occurs at a higher temperature when the sample is heated up at a faster rate. The weight losses of the samples start from the melting temperature through temperature of coalescence and continue up to about 750°C.

4.2.4 Thermogravimetric Investigations

The rate of decomposition reactions occurring in the investigated sample under the action of heat may be studied by means of a thermo-balance, an apparatus for continuously measuring the weight of a material heated at an adjustable rate. The weight loss curves thus obtained make it possible to derive the rate of loss in weight
as a function of temperature and time. These curves are known as devolatization curves.

Thermogravimetric investigations are normally carried out in two different ways, (a) The rate of loss in weight as a function of time at constant temperature, (b) The rate of loss in weight as a function of temperature at constant heating rate.

When an investigated sample is heated at constant temperature, the devolatization curve reaches a limiting value while the rate of decomposition decreases as a function of time. The shape of the curves depends on the temperature used.

When such a sample is heated at constant heating rate, the devolatization rate passes through a maximum. An increase in heating rate causes the characteristics temperatures to shift towards higher values[25,26].

4.3 Polarized-Light Technique

The use of the reflected polarized-light at normal incidence in the study of the structure of metals and alloys may be divided under the following headings, (a) examination of the structural characteristics of a homogeneous phase and (b) identification of inclusions and differentiation between various phases of a complex structure.

The polarized-light technique provides a powerful tool to determine quantitatively the optical properties of transparent, translucent and opaque materials. This technique was initially restricted to mineralogy; but in recent years, it is being widely applied in the field of metallurgy, chemistry, biology, crime detection, military intelligence, medicine, ceramic technology and various branches of industrial technology. Various aspects of this technique have been described in detail by a number of authors[27-34]. Hallimond has discussed the design and use of the polarizing microscope. Conn and Bradshaw[28] have described its
application to metals and ores. Mott and Haines[29] have discussed its application to the examination of a number of anisotropic metals. Marshall[30] and Dale[31] have discussed optics of crystals. Hartshorne and Stuart[32] have given a good description for the microscopic examination of uniaxial and biaxial crystals under polarized-light. A review of the use of polarizing microscopy in organic chemistry and biology is also given by Vickers[33].

Recent studies by several groups on the structural conditions of graphitizability have established the fact that polarized-light microscopy has been found well-suited to the studies of carbonization and graphitization because, (a) the strong optical characteristic of the graphite crystal begins with the parallel alignment of mesophase molecules and (b) the high viscosity of the mesophase permits microstructures formed in the plastic mesophase to be cooled to room temperature with little apparent disruption. Thus the polarized-light response on a section polished at room temperature can be used to identify the orientation of the intersections of mesophase layers with the plane of the section. Most microstructures are brought out with best contrast when the polarizers are crossed. Under this condition the extinction contours define the loci of layers lying either parallel or perpendicular to the plane of polarization of the incident light and the specific orientation can be distinguished for any particular region by the use of sensitive-tint plate.

4.3.1 Description of the apparatus and working principle.

Generally the polarizing microscope is an ordinary compound microscope provided with calcite polarizing prisms, usually discs of 'polaroid' above and below the stage, and some convenient means of altering the orientation of the object with reference to the plane of vibration of the light incident upon it. There is a provision
to insert the auxiliary lenses and compensators into the path of the light through the
instrument.

The polarizing microscope has undergone many modifications because of its wide
applications, but in principle all types are the same and do not differ essentially
from one another. The arrangement of the main components of a typical modern
polarizing microscope are described below:

The incident light passes through the polaroid disc, the polarizer, and thus
constrained to vibrate in one plane only. The polarizer can be rotated in its own
plane and the angle of rotation can be read against a fixed mark from divisions on
the metal ring in which it is mounted. A second polaroid disc, the analyzer, is
mounted in the body tube of the instrument. The analyzer can be rotated or
withdrawn from the field of view to enable a sample to be viewed in unpolarized-
light. When both the polarizer and analyzer are in 0°-0° position (as marked in the
scale) they are said to be in "crossed position", and they will not permit light to
reach the eye-piece so long as the medium between them is entirely isotropic. This
is because light emerging from the polarizer is completely extinguished by the
analyzer according to the principle underlying the well known Malus's experiment
in optics.

The specimen under investigation, mounted in a quick-setting acrylic resin or on a
glass slide, is placed on a circular stage. This specimen, which can be held in
position by means of a clamp attached to the stage, is capable of movement in two
directions in the plane of the stage. To permit easy return to a certain specimen
point the co-ordinate positions can be read against millimeter scales. The stage can
be rotated in its own plane and is provided with centering screws and 'click stops' at
intervals of 45°. The stage is also provided with a clamp to arrest the motion if
desired.
Above the objective lens is a slot in the body tube of the instrument through which the compensator or tint plate is inserted. The tint plate, which is a gypsum plate, is placed at an angle of 45° to the vibration planes of the polarizer and the analyzer, when they are in the crossed-position.

Also, there is a Bertrand lens in the microscope body which can be swung in or out of the field of the view. This Bertrand lens and the eye-piece act together to constitute a low-power microscope which can be focussed on the upper focal plane of the objective. The main purpose of this combination, however, is to give an enlarged image of the interference figures which are formed in this plane under certain conditions. There is an iris diaphragm above the Bertrand lens which can be used to isolate the interference figure of the crystal occupying the centre of the field of view.

The condensing lens system is situated between the rotating stage and the polarizer. Its primary function is to bring the incident light to a focus in the plane of the specimen. The eye-piece lens system, fitted to the microscope body, is of the binocular type, having a certain magnification. This together with the different objectives produces the overall magnification ranging from X25 - X1000.

