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THE FORMATION OF GRAPHITIZABLE CARBONS VIA MESOPHASE: CHEMICAL AND KINETIC CONSIDERATIONS

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I. INTRODUCTION

In general terms carbonaceous substances are either isotropic (non-graphitizing) or anisotropic (graphitizing). Polycrystalline manu-factured graphites, of major industrial importance, are based upon graphitizing coke from petroleum pitch (grist) and coal-tar pitch (binder). The crystallographic order established in the cokes capable of graphitization originates in the formation from the pitch of a liquid crystal system called mesophase. The objective of this article is to discuss aspects of the chemical kinetics of the for-mation of mesophase.

II. OPTICAL TEXTURE

The isotropic carbons are thought to possess only small-scale crys-tallographic order, i.e., the parallelism of associated (grouped or stacked) constituent lamellar molecules extends over short distances (about 1-5 nm). Conversely, for the anisotropic carbons, these possess a long-range crystallographic order, i.e., the parallelism of associated constituent lamellar molecules extends over much longer distances (as much as 500 μm). It is to be noted that in these anisotropic carbons of heat treatment temperature (HTT) < 1700 K, the stacking of the constituent molecules is only approx-imately parallel.

     The terms *isotropic* and *anisotropic* are convenient to use in this context because of the extensive application of the polarized light optical microscope in studies of the formation of mesophase to establish carbon structure or optical texture. This approach usually requires the carbon specimen to be mounted in a suitable thermosetting resin and a polished surface to be prepared. The polishing must be of a high quality and free from scratch marks.

     A convenient microscopic technique is to use parallel polars in the light beam in conjunction with a half-wave retarder plate inserted between the surface of the carbon specimen and the analyzer. In this way, via dispersion effects, interference colors are created,

usually yellows, blues, and purples, which characterize the aniso-
tropic carbon in terms of size of colored (isochromatic) areas, the
orientation of the stacked constituent lamellae relative to the plane
of the polarized light and the actual color. This characterization
is of the *optical texture* (Figures 1 and 2). The isotropic carbons
when examined in this way only exhibit a purple color which is inde-
pendent of the angle of rotation of the specimen stage. The purple
color is of a lighter shade than seen with the anisotropic carbons.
When the anisotropic carbons are studied in the optical microscope,
then on rotation of the specimen stage or inversion of the half-
wave plate, the yellow areas become blue, and the blue areas become
yellow. The purple areas remain unchanged.

These differences in optical activity between the isotropic
and anisotropic carbons are due, basically, to the differences in
the range of crystallographic order explained above. With the iso-
tropic carbons, the range of order of 1–5 nm is much smaller than
the resolution of the optical microscope, or wavelength of light
used, i.e., about 500 nm. Although the structure can be said to be
anisotropic on the size scale of 1–5 nm, it is essentially isotropic
to the light beam. However, with the anisotropic carbons the range
of crystallographic order extends from 0.5 μm (500 nm) to about
500 μm, and to the light beam the material has bulk anisotropy, i.e.,
it exhibits significant differences in optical properties (absorption)
and refraction in two structural dimensions parallel and perpen-
dicular to the parallelism of the constituent lamellar molecules.

With few exceptions, e.g., the carbonization of saccharose,
isotropic carbons are formed from parent materials which do not fuse
on carbonization. Common examples are carbons, made from coconut,
wood, thermosetting resins, or highly cross-linked polymers and low-
rank coal substances. Isotropic carbons of high surface area can
be made from polyvinylidene chloride which may fuse depending upon
rates of carbonization (but the fluidity is not as described below).
These isotropic carbons adopt the overall morphology of the parent
materials and possess a molecular structure (i.e., a structure based
upon lamellar graphite-like (not graphitic) molecules bonded

Fig. 1. Optical micrograph of polished surface of a carbon, from
Ashland A200 petroleum pitch, HTT 800 K, using polarized light
showing domains in the optical texture.
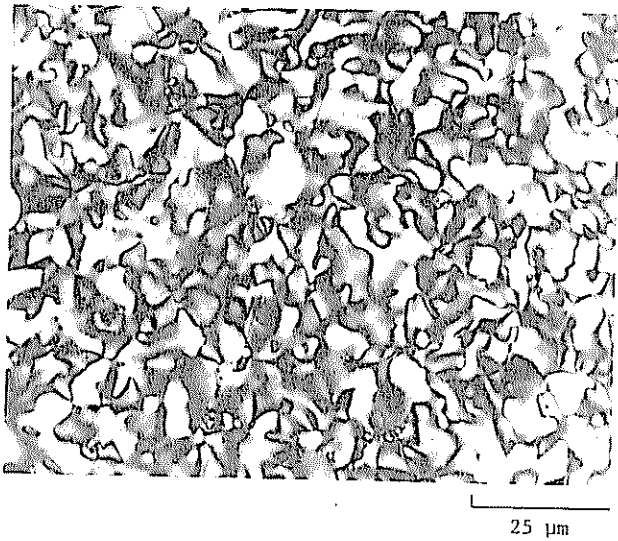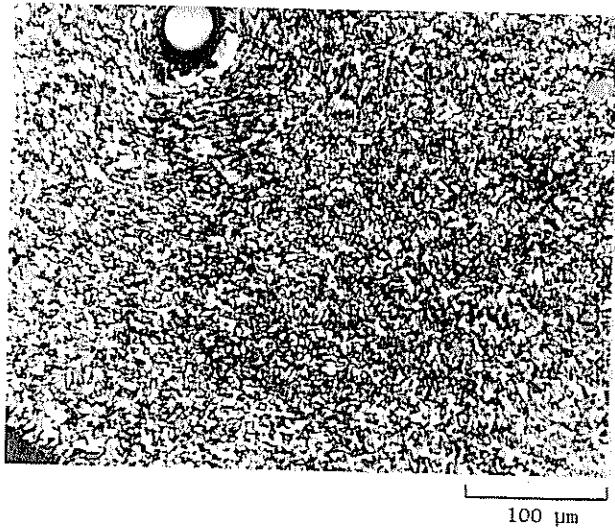
100 μm