The illumination of the microscope is provided by a low voltage 15 watt quartz-iodide bulb, the power supply of which is controlled from a regulating transformer. This lamp generally operates on 6 V, 15 watt a-c supply and contains a fixed condenser. The bulb is inserted in a well-ventilated housing with a circular opening for the emission of light.

The body tube of the microscope allows a camera adapter to be fitted after the analyzer. The adapter is supplied with a definite magnifying eye-piece. The camera used for photography is a 35 mm Kam ES-2.
Chapter 4

4.4 Infrared Spectroscopy (IR)

Infrared spectroscopy has become an indispensable tool for finding structural information of organic substances. Infrared spectroscopy study provides valuable information concerning the nature and variation with carbon content of the substituent groups in coal structure, as well as the nature of the aromatic systems. It is applicable to characterize both the organic and inorganic part of the coal sample. The infrared spectroscopy has been used first by Cannon and Sutherland[35] to characterize the presence of functional group in the composite samples.

Its application to organic systems has been made in the areas of both quantitative and qualitative analysis. Qualitative analysis, however, being more common tool of analysis in organic chemistry. In general, many organic chemists use this method as a routine work to examine unknown materials, both in crude and pure states for functional group and other structural information.

In the hands of the physical chemist, this method can provide more detailed information about molecular structures. For example, bond lengths, bond distances and thermodynamic properties in many cases can be determined through mathematical analysis of spectral data.

Band positions in infrared spectra are presented either as wave numbers or wave lengths. The wave number unit (cm\(^{-1}\)) is used most often since it is directly proportional to the energy of the vibration of molecules. Band intensities are expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance. \(A = \log_{10}(1/T)\). The frequency or wave length of absorption
depends on the relative masses of the atoms, the force constants of the bonds and the geometry of the atom.

4.4.1 Techniques used in IR spectroscopy

Two important techniques have been developed for the infra-red examination of the sample. One of these is the thin-section technique, which was first successfully applied by Cannon and Sutherland[35] and later by Orchin and Co-workers[36]. Another one is Nujol technique, which was used by Gordon & co-workers[37] and Cannon[38].

Potassium bromide (KBr.) pellet technique, developed by Schiedt[39] has given excellent results. The sample to be examined is ground in the presence of potassium bromide and compressed under high pressure to yield very translucent tablets. The loss through scattering is reduced by the relatively small difference between the refractive indices of the sample and the surrounding medium. The advantage of the potassium bromide technique is that, potassium bromide does not produce specific absorption bands in the region (2.5-15 μm) so that the whole of the region is accessible. Moreover, the tablets are stable.

4.4.2 Working Principle

A very simple molecule can give an extremely complex spectrum. The organic chemist take advantages of this complexity when the spectrum of an unknown compound against that of an authentic sample is investigated. A peak-by-peak correlation is an excellent evidence for identification. Although the infra-red spectrum is characteristic of the entire molecule, certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule.
Generally there are five regions of absorption which can be related to the different modes of vibration of the aromatic system. We can obtain structural information from these absorption spectra. These are (1) aromatic C=H stretching region, (2) overtone region, (3) aromatic ring (C=C) vibrations region, (4) in-plane bending region and (5) out-of-plane bending region.

4.5 X-ray Diffraction

The history of X-ray studies on carbon and graphite is closely linked with the development of theories and experiments in the field of X-ray diffraction. As a matter of fact, graphite was one of the first substances investigated by X-ray diffraction. Ewald[41] demonstrated the hexagonal symmetry of a graphite single crystal by means of a Laue photograph and concluded from a qualitative interpretation that the number of nearest neighbors should be different from that in diamond. Bragg[42] measured the first interlayer spacing. Debye and Scherrer[43,44] and Hull[45] made the first attempts to determine the crystal structure from powder diagrams. Though Debye and Scherrer found the correct structure of the graphitic layers, they gave a wrong sequence for the layer stacking. Hull found the right sequence for the layer stacking but gave a wrong structure for the layers. The correct structure of the hexagonal form was first published by Hassel and Mark[46], followed shortly by Bernal[47]. The structure of the rhombohedral form was determined later by Lipson and Stokes[48].

The main structural difference between amorphous carbon and graphite is due to their different sizes of ordered domains, and not in the arrangement of atoms within those domains. The concept of the crystallite size as the main cause of the line broadening in amorphous carbons has been predominant in most of the early work. The gradual transition from the random layer structure to the graphite lattice was
first interpreted quantitatively by Franklin[49] and in a different way by Houska and Warren[50].

Many researchers like Hofmann & Wilm[51] and Bacon[52,53] have published information on the variation of crystalline size of the interlayer spacing of graphite. Franklin[49], in her studies of both non-graphitic and graphitic carbons, concludes that the measured interlayer spacing are mean values only. She suggests that to a first approximation the groups of oriented and disoriented layers in a graphitic carbon retain the spacings of 3.354\AA{} and 3.44\AA{} respectively, which are characteristics of highly crystalline graphite and non-graphitic carbon.

4.5.1 Working Principle:
X-rays are the most direct tool for studying the structural regularities and irregularities of solids. When X-rays strike a crystalline substance, the ordered arrangement of the atoms gives rise to coherent scattering and diffraction pattern. When the angle of reflection is slightly larger or smaller, the rays reflected by neighbouring atoms will differ in phase. For more distant atoms this phase-difference may build up to such a degree as to cause the intensity of the reflected radiation to fall to zero.

The crystalline regions existing in carbon crystallites are so small that the more distant atoms needed to cause zero-intensity are absent. This explains why the diffraction pattern reveals wide diffuse bands. Moreover, carbon is only partly composed of crystalline material and the three-dimensional arrangement is not regular. As a result, the Compton scattering is relatively strong and therefore has an appreciable effect upon the X-ray pattern. It has been established that Compton dispersion produces the continuous background of X-ray pattern, which is also
dependent on the scattering angle. With crystalline substances such a background does not cause difficulties.

The average carbon black without additional heat-treatment gives an X-ray pattern of only 3 diffuse peaks, from which it is not possible to deduce a unique structure. With heat treatment the pattern sharpens sufficiently to allow a definite structure determination, and from the structure of the heat treated black it is possible to summarise the structure of the original black.

It has long been recognized that the pattern is essentially of graphite. In most of the X-ray studies of carbon black it had been assumed at the outset that the patterns could be treated as crystalline powder patterns, and indexed in terms of the graphite structure.

From a Fourier integral analysis of the scattering curve, it was found that the distribution of the neighboring atoms was exactly that of atoms in a single layer of the graphite structure. Although this result indicated strongly the existence of the single graphite layers in the carbon black structure, it was not possible to determine uniquely the relative arrangement of the layers. The question as to whether carbon black was finely divided graphite crystals, or was another form of carbon with a lower degree of order, could not be answered definitely. Heat treated carbonized samples can give more definite answer because in absence of air the diffraction pattern sharpens considerably and more peaks appear.

The structure of the graphite carbons is intermediate between the three dimensional crystalline structure of graphite and the random layer structure of the non graphitic carbons. In the graphitic carbons the graphite like layers are grouped in parallel packets within which there is a random distribution of oriented and dis-oriented layers.
Thus, there exist in the graphitizing carbons two distinct and well-defined values of the inter-layer spacing; 3.44 Å, when the structure is perfectly non-graphitic, and 3.354 Å, in true graphites. Intermediate values are observed for all partially graphitic carbons, and the spacing decreases as the degree of graphitization increases.

4.6 Torque Magnetometer for Magnetic Anisotropy Measurement

A simple form of torque can be measured by suspending the sample from a fibre with known torsion constant[54]. If the magnetic field is applied, the torque from the sample will twist the fibre and we can measure how much we have to rotate the upper point of suspension of the fibre to bring the sample back to its original position. If the turn angle lies within the range where the turn angle is directly proportional to the torque, the torque from the sample can easily be calculated. The sample is rigidly connected to a mirror and the compensation coil. The whole assembly is freely suspended in a thin fibre and the coil is located in the field from a pair of permanent magnets. A laser beam is made to shine on the mirror, the image of the light source then moves as soon as some torque acts on the sample and hence turns the mirror. A photodetector detects the movement of the reflected beam and via an amplifier generates a current through the compensation coil which inhibits the motion.

4.7 Materials Preparation

4.7.1 Choice of Samples

The following aromatic organic ring compounds having purities greater than 98% were selected for examining the graphitization process and the associated properties.
Pure carbons may be produced from any organic material by heating it to a sufficiently high temperature. If the carbonization process is nearer to 3000°C, it is closer to the structure of graphite. The problem, therefore, is to prepare a pure carbon at a relatively low temperature.

Analytical grade anthracene and phenanthrene were intimately mixed with AlCl₃ in different mole ratios such as 32:0, 32:1, 32:2, 32:3. Pyrolysis of the composite samples were then carried out by sealed tube techniques.

The samples were taken in pyrex tubes of 16.5 cm in length 1.26 cm in internal diameter and 0.15 cm in thickness and each tube in turn was placed inside a steel bomb which was fitted with screw caps at both ends. The whole arrangement was carefully placed in a solenoidal furnace and was then subjected to particular power input corresponding to the desired heat-treatment at a particular temperature and duration. A heating rate of 10°C/min. was adopted by the temperature controller.

During pyrolysis the pressure inside the sealed tube increased because of the presence of H₂ and other hydrocarbon gases which were evolved. After allowing the tube to cool to room temperature, the pyrolytic sample was then collected by opening the sealed tube inside a specially designed safety box to avoid any possible blow or blast due to high pressure inside.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Structure</th>
<th>Melting point °C</th>
<th>Boiling point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Anthracene C₁₄ H₁₀</td>
<td><img src="image" alt="Structure" /></td>
<td>216</td>
<td>340</td>
</tr>
<tr>
<td>2. Phenanthrene C₁₄ H₁₀</td>
<td><img src="image" alt="Structure" /></td>
<td>99</td>
<td>338</td>
</tr>
</tbody>
</table>
The safety box consists of a mechanical device for cutting the sealed tube inside it with a diamond edge, having no risk of explosion. The sealed tube containing the heat-treated sample was placed inside the safety box in a horizontal position with the diamond edge, a strong push was transmitted to the cutting area from below using a screw, as a result the tube was found to open very easily. The pyrolyzed sample was then separated from the inside of the tube and then dried and embedded in a cold-setting mounting resin in the manner described below:

4.7.2 Infra-red spectroscopy (IR)

The pyrolyzed samples were prepared by pressed-disc technique, which depends upon the fact that dry powdered potassium bromide or other alkali metal halides could be pressed under pressure in vacuum to form transparent discs. The sample (0.5 - 1.0mg) is intimately mixed with approximately 100-200mg of dry powdered potassium bromide. Mixing was affected by thorough grinding in a smooth agate mortar. The mixture was pressed with special dies under a pressure of 10000-15000 pounds per square inch into a transparent disc. The quality of the spectrum depends on the intimacy of mixing and the reduction of the suspended particles to 2 µm or less. Micro-disks of 0.5 - 1.0mm in diameter were thus prepared to be used with a beam condenser. The micro-disc technique permits examination of samples as small as 1 microgram. Pellets obtained from such a mixture were found to have good spectral qualities.