25 μm

Fig. 2. Optical micrograph of polished surface of a carbon, from
Gilsonite pitch, HTT 800 K, using polarized light showing mosaics
in the optical texture.

together to give essentially a disordered polymeric system) based
upon that of the parent polymeric structure, e.g., the cellulose or
lignin system.

On the other hand, the anisotropic carbons are almost totally
formed during the pyrolysis and carbonization of parent materials
which do pass through a fluid phase. Common examples are coal-tar
pitch, petroleum pitch, solvent-refined coals, polyvinyl chloride,
and aromatic compounds. It is found that the coke or carbon formed
during the carbonization of these materials is anisotropic in optical
texture and must therefore possess a relatively high degree of crys-
tallographic order at the moment of its formation. This is self-
evident in view of the graphitizability of these carbons, this proc-
ess of graphitization involving the perfection of an already existing
crystallographic order rather than a subsequent major reordering on
recrystallization.

Such anisotropic carbons are seen to grow from the isotropic
melt of pitch or coal, and it is intriguing to know the exact
mechanism of this growth process. Can the growth of this anisotropic
carbon be considered as a form of crystallization or perhaps a pre-
cipitation? *It is the examination of the mechanism of the growth
process which constitutes the objective of this chapter.*

III. MESOPHASE

A.   Lamellar Nematic Liquid Crystals

There already exist several review articles describing in some detail
how the anisotropic carbon originates from the isotropic melt of
pitch. Brooks and Taylor [1] initially advanced the proposal that
from within the isotropic melt of pitch there grows a new phase,
more viscous than the parent pitch, but of anisotropic texture, and
yet able to flow. Brooks and Taylor's proposal was that this new
phase was a *nematic liquid crystal* for which class of substance there
now exists a comprehensive literature [2-4]. Nematic liquid crystals
are distinguished from other forms of liquid crystal systems in that

the lamellar constituent molecules of pitch precursors or the rodlike
molecules of conventional liquid crystals are stacked approximately
parallel to each other, other types of order being absent. Liquid
crystal systems have been known for about 100 years, and to distin-
guish them here from the more unusual systems based on lamellar
(planar) aromatic molecules, they are referred to as *conventional
liquid crystals*. Further, in order to understand more thoroughly
the flow properties and structural behavior of this new phase a
direct comparison with liquid crystal behavior can be made. How-
ever, it must be appreciated that with increasing HTT of the iso-
tropic melt this newly formed phase will cease to have flow properties
and will assume the rigidity of semicoke. Thus, the model which
emerges from these considerations is, initially, the formation of a
lamellar nematic liquid crystal phase, with flow properties, and
that, secondly, this becomes progressively more viscous with increas-
ing HTT and/or isothermal duration of the experiment until a "solid"
semicoke results. The increase in viscosity is thought to be due to
a process of polymerization of the constituent molecules of the
liquid crystal phase between molecules essentially in one layer and
possibly of molecules in different layers (cross-linkage).

From the viewpoint of discussing this model process it is con-
enient to consider the beginnings of the creation of the anisotropic
plastic phase as being the formation of lamellar nematic liquid
crystals. Once this structure is established then the polymeriza-
tion processes which created the molecules now forming the liquid
crystals will continue within the liquid crystal. This polymerized
lamellar nematic liquid crystal is termed *mesophase* (i.e., the phase
intermediate between the isotropic liquid pitch and the solid semi-
coke). In discussions of the origins of the mesophase it is not
usual to distinguish the initial lamellar nematic liquid crystal
system from its partly polymerized derivative, i.e., mesophase.