Special care was taken in handling salt cells and plates. Moisture-free samples were used. Finger touch with optical surfaces was avoided. Care was taken to prevent contamination with silicon, which was hard to remove and have strong absorption patterns. The prepared pellets were stored in a desiccator to protect it from moisture.
Infra-red spectra of these samples were recorded in the region 400 - 4000 cm\(^{-1}\) KBr pellet technique using IR-470 Shimadzu double beam spectrophotometer with its base line 0, transmission expansion-5 and scan time 7 minutes.

4.7.3 Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) of the samples.

Partially carbonized samples which had not passed through the carbonaceous mesophase formation due to prolonged heating were chosen for DTA and TGA. The pyrolyzed sample separated from inside the tube was dried and ground in a pestle and mortar.

The experimental details of DTA and TGA are described above. The samples were subjected to DTA and TGA using thermal analysis TAS-100 manufactured by Rigaku Corporation, Japan. The heating rate was maintained at 10°C per minute. The sample (20 mg) was heated in the inconel head to 700°C with dry alumina being employed as the inert material in the reference cell. As the DTA traces of the composite samples gave initial endothermic peaks associated with the melting of the specimen, the heat of fusion for the samples were computed from the area covered by the peaks\(^{[55,56]}\). Taking the heat energy values for benzoic acid as a standard the energy values for all the samples were calculated.

The TGA has been used for quantitative analysis of the samples and it has been carried out to find the losses of volatile matters and to see the thermal behaviour of the sample.
4.7.4 Heat of fusion

The heat of fusion is calculated from the 1st endothermic peak area of the DTA curve.

The area enclosed by the peak has to be accurately determined for quantitative work. Norton[57] was perhaps the first to attempt a quantitative DTA of high alumina clays. In his method two tangents were drawn on both sides of the peak and a straight line AB joined the points of tendency. The area enclosed by ABC formed the peak-area. In the method of Speil et al.[58], the line AB was obtained by joining two points where the curve starts and ends.

The delineation of the peak area for a curve showing a considerable base line shift is described by Berg[59]. In this method the extra-polated line from BE meets the vertical line drawn from the peak D. The space enclosed by ADBC is the peak area (Fig. 4.5c). The other methods of delineating peak area of the curves that don't return to the base line are illustrated in the Figs 4.5(d,e,f). Dean[60], has suggested the determination of peak area by determining the cosecant of the peak angle of Fig. 4.5g. The peak area is obtained with a planimeter and also by weighing the cutout area of the curve drawn on transparent paper.

4.7.5 X-ray Analysis

The samples were analyzed by X-ray diffractometer (Model No JDX-8P JEOL CO. Ltd., Tokyo, Japan). The pyrolyzed sample was crushed into fine powder by using pestle and mortar. The sample on a glass slide was then placed into the diffractometer (Model Nu JDX-8P). Different diffraction graphs were obtained by using an automatic recorder. From the positions of the symmetrical diffraction peaks the interlayer spacing "d" was calculated using Bragg's equation. And then using the following formula Miller indices were calculated.
where, \( a = b = 2.456 \) and \( c = 10.044 \)

4.7.6 Micrographic preparation of samples for polarized-light technique

Mesophase samples for observation by reflected polarized-light microscopy were obtained by heating the original composite sample (1.0g) individually in sealed tube inside the solenoidal furnace as before to the desired temperature in which investigation was necessary.

A brass tube of 4.5cm in length and 3.3cm O.D. X 10 SWG with one end accurately machined to a flat finish was taken. A piece of metal plate was also taken and its surface was smeared lightly with vaseline. The inside wall of the tube was also coated with vaseline prevent adhesion to the mount. The heat-treated sample was then placed on the plate facing downwards and the tube was placed over the sample. The plastic powder (kwick liquid No 20-3566) was then poured on the tube and it was saturated with the liquid methyl methacrylate (kwick liquid No 20-3568). The slurry was kept gently stirred at the beginning to prevent air bubbles adhering to the sample. After 10-15 minutes, the mould was lifted off the plate and the mount was tapped through with a rod and hammer.

The mounted samples were then ground on progressively finer grades of water proof silicon carbide papers, using tap water as lubricant and progressing from 120 to 600 grit to expose the carbonized residue in the way described as follows: The silicon carbide paper in the form of a disc was fixed on the top of a rotator and the sample was allowed to be rubbed by the silicon paper when the disc was kept on rotation. Light but steady pressure was applied on the sample while it was rubbed by the carbide paper, maintaining the same direction of grinding on each paper.
During each stage, the direction of polish was maintained constant except for reversals made at regular intervals by lifting and rotating the sample by 180° accordingly the sample could not move about the wheel but could only move laterally between the centre and the periphery. The sample was washed with tap water before using with another comparatively finer grade of carbide paper.

The best results were found by using fresh paper for each sample and by grinding further than what was necessary at each grit level to remove the scratches from the preceding paper. After the final grinding on 600-grit paper, the surface of the sample appeared bright independent of the level of heat-treatment.

Subsequent polishing was done with Hyprez-diamond lapping compounds (3μ size followed by 0.03μ size) on a wet polishing Texnet cloth supplied by Buehler Limited, U.S.A. in the way described as follows:

The coarse grade Hyprez-diamond compound of micron size was spread over the polishing Texnet cloth fixed on one of the rotating disc of the Shimadzu polisher and the sample was kept on rubbing for about five minutes and then washed thoroughly with tap water. Then the finer grade Hyprez-diamond compound of micron size was spread over another polishing Texnet cloth fixed on the other rotating disc of the polisher and the sample was again kept on rubbing for five minutes.