When the polished surfaces of graphitizing carbons are examined
in the optical microscope using the half-wave plate as described
above, one can see colored areas of different size and shape. Some
carbons, e.g., from A200 Ashland petroleum pitch, possess larger

colored areas, about 100 µm in dimension (called domains) or flow-
type anisotropy, when the isochromatic areas are elongated and narrow
(e.g., 150 µm by 20 µm; Figure 1). Other carbons, e.g., from
Gilsonite pitch, possess smaller anisotropic areas about 5 µm in size
(often isometric) and called larger mosaics (Figure 2). Some cokes,
e.g., from coking coals, possess very small anisotropic units about
0.2 µm in size (fine mosaics). The shape and size of these iso-
chromatic growth units are functions primarily of the chemical prop-
erties of the parent pitch substance and its previous shear history
established by the conditions of carbonization, e.g., turbulent flow
of the pitch in a vertical tube furnace during rapid carbonization
or quiescent conditions of slow carbonizations in a horizontal tube
furnace. The flow pattern of mesophase and the way in which the
basic lamellar structure of mesophase establish the defect structures
of graphite (disclinations) are described by White et al. [5,6].
The relevance of considerations of mesophase including the chemical
mechanism associated with variations of optical texture is reviewed
by Marsh and co-workers [7-9].

B. Origins of Mesophase: Fluidity and Reactivity

An assessment of the literature shows that, so far, little attentic
has been directed toward a detailed understanding of one aspect of
the above comprehensive overviews of the properties of mesophase,
namely, the detail of the mechanism of its formation from the iso-
tropic melt of parent pitch substance. The situation as currently
understood is as follows. The growth of liquid crystals and meso-
phase in carbonizations is a general phenomenon, i.e., it is not de-
pendent upon the formation of a limited number of specific chemical
compounds.

The phenomenon is observed when the starting material is coal-
tar pitch, a petroleum pitch, an asphaltene, a solvent-refined coal,
polyvinyl chloride, Gilsonite pitch, or polycyclic aromatic compounds
(often used as model compounds). It is apparently not yet possible
to produce mesophase from such compounds as benzene and phenol.

Those materials which do form mesophase exhibit large variations in initial chemical composition. Recent attempts to analyze the molecular constituents of petroleum pitch and coal extracts [10-12] only serve to illustrate their extreme complexity of molecular structure. Each of these materials must contain several hundreds of individual compounds. The degree of aromaticity varies considerably from about 7% of aromatic hydrogen atoms in Gilsonite pitch [13] to above 90% in coal-tar pitch [14]. The molecules in petroleum are predominately nonaromatic, being composed of six-membered ring systems (mostly alicyclic with some aromatic) linked by methylene bridges and associated with alkyl groupings, etc., as well as a variety of heteroatoms, in and out of ring systems. This complexity of original chemical composition of petroleum substance is compounded by the several cracking and distillation processes to which the petroleum is subjected. Thus, the final petroleum pitch can have origins in vacuum distillation or ethylene cracking plants, not to mention further chemical treatment such as air blowing, to modify the chemical composition of the marketed petroleum pitch.

Attempts have been made to simplify the chemistry of the carbonizing system very considerably by starting with *one* organic compound, e.g., anthracene (I), Figure 3 [16,17]. Anthracene was sealed .n gold tubes and carbonized to about 875 K under hydraulic pressures to monitor the formation of mesophase.

Indeed, in similar experiments, mesophase could be formed from naphthalene (II) and phenanthrene (III), Figure 3. Marsh and Evans [17] attempted to analyze the various intermediate compounds formed during the carbonization of anthracene and which eventually are incorporated into the substance of anisotropic semicoke. An AEI MS9 mass spectrometer was used, in conjunction with a hot filament at low voltages to study molecular weights in the range up to 1000 amu. Initially, the anthracene dimerized, trimerized, etc., but subsequently with increasing HTT, underwent extensive molecular fragmentation as well as polymerization. The analysis showed extensive formation of substituted derivatives of smaller molecules (< 400 amu) and that a great many aromatic ring systems could be detected
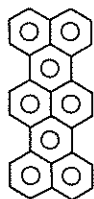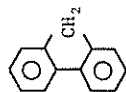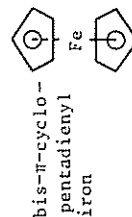
(I) Anthracene

(II) Naphthalene

(III) Phenanthrene

(IV) Acenaphthylene

(V) Terrylene

(VI) 1,14,7,8 – Dibenzo peropyrene

(VII) Dibenzo
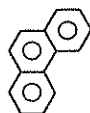
(VIII) Free radical from benzanthrene
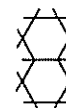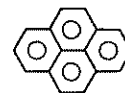
Free radical from naphthanthrene

(IX) Biphenyl

(X) Fluorene

(XI) Dibenzyl

(XII) Decalin

(XIII) Tetralin

(XIV) Indene

bis-π-cyclo-pentadienyl iron

(XV) Ferrocene

(XVI) Chrysene

(XVII) Pyrene

(XVIII) Phenazine
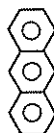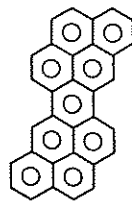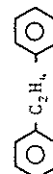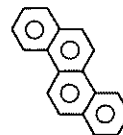
(XIX) Diphenyl sulfide
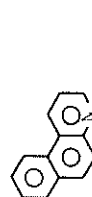
(XX) 5,6 – Benzoquin-oline
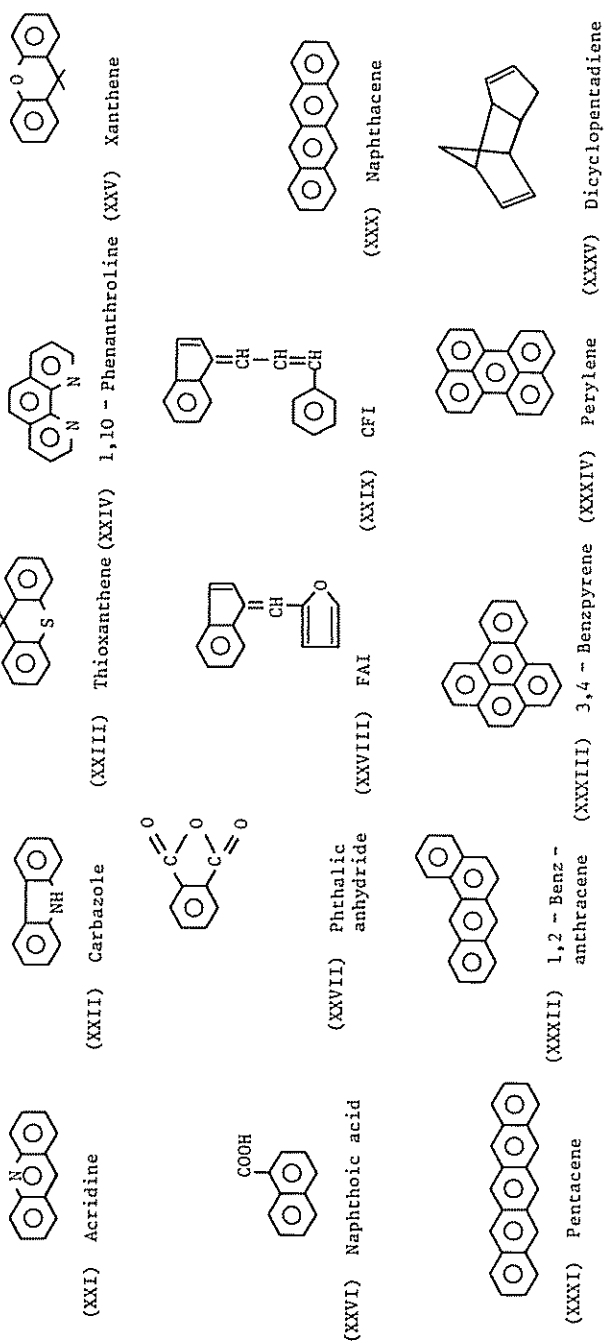
Fig. 3. Structural formulae of organic molecules.

(> 400 amu). Methylation, phenylation, etc., also occurred. The overall result was that the black pitch which resulted from the carbonization of anthracene and which was the precursor of mesophase was probably as complicated in terms of molecular structure as coal-tar and petroleum pitch. A similar situation was found with the carbonization of polyvinylchloride [13]. Here, the starting material is a white solid which melts and loses hydrogen chloride and other volatile materials to leave in the carbonization system a black pitchlike substance. Examination of this pitchlike substance by mass spectrometry revealed essentially an "envelope" of molecular species extending over several hundred atomic mass units. Again, an extremely complex mixture of chemical species formed the chemical composition of this pitch. It is from these extremely complex parent pitch substances that the liquid crystal phase and mesophase can develop.

Although optical microscopy has been used extensively to monitor the growth of mesophase, the processes occurring to establish its existence are beyond the limits of resolution of the microscope. One really has to consider molecular processes. The extreme complexity not only of initial molecular composition but of the pyrolysis processes of carbonization must be emphasized. It will not be possible, ever, to know in detail the chemistry of these pyrolytic reactions. Overall, though, there is an increase in average molecular weight and size. This occurs with increasing carbonization temperature such that as the molecular weight increases so also do the fluidity of the liquid phase and the diffusivity of the molecules within the liquid phase. Although most carbonization systems use progressive heating procedures, this increase in HTT is not necessary

to mesophase growth which can be studied isothermally, where, according to Honda et al. [18], time and temperature have been shown to be dependent functions of the conditions of carbonization. Basically, similar effects can be observed at a lower HTT and longer duration of carbonization and a higher HTT (isothermal) and shorter duration of carbonization.

These effects can best be illustrated by reference to some delicate experimentation of Lewis [19]. Petroleum and coal-tar pitches were maintained isothermally at an HTT of 673 K in a modified Kofler hot stage attached to an optical microscope. Eventually, growing from within the fluid isotropic phase of pitch small growth units (size about 0.5 µm) of liquid crystals (mesophase) could be detected in the optical microscope. Lewis [19] now raised the temperature of his hot-stage furnace rather quickly by a few degrees Kelvin only, when the liquid crystal phase was seen to disappear and to reappear when the temperature was lowered to its original value. This cycling process could be repeated only a few times. After several such cycles the anisotropic phase had evidently polymerized sufficiently such that another increase in temperature was not able to dissociate the liquid crystal phase. What Lewis [19] was evidently simulating in his experiments was the reversible transition from the isotropic phase (liquid) to the anisotropic phase (plastic) of those rodlike polar molecules which are known to form the conventional nematic liquid crystal systems (see References 2–4). Lewis [19] also observed for low viscosity isotropic phases that 5–10% of mesophase in small spherules is formed from the isotropic pitch on cooling from 673 K to room temperature.