Final polishing of the sample was carried out by the high parity Linde Alpha Alumina powder. The powder was first wetted with distil water and the sample was rubbed gently by hand in the same direction for about ten minutes. The final polishing time varies with the nature of the sample. When the final polishing was completed it resulted in a highly polished surface having a bright lustre, the characteristic of carbonaceous mesophase which proved suitable for observation by polarized-light microscopy.
4.7.7 Polarized-light microscopy

Samples prepared in the above manner were observed and photographed with a Reichert 'METABELT' polarizing microscope using reflected polarized-light. Colour photographs of the mesophase spheres and of subsequent heat treated samples were obtained using Fuji colour films super Asa dito 100-21. The coloured mesophase spheres were produced by the insertion of a gypsum plate inclined to the analyzer at an angle of $45^\circ$ itself and the sample under observation. The analyzer and the polarizer remained cross with respect to each other. This is the so-called the Sensitive Tint Technique[3,27]. The light source of the microscope was a 6V, 15W low-voltage halogen bulb. An exposure time of 5 minutes per photograph was used. A suitable area of each specimen was photographed so that at least some clear mesophase could be counted.

4.7.8 Magnetic Anisotropy

The sample was mounted at the end of a Quartz rod which is nonmagnetic, tough and has low thermal conductivity. The upper end of the Quartz rod was attached to a brass rod to which the mirror and the compensation coil were fixed. The whole assemble was suspended by a Quartz fibre. The Quartz was chosen for its large tensile strength and small torsion constant. The elasticity in the longitudinal direction was very low, which prevented low frequency oscillations along the axis of suspension. A torque magnetometer with proportional integrating differentiating compensation and having sensitivity of the order of $10^{-6}$Nm has been used.
Fig. 4.1 Heating Curve of Simple and Reference Substance

Fig. 4.2 DTA Curve
Fig 4.3 DTA thermocouple assembly

Furnace atmosphere control

Fig 4.4 Block diagram of a differential thermal analysis equipment (S) sample thermocouple (R) reference thermocouple (M) monitor thermocouple
Chapter 4

Fig 4.5 Method of delineation of peak area

h. The peak area of benzolic acid

Fig 4.6 Methods of delineation of peak area
Reference


42. Bragg, W.H., measurement carried out in 1914 and quoted in X-ray and crystal structure (Bragg, W.H. and Bragg, W.L. edes), Bell & Sons London 3rd ed. 1918, 174.


Chapter-4

Experimental


60. Dean, L.A., Soc., 1947, 63, 95
Chapter - 5

Results and Discussion
5.1 Introductory aspects

IR spectra have been used as a potential tool for investigating the structures of the carbonized samples and also to locate important properties like stretching and bending of bonds. DTA has been employed to examine the temperature region of the mesophase formation. The heat of fusion has been calculated from the 1st endothermic peak area for each DTA curve. TGA has been used for quantitative analysis of the sample. Interlayer spacing, Miller indices, relative intensity and widths of the diffraction lines have been calculated from X-ray diffractograms. In the present study the mesophase formation has been examined and polarized-light photomicrographs of the various samples during mesophase formation have been taken in order to study the nucleation, growth and coalescence processes of the mesophase spherules at different heat-treatment temperatures. Magnetic anisotropic is looked for in all the samples using a sensitive torque magnetometer.

5.2 Intra-red Spectroscopy

IR band commences at frequency 3040 cm$^{-1}$ indicating the presence of an aromatic C-H stretching vibration or C-H bond. In actual practice, C-H stretching vibrations associated with methyl and methylene groups are generally observed in the region between 2960-2850 cm$^{-1}$ and IR band commences to appear at 2900-2920 cm$^{-1}$, indicating the presence of an aliphatic C-H stretching vibration. Weak bands between 1787 and 1950 cm$^{-1}$ are usually assigned to over tones and combination tones which disappear rather rapidly as reaction proceeds. Bands in the 1286-1623 cm$^{-1}$ region are caused by aromatic ring stretching vibrations. Their shift and broadening upon carbonization is evident from the progressive broadening of the peaks. This is interpreted to be a result of the presence of quinoid structure (Figs. 5.1 & 5.2). The band at 906 cm$^{-1}$ shows a steady decrease in its intensity as
pressure is increased and finally disappeared completely. This is due to the loss of aromatic character, which is shown to be very poor.

The distinct IR bands between 722 and 882 cm\(^{-1}\) remain even after carbonization at the highest pressures. They are both characteristic of the IR spectra of anthracene and phenanthrene and their polymeric products. The analysis of the IR spectra obtained in this investigation suggests that reaction proceeds through the 9,10 positions of anthracene and phenanthrene in the graphs of Figs. 5.1 & 5.2 with the formation of quinoid structures[1].

The stronger peaks indicate C-H out of plane bending at 995 and 883 cm\(^{-1}\). Skeletal deformation at 490, 465 & 420 cm\(^{-1}\) are sharply reduced. Background intensities are increased markedly due to strong absorption throughout the range of wave numbers.

### Summary of the characteristic absorption due to anthracene and phenanthrene and their products.

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>3040-3010</td>
<td>Aromatic C-H Stretching</td>
</tr>
<tr>
<td>2915-2850</td>
<td>Aliphatic C-H Stretching</td>
</tr>
<tr>
<td>2360-2350</td>
<td>The weak C=C C Stretching</td>
</tr>
<tr>
<td>1610-1590</td>
<td>C=C Stretching (ring stretch)</td>
</tr>
<tr>
<td>1250-1485</td>
<td>C-H bending medium</td>
</tr>
<tr>
<td>1035-1195</td>
<td>In plane C-H bend (IR active)</td>
</tr>
<tr>
<td>995-935</td>
<td>C-H rocking, strong characteristic</td>
</tr>
<tr>
<td>880-898</td>
<td>C-H rocking, Strong characteristic</td>
</tr>
<tr>
<td>870-815</td>
<td>C-H deformation</td>
</tr>
<tr>
<td>900-675</td>
<td>Out of plane ring bending</td>
</tr>
<tr>
<td>615</td>
<td>==C-H bend fundamental</td>
</tr>
<tr>
<td>471-420</td>
<td>Out of plane ring C=C bend( or wagging)</td>
</tr>
</tbody>
</table>
Chapter 5