The processes which occur during the formation of mesophase in the more usual of carbonization systems would therefore appear to be

somewhat as follows (under isothermal or nonisothermal conditions).
The process of pyrolysis of the pitch substances eventually estab-
lishes a system with a chemical composition which is increasing in
molecular weight and molecular size. Mesophase formation is assumed
to be specific to these larger molecules which are essentially (but
not exactly) planar. In this liquid system, as in all liquid systems,
there is a dynamic, reversible association of constituent molecules.
Liquids do not exhibit the random (or amorphous) distribution of
molecules or atoms as is found in the gas phase. As the concentra-
tion of molecules of larger size increases with duration and tempera-
ture of carbonization, the frequency and duration of their dynamic
reversible association must also increase. Eventually, the increase
in concentration of these larger molecules is such that a critical
condition is exceeded, and a situation is created where a transition
to a liquid crystal phase is possible. The particular properties
of these liquid crystal systems must be emphasized. Whereas in the
"conventional" liquid crystal systems [2-4] the anisotropic liquid
crystal phase is established by reduction of the mobility (kinetic
energy) of the constituent molecules by lowering the temperature to
create that delicate energy balance whereby that particular molecular
arrangement in the liquid crystal is maintained, so in pitch pyrolysis
the mobility of the molecular species is lowered, not by decreasing
the temperature but by increasing the molecular weight (by inducing
polymerization, until at a critical condition of concentration, fluid-
ity, and temperature the situation (energy balance) is created leading
to liquid crystal formation. This essentially is the process of
Lewis [19]. An essential difference exists, however, between the
two systems, i.e., of conventional liquid crystals and of pitch
pyrolysis. This difference is that whereas the conventional liquid
crystals are chemically stable, the pitch pyrolyzing system is still
chemically very reactive. Once the liquid crystal system from pitch
has been created, then further duration of experimentation or in-
creased HTT will cause a continuation of the process of polymeriza-
tion, this time within the liquid crystal phase to establish a solid
phase, the semicoke, via the mesophase, insoluble (as is mesophase)

in the usual solvents for pitch, i.e., quinoline, pyridine, benzene, or chloroform.

The actual formation or initiation of the liquid crystal phase must be by a process which is physical in nature. Any covalent chemical bonding between components must be insignificant. The initiation can be considered as a continuing growth of the normal associations of molecules in the liquid phase whereby the progressive increase in molecular weight of the pyrolysis system may be equated to a decrease in temperature in the conventional systems. This is true for both isothermal and nonisothermal carbonization systems. It is just conceivable that extremely rapid carbonizations of pitch substances may create isotropic carbon (not enough time to create the liquid crystal systems) but these have not been reported as yet. Rapid carbonizations of coal substances have been studied by Patrick et al. [20], but here, the rapid rise in temperature reduces the loss of volatile material which is carbonized within the system to give *enhanced* anisotropy within the resultant coke.

The large planar molecules of the pitch system must behave in a similar way to the rodlike molecules capable of forming conventional liquid crystals. This rather unique and very sensitive property is the essential operating factor to mesophase growth and (eventually) formation of anisotropic coke. Whereas the rodlike molecules forming liquid crystals rely on rigid molecular structures with strong polar constituents to create the coulombic forces necessary to stabilize the liquid crystals over a specific range of temperature, it is the large van der Waals forces between the lamellar molecules which maintain the stability of liquid crystals in the pitch systems over their range of thermal stability.

So, it would appear that the two most important factors in the formation of liquid crystals in pitch systems are the size of the molecular units (probably greater than 1000 amu and created by the dimerization of units about 500 amu which would be soluble in the pitch) and their planarity. If the size of the molecules and the range of their size are not large enough, then the overall van der Waals forces interacting at overlap are not sufficient to prevent

rapid dissociation ($< 10^{-8}$ sec). The size has to be sufficient to
hold the molecules together despite the progressive increase in HTT
of most carbonizing systems, until further polymerization within the
liquid crystal system is sufficient to prevent thermal dissociation.
If the molecules are not sufficiently planar and/or contain nonplanar
substituents then there now exists a steric barrier to the maximizing
of the van der Waals forces. This means that the molecules are
never close enough together to create a stable association.

In terms of formation of anisotropic carbon, two rather spe-
cialized phenomena must be occurring. The first, of course, is the
actual formation of the liquid crystal system itself in which the
constituent planar molecules are stacked parallel to each other.
Other forms of crystallographic order are absent. This is sufficient,
however, to create a structure in the semicoke which is amenable to
graphitization, i.e., the ordering of molecules within the liquid
crystal and semicoke is sufficiently good that limited movement of
carbon atoms or small groups of atoms is sufficient to establish
the graphitic lattice. The second specialized (or delicate) phe-
nomenon is concerned with the chemical reactivities of the molecular
constituents. These reactivities are sufficient to promote polymer-
ization processes and yet permit the establishment of a *physical*
liquid crystal system. If the reactivities of the molecular system
are too high, then polymerizations can occur at a rapid rate within
the fluid pitch phase at a temperature which is too low for the
establishment of the liquid crystal structure and resultant carbons
become isotropic, e.g., as found in carbons prepared from
phenolformaldehyde-type resins.