Results and Discussion

5.3. Differential Thermal Analysis

The DTA traces of partially carbonized anthracene and phenanthrene with the mixture of AlCl₃ in different mole ratios are presented in Figs 5.3 & 5.4. For the DTA traces of the samples, a common characteristic is the presence of initial large endotherm due to melting of the tarry substance. The 2nd large endotherm shows the boiling point of the substance (Table-5.1) and these two endotherms are followed by small fluctuations in the trace before a smooth trace returns. The temperature at which all the fluctuations terminate just before the smooth trace starts is the temperature of complete coalescence in the case of carbonaceous mesophase. This process may then repeat itself till the sample is decomposed to produce a mosaic having complete coalescence of the mesophase.

The DTA traces show that the initial large endotherm gradually increases in size with the addition of AlCl₃. This increase of the initial large endotherm indicates an increase in the heat of fusion which indicates the consequent increase of activation energy[2] and hence the graphitizing power. The calculated values of heat of fusion of composite samples (Table-5.2) from the 1st endothermic peak area of each DTA trace are graphically shown in Fig 5.5.

The function of AlCl₃ is to cause the chain-stripping and associated reactions allowing planar distribution of the aromatic rings which is an essential prerequisite for the formation of graphite.
5.4 Thermogravimetric Analysis

The TGA traces of the same samples are presented in Figs. 5.6 & 5.7. The weight losses of the samples start from around 373 K and substantially continued up to the coalescence temperature due to the elimination of hydrogen and other hydrocarbon gases. The TGA results show that the carbon yield is increased with the addition of AlCl₃ which is supported by Blayden's assumption[3].

5.5 X-ray

In the graphite-like carbon the extent of ordering that is associated with increasing order of graphitization can be estimated from X-ray diffraction patterns. Whatever the degree of graphitization diffuse bands can be identified which have angular positions that correspond roughly to the respective diffractive lines of the graphite (001, 002, etc.) Figs. 5.8 & 5.9.

Interference effects arise between X-rays scattered by different parts of the electron cloud surrounding the nucleus in the individual atoms. This interference is responsible for the decline in the scattering power of an atom with increasing scattering angle and is indicated by the scattering factor. When the atoms form a 3-dimensional periodic array the material forms a crystal and the interference effect produced by the atoms can be analysed in terms of the scattering from the crystal formed. The sequential development of the interference effects brought about by increasing the order in the atomic arrays is of importance. The consequence of short range order in otherwise random atomic arrays is that incoherent scattering of X-rays produce diffraction cones called "diffraction halos".
When the short range order is sufficiently extensive for the ordered groups to form recognizable crystallite which, however, are randomly arrayed with respect to each other, the rings sharpen into forms which are characteristics of diffraction by polycrystalline aggregates.

Due to the form-factor the scattering curves deviate successively from the scattering factor for a point atom as we go further away from the inner core of the atom. The outermost, the more weakly bound electrons, make an appreciable contribution to the total scattering only at small angles. The valence electrons are not usually distributed in a spherically symmetrical manner, but are probably localized along bonding directions between atoms. Because of the relatively small contributions that these outer electrons make to the scattering factors of heavy atoms, such deviations from spherical symmetry are normally negligible in X-ray diffraction. On the other hand, in organic molecules containing light elements like carbons, the valence electrons contribute a major fraction of the total scattering. The effect of directional bonding on scattering factors is, therefore, important and may become measurable.

An experimental approach has been made to investigate the effect of the catalyst on bonding by comparing the scattering intensity against inverse of d which is representative of the form-factor and can reflect on the contributions of valence electrons to scattering and hence the process of crystallization (Figs. 5.10 & 5.11).

The intermediate stage, between disordered state of non-graphitic carbon and the ordered state of graphite, can be thought of as small layers of graphite-like structures which are stacked in parallel groups but not mutually oriented. From the
shape of the diffused bands that correspond to the spectral lines of indices (hkl) of ordered graphite we can estimate the extent of ordering [4].

In an attempt to produce an alternating structure, the variation of the apparent interlayer spacing with the degree of graphitization and its constancy in both the non-graphitic carbons and in graphite is considered. This is done by taking into account the different shapes of (001), (002), (003) and (004) lines and the apparent interlayer spacings.

The effect of catalytic agent (AlCl₃) on the graphitizing tendency is investigated from the shape of the bands[5,6]. It is observed that with increasing amount of AlCl₃ the sharpness of the diffraction lines (hkl) increases. The area under the peaks represent the number of atoms contributing to the scattering of X-rays and the widths of the peaks represent the radii of the spheres within which the atoms are distributed.

Since the widths of different peaks are different, the estimation of the width of a peak is made by taking the ratio of the area under the peak by the corresponding height. Data of crystallographic parameters of composite samples from anthracene and phenanthrene are shown in Table 5.3 and Table 5.4 respectively.

The (hkl) lines become sharper as the degree of graphitization increases which is associated with the increase in the number of oriented layers. Sharpening of the bands corresponds to the reduction of the radii of the spheres within which the atoms are distributed. The diffraction data, therefore, indicates a trend towards graphitization with increasing amount of the catalytic agent which is in agreement with the observations made using IR spectroscopy[1], DTA and TGA[7].
5.6. Polarized-Light Photomicrographs

The development of the carbonaceous mesophase for anthracene and its composites under study is illustrated in plates 5.1 to 5.4; and that of phenanthrene and its composites is illustrated in plates 5.5 to 5.8 respectively.

In the case of mesophase formation in anthracene, spherules just start to appear at 460°C (Plate 5.1). Plates 5.2 and 5.3 show further growth of mesophase in anthracene with AlCl₃ for the ratios of 32:1 and 32:2 respectively at the same temperature. Finally, temperature being kept constant complete coalescence is found to take place forming a mosaic pattern for the mole ratio of 32:3 (Plate 5.4).

In case of phenanthrene typical mesophase spherules are present at 530°C (Plate 5.5). With the addition of AlCl₃ they start to coalesce, forming larger spherules. Plate 5.6 shows the picture of such a coalescence at the same temperature with the mole ratio of 32:1. For higher mole ratio of 32:2, the growing mesophase spherules coalescence to form relatively complex bulk mesophase at the same temperature (Plate 5.7). Plate 5.8 shows that complete coalescence giving rise to a mosaic texture takes place at 530°C in the case of phenanthrene with AlCl₃ in the mole ratio of 32:3.

Mesophase intervals are found to be shortened with the addition of AlCl₃. This clearly indicates that the degree of graphitization is increased with addition of AlCl₃.

The photomicrographs of mesophase of both the samples indicate that the mesophase interval is shortened with the gradual increase of the catalyst. From literature it was seen that the mesophase interval was formed during the temperature interval of 460°C to 531°C for anthracene and for phenanthrene the
corresponding temperature interval was 530°C to 550°C[8]. But in the present investigation the mesophase formation and its growth is found to be at 460°C for anthracene and its composites and for phenanthrene and its composites it is at 530°C. Here the mesophase intervals are found to be completely diminished with the addition of AlCl₃ in different mole ratios.

The crystalline structure of the carbon is found to be influenced by the heating rate during carbonization. An increase in the heating rate leads to a marked deterioration of the pre-order since sufficient time is not available to the atoms to occupy the minimum energy positions. The slow heating rate must be maintained in the range of mesophase formation. Carbonization in a sealed tube generally produce a higher carbon yield compared with carbonization in an open crucible. On the other hand, a gas pressure during pyrolysis causes a poor microstructure in the residue. High gas pressures of evaporated hydrocarbons lead to high carbon yield and to hard carbons. Carbonization in a sealed tube provides the condition for a combined liquid and gas phase pyrolysis.

5.7. Magnetic Anisotropy

Although magnetic anisotropy is a prominent property for ferromagnetic materials with crystalline anisotropy, diamagnetic materials can also show magnetic anisotropy due to asymmetric nature of the orbitals of the covalent electrons.

For an ideal torque measurement one has to prepare a disc containing the hexagonal c-axis and one of the axes of the ab-plane. However, most of the specimens prepared were not thick enough for the preparation of the ideal disc needed for torque measurement. However, some of the specimens were moderately
thick to contain a component of the c-axis, when slanting planes were cut from the specimens.

Most of the specimens thus prepared showed practically no magnetic anisotropy except the one noted as 32:3 (A). This specimen showed a very clear two-fold magnetic anisotropy (Fig. 5.12). Although this specimen was not an ideal one, it contained a component of the c-axis and a direction of ab-plane of the hexagonally grown graphite. Since the specimens were not ideal and anisotropy could not be found in the specimens other than the one with 32:3(A), we have not quantified the results at the present stage and only a qualitative explanation is provided.

The magnetic anisotropy in this case occurs because the orbital motion of the electrons and the associated angular momenta tend to orient themselves in such a way as to make the electron loops approach the positive ions. A crystalline material or an amorphous material with a preferred orientation of the bonds will thus show anisotropic angular momenta and the associated magnetic moments will also be anisotropic. In a magnetic field such a diamagnetic specimen will experience a magnetic torque energy which is given by \( \tau = \frac{\delta E_k}{\delta \theta} \)

where \( E_k \) indicates the anisotropy energy.
### Table: 5.1

Thermal characteristics of the carbonized composite samples by differential thermal analysis.

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<th>Compound</th>
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<th>m.p(°C) Differential thermal analysis</th>
<th>b.p(°C) International critical tables</th>
<th>b.p(°C) Differential thermal analysis</th>
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Table-5.3

Different crystallographic parameters of composite samples from Anthracene.

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Different crystallographic parameters of composite samples from phenanthrene.

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Chapter 5

Results and Discussion

Fig. 5.1 INFRARED ABSORPTION SPECTRUM OF CARBON PRODUCT FROM ANTHRACENE AND ANTHRACENE WITH DIFFERENT AMOUNT OF CATALYST.
Fig. 5-2: Infrared absorption spectrum of carbon product from phenanthrene and phenanthrene with different amount of catalyst.
Fig. 5.3 DTA traces of Anthracene with AlCl₃ in different mole ratios
Fig. 5.4 DTA traces of Phenanthrene with AlCl₃ in different mole ratios
Chapter 5

Results and Discussion

Fig. 5.5 Variation of Heat of Fusion with Different Mole Ratios of AlCl₃
Figure 5.6: TGA traces of Anthracene with AlCl₃ in different mole ratios.
Fig. 5.7 TGA traces of Phenanthrene with AlCl₃ in different mole ratios.
Fig. 5-8 INTENSITY PATTERNS OF XRD OF CARBONISED COMPOSITE SAMPLES COMPRISING OF ANTHRACENE AND \( \text{AlCl}_3 \) IN DIFFERENT PROPORTIONS
Fig.5-9. Intensity patterns of XRD of carbonised composite samples comprising of phenanthrene and \( \text{AlCl}_3 \) in different proportions.
Fig. 10a. Scattering factor
A=32:0

Fig. 10b. Scattering factor
A=32:1
Fig 10c. Scattering factor
A = 32.2

Fig 10d. Scattering factor
A = 32.3
Chapter 5

Fig. 10a. Scattering factor
A = 32:4

Fig. 10b. Scattering factor
A = 32:5

123
Chapter 5

Results and Discussion

Fig. 11a. Scattering factor
P = 32:0

Fig. 11b. Scattering factor
P = 32:1
Fig. 11c. Scattering factor
$P=32:2$

Fig. 11d. Scattering factor
$P=32:3$
Chapter 5

Results and Discussion

Fig. 11a, Scattering factor
P = 32.4

Fig. 11b, Scattering factor
F = 32:5
Plate 5.1  Mesophase spherules in anthracene heat treated to 460°C for 4 hrs

Plate 5.2  Mesophase development in anthracene with AlCl₃ in mole ratio of 32:1 heat treated to 460°C for 4 hrs.
Plate 5.3 Mesophase development in anthracene with AlCl$_3$ in mole ratio of 32:2 heat treated to 460°C for 4 hrs.