C. Growth of Mesophase

The growth of liquid crystals and mesophase from the pitch phase is
thus dependent upon a rather critical set of conditions involving
size of molecules, a quite planar configuration, an effective con-
centration of such molecules, and the heat treatment temperature
and the fluidity of the system.

What appears *not* to be critical to actual formation or appearance of mesophase are the details of structure or composition of those molecules forming the liquid crystals, the rates of heating (over a wide range of 0.1 to 10^3 K min^{-1}), and the physical description of the carbonizing system, quiescent or turbulent. Rapid stirring or pulsation of the carbonization system may influence the shape of the growth units of mesophase but not their actual formation.

That the growth of mesophase is not sensitive to the details of structure or composition of its constituent molecules explains the origins of mesophase in so many pitchlike substances of quite different chemical compositions. At that value of HTT where mesophase is beginning to grow the pyrolysis process has created a large number of molecular species which have only two common properties, i.e., they are essentially lamellar and large. The detail of numbers of ring systems, their method of bonding together, the number of vacancies and their size within the lamellar molecule, the presence and position of heteroatoms, and the degree of aromaticity are unimportant to the origin of mesophase.

Although it is stressed that the details of structure or composition of the lamellar molecules forming mesophase are not important in terms of formation of mesophase, it must equally be stressed that the chemical reactivity of initial and intermediate molecules can influence, markedly, the resultant viscosity of the mesophase and the manner of coalescence of the growth of mesophase. Marsh and Smith [9] elaborated upon these ideas. (Note: If the reactivities of the constituent molecules are too high then isotropic carbon will be produced. We are concerned here with molecules whose chemical reactivities are, overall, relatively low, such that mesophase is created.) Variations exist in chemical reactivities of "molecules" within mesophase. When molecules forming the mesophase are relatively more reactive than the molecules in mesophase from other sources then polymerization within the mesophase, relatively, is more extensive at lower temperatures of formation of mesophase (about 675 K). Consequently, the mesophase growth units lack an

ability to flow and hence to coalesce on contact. This relatively
high viscosity, thus, can ultimately affect the optical texture of
the resultant anisotropic carbons. High viscosity appears to favor
the formation of mosaics and low viscosity the formation of domains
[19]. The differences in optical texture of carbon from different
parent materials, which are discussed above in terms of domains,
flow-type anisotropy, and mosaics, must be directly attributable to
differences in viscosity of the mesophase, this, in turn, being in-
fluenced by chemical reactivities of those molecules present in the
carbonizing system and in the formation of the nematic liquid crys-
tals and mesophase.

The irrelevance of the detail of structure or composition of
lamellar molecules in the formation of mesophase is illustrated in
two series of experiments. Marsh et al. [21] carbonized, singly,
anthracene (I), naphthalene (II), phenanthrene (III), and
acenaphthylene (IV) (Figure 3) and noted the formation of mesophase.
They then cocarbonized a mixture with 25% of each of these four
compounds and obtained similar mesophase, despite the much greater
chemical heterogeneity of the cocarbonizing system. Yamashita and
Ouchi [22] examined a pyrolysis system, not based upon the usual
type of pitch substance, but on a 3,5-dimethylphenol-formaldehyde
resin. The system which was isotropic in polarized light optical
microscopy at 673 K suddenly became anisotropic (fine mosaics) at
about 703 K. It was estimated that the molecular weight of the
dimethylphenol-formaldehyde polymer was about 1380 amu. The evo-
lution (per polymer molecule) of only about 0.5 molecules of H_2O
and CH_4 and smaller amounts of H_2 and CO in going between 673 and
703 K was indicative of further polymerization. Yamashita and
Ouchi [22] consider that the mesophase is formed from planar mole-
cules made up of benzene rings linked by methylene bridges and ether
bridges. They are not large aromatic condensed ring structures, but
the essential planarity is sufficient to enable mesophase to be
formed, although the chemical reactivity is sufficiently high to
create only a fine mosaic optical texture in the resultant aniso-
tropic carbon.

Marsh et al. [23] studied the cocarbonization of mixtures of pitch substances (i.e., blends) as well as of pitch substances with coals, and monitored, by optical microscopy, the optical textures of carbons from the blends. Again, a physical phenomenon, rather than a chemical phenomenon, was observed. It would appear as though, in cocarbonization systems, the individual components pyrolyze or undergo their usual chemical rearrangements quite independently of the presence of the other components. This aspect of the pyrolysis process was mentioned by Evans and Marsh [17] and is probably associated with very distinct temperature zones of chemical reactivity, such that for two components the zones do not overlap and interaction of the components does not result.

Marsh et al. [23] observed the dominance of one component (A) of the blend over the second component (B) in terms of optical texture. Particularly for the coal-pitch systems, when the coal gave a coke with fine-mosaic anisotropy, addition of 25% of pitch was sufficient to produce, in the resultant coke from the blend, an optical texture almost identical to that of the minor component, i.e., the pitch. When using an A200 Ashland petroleum pitch which gives a coke of large domain texture ($\sim$ 200 μm), the coke from the coal-pitch system (75:25) resembled that of the pitch coke. Similar effects were observed when pitch materials were cocarbonized, i.e., that component which gave a coke with larger domains could dominate the optical texture of the coke from the blend, when present as a minority component.

When considering the origins of these phenomena, account should be taken of possible *physical* and *chemical* modifications caused by the blending process (Mochida [24]). Four possible explanations can be summarized as follows:

1. Mesophase from one component, during the stage of its formation can physically incorporate within itself molecules from the second component without chemical bonding.

2. The fluid phase made up of the two components may behave as a more suitable solvent of low viscosity for the physical transformation of large molecules into mesophase.

3. The molecules of the components of the blends may chemically
    interact, so controlling the rates of condensation and the
    structures of those intermediate molecules leading to the
    formation of mesophase. If the rate of condensation is
    too rapid then the ability to form liquid crystals is re-
    duced. If the rate is too slow then often volatile material,
    which could act as a solvent, is lost. The optical texture
    of resultant cokes could then be very sensitive to the re-
    activity and role of solvent of new intermediates formed in
    a carbonization of pitch blends.

4. There may be reactions occurring in carbonizations of blends
    other than condensation reactions as mentioned above.
    Hydrogenation and transalkylation are possible between com-
    ponent molecules. Hydrogenation will reduce the melting
    point and viscosity of an aromatic compound. Transalky-
    lation may increase the affinity of large aromatic molecules
    for the less aromatic molecules of the carbonizing matrix
    as well as disturb the aromatic π-π interactions responsible
    perhaps for the formation or initiation of the nematic
    liquid crystals.

Figure 4 is a diagram illustrating how the size of the optical tex-
ture of a carbon could vary with the composition of the parent pitch
blend. Figure 5 (left-side circle) is a diagram showing the en-
trainment of the smaller molecules of the pitch blend in the liquid
crystals formed by the larger molecules (explanation 1 above).
This entrainment prevents further chemical reaction (polymerization)
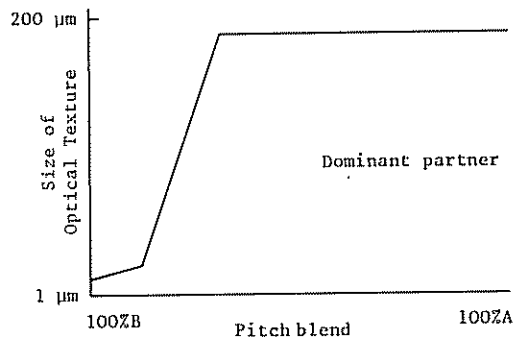
Fig. 4. Diagram of variation of size of optical texture with blend
composition:dominant partner effect [23].
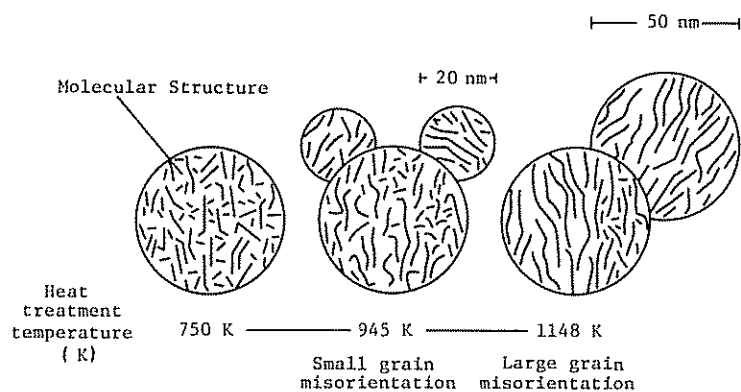
Fig. 5. Diagram of arrangement of small and large molecules within mesophase [25].

between the molecules of the second component (giving in the result-ant cokes only the small mosaics), this polymerization being respon-sible for an enhanced viscosity and smaller mosaic size of aniso-tropic growth unit. The overall fluidity and coalescence properties of the mesophase from the cocarbonization is consequently similar to that in cokes from the pitch with the dominating molecular compo-sitions. This experimentation further emphasizes the physical na-:ure of the process of liquid crystal formation from the pitch materials. (See Section VI.B.)

This trapping of smaller molecules within the structure of mesophase has been demonstrated experimentally by Marsh and Crawford [25] using phase-contrast electron microscopy which resolves the constituent molecules of mesophase as lattice images. Mochida et al. [26], using vapor pressure osmometry of chloroform or benzene solu-tions obtained by reductive ethylation of mesophase from Kureha petroleum pitch and a coal-tar pitch, estimated that the spheres of mesophase consist of molecules with a weight distribution from 400 to 3000.