Plate 5.4 Mosaic formation in anthracene with AlCl$_3$ in mole ratio of 32:3 heat treated to 460°C for 4 hrs.
Plate 5.5  Mesophase spherules in phenanthrene heat treated to 530°C for 5 hrs.

Plate 5.6  Mesophase development in phenanthrene with AlCl₃ in mole ratio of 32:1 heat treated to 530°C for 5 hrs.
Plate 5.7 Mesophase development in phenanthrene with AlCl₃ in mole ratio of 32:2 heat treated to 530°C for 5 hrs.

Plate 5.8 Mosaic formation in phenanthrene with AlCl₃ in mole ratio of 32:3 heat treated to 530°C for 5 hrs.
Chapter 5

Results and Discussion

Fig. 5.12. Angular Variation of Torque for Different Magnetic Fields.
Chapter-5

Results and Discussion

Reference:


Chapter - 6

Conclusion
Conclusions

The objective of this research was to study the improvement of precursor states for graphitization of simple aromatic organic compounds such as anthracene and phenanthrene under the influence of a catalyst like AlCl₃.

For this purpose, different techniques such as DTA, TGA, IR, XRD, Polarised-light micrography and Torque magnetometer with PHI compensation were adopted.

The catalyst remains as it is in the system at the end of the carbonisation process. This may be due to some kind of strong interaction between the AlCl₃ and the high molecular weight aromatic hydrocarbons of the reaction mixture. The different DTA and TGA behaviour of both systems at higher temperatures, clearly indicates that chemical changes are brought about by the catalyst.

The DTA traces obtained for the composite samples under study (Figs. 5.3 & 5.4) clearly indicate that endothermal processes of decompositions in the initial portions of curves become wider with increasing the catalyst in all the samples.

The DTA traces of anthracene and phenanthrene (Figs. 5.3 & 5.4) have relatively wider initial endothermic peaks with increasing amount of AlCl₃. Widening of the initial endotherm means that the heat of fusion and so the activation energy gradually increase with increasing amount of AlCl₃ (Fig. 5.5). This indicates that carbons obtained from the pure aromatic samples in presence of AlCl₃ have relatively more graphitizing power.

As the amount of AlCl₃ added to the sample is gradually increased the mesophase interval becomes significantly shorter which indicates the increasing degree of graphitization. This is entirely a new phenomenon which appears to arise because of bubble formation occurring in the samples at the temperature of the formation of mesophase spherules.
The TGA traces (Figs. 5.6 & 5.7) obtained for the samples predict the increase in yield of carbon with the increase of AlCl₃. The greater the yield of carbon, the greater is the degree of graphitization.

In IR-spectra, the aromatization is increased with the increase of catalyst which is also the indication of the increase of degree of graphitization.

From X-ray study, we can see that the interlayer spacing decreases with the increase of catalyst showing another indication of increasing degree of graphitization.

While the interlayer spacing is constant at 3.44 Å in the non-graphitic carbons and at 3.354 Å in graphite, the apparent interlayer spacing in the graphitic carbons decreases with the progress of carbonization and graphitization. This apparent interlayer spacing is in reality a mean value. In all graphitic carbons, whatever be the degree of graphitization, the small groups of orientated and disorienated layers within the parallel layer packets retain the structural characteristic of crystalline graphite and of the non-graphitic carbons respectively. Among the orientated layers the interlayer spacing is constant and is always equal to that in graphite which is 3.354 Å.

The structure of the graphitic carbons is the simplest which is found to be consistent with all the experimental results. We can see that the interlayer spacing decreases with the increasing amount of the catalyst. This indicates an increase in magnitude of graphitizability. Measurements of the width of different diffraction lines show that there is a mixture of at least two interlayer spacing in the graphitic carbons. We are, therefore, led to the conclusion that the graphitic carbons contain a mixture of oriented and disoriented layers, the spacing of the latter being greater than that of the former.
Polarised-light photomicrographs (plates 5.1 to 5.8) obtained for the composite samples at different mole ratios indicate that the compounds pass through the carbonaceous mesophase transformation fulfilling the general features of mesophase and hence, they are all graphitizable. Photomicrographs of mesophase of both the samples indicate that the mesophase intervals are found to be shortened for higher percentage of the catalyst with the parent samples. This means that the degree of graphitization increases as the amount of the catalyst added is increased.

The result of the heat of fusion carried out on the composite samples shown graphically in Fig 5.5 also support the nucleation and growth of the spherules at different heat-treatment temperature at different ratios.

Interlayer spacing results indicate that carbons produced from mixtures of anthracene and phenanthrene are highly graphitizable.

The interesting result of two-fold anisotropy for the sample prepared with 32:3 ratio of anthracene and the catalyst is related to the observed optical anisotropy because both the phenomena originate from the nonspherical distributions of the electron clouds. The absence of such anisotropy in other specimens is not very clear, although, as a possible reason, we may attribute it to the absence of the hexagonal axis in these specimens. Further study in this field is, therefore, needed.