Similar effects to those reported by Marsh et al. [23] are discussed by Mochida et al. [27,28], these authors studying espe-cially the cocarbonization of soluble (S) and insoluble fractions (I)

[using benzene (B), acetone (A), and heptane (H) as solvents] of
solvent refined coals (SRC), a coal-tar pitch (CP), an ethylene
tar (ET), and a Kureha thermal-cracked crude derivative. The ob-
jective of the work was to obtain a better understanding of the
compatability of pitch fractions during cocarbonizations in terms
of the development of flow-type anisotropy in resultant cokes.

Carbonization behavior was characterized in terms of flow-type
anisotropy, mosaic (> 10 μm), fine mosaic (< 10 μm), and isotropic
carbon in the optical textures of resultant cokes. The various
fractions were characterized by ultimate analyses, [^{1}H]NMR and
[^{13}C]NMR (reproduced in Table 1). Carbonizations were at heating
rates of 150 K h^{-1} to 673-873 K, soaking for 2 h.

Essential results may be summarized in Table 2. Mochida et al.
[28] looked for correlations of compatability with the chemical
structure of the pitch fraction. It is obvious that the ethylene
tar derivative with its low molecular weight and low aromaticity
(carbon atoms) will not yield a coke with flow-type anisotropy.
These authors tried to explain the order in compatability of soluble
fractions (KP-BS > KP-AS > No.1-AS > No.1-HS > CP-BS > No.2-AS
> No.2-HS > ET-BS) in terms of average values of their molecular
weight, degree of aromaticity and distribution of hydrogen atoms
(Table 1) *without* success. However, correlations of chemical
structures with carbonization reactivity for blends may not be
straightforward. Many factors may work together. It was considered
(in one system) that the variations in the distributions of sizes of
molecules (same average molecular weight) could influence carboniza-
tion properties. An average (statistical) description of the complex
pitch substance may provide little information which can be corre-
lated with carbonization behavior. (See also Section VI.)

Thus, it would appear that much greater detail of chemical
specification is needed to predict carbonization behavior. Mochida
et al. suggest that separation of molecular constituents by liquid
chromatography and followed by chemical analyses may be necessary.
However, Mochida et al. [29] varied the amounts of No.1-BS and
No.2-BI material in cocarbonizations and found what Marsh et al. [23]

Table 1. Some Properties of Fractionated Pitches [28]

		Fractions	Yield (wt%)	Analysis (wt%)						[1H]NMR*					[13H]NMR	Molecular weight
				C	H	N	S	Ash	H/C	H_a/H	H_i/H	H_o/H	H_r/H	f_a	f_a	
No. 1		BS	58.6	91.4	6.2	1.11	0.04	Trace	0.81	0.62	0.24	0.13	0.014	0.85		280
		AS (in BS)	40.7	90.7	5.8	1.74	--	Trace	0.77	0.58	0.26	0.13	0.019	0.85	0.83	330
		HS (in BS)	51.7	92.4	6.1	0.86	---	Trace	0.79	0.62	0.23	0.13	0.021	0.86		250
		BI	41.4	87.1	5.0	2.33	0.26	0.76	0.68							
No. 2		BS	57.4	91.4	6.2	1.11	0.04	Trace	0.81	0.72	0.16	0.11	0.012	0.90		350
		AS (in BS)	40.1	91.0	5.4	1.10	--	0.22	0.71	0.71	0.19	0.09	0	0.90	0.88	450
		HS (in BS)	51.0	91.5	5.8	0.82	--	0.04	0.76	0.71	0.16	0.13	0.012	0.89		300
		BI	42.6	87.2	4.4	1.74	0.15	0.79	0.60							
KP		BS	35.0	94.0	5.1	0.12	--	Trace	0.65	0.76	0.17	0.06	0.011	0.94		400
		Al-BS (in BS)	32.2	94.4	4.8	0.49	--	Trace	0.61	0.83	0.14	0.03	0	0.93	0.92	530
		AS (in BS)	64.5	94.0	5.3	0.11	--	Trace	0.68	0.76	0.20	0.04	0	0.92		340
ET		As received		92.8	7.3	0.09	--	Trace	0.95	0.50	0.36	0.12	0.019	0.77	0.76	230
CP		BS	89.0	92.0	5.3	1.11	--	Trace	0.69	0.84	0.14	0.016	0	0.95		270

*H_a: τ value (ppm) 6.30-9.30 aromatic; H_i: τ value (ppm) 2.00-4.00, α-aliphatic, α-methyl; H_o: τ value (ppm) 1.00-2.00, β-methyl, methylene and methine except for α ones; H_r: τ value (ppm) 0.50-1.00, methyl except for α and β ones.

Table 2. Optical Texture of Polished Surfaces of Carbons from Pitch
          Materials and Pitch Components [28]

Carbonized material*	Optical texture
No. 1 SRC original	Flow
No. 2 SRC original	Mosaic
No. 1 SRC original + $AlCl_3$ or dicyclopentadiene	Larger flow
No. 2 SRC original or dicyclopentadiene	Fine mosaic
No. 1-BS	Flow
No. 1-BI	Isotropic (nonfusing)
No. 2-BS	Flow
No. 2-BI	Isotropic (nonfusing)
No. 1-BS + No. 2-BS	Flow
No. 1-BI + No. 2-BI	Isotropic
No. 1-BS + No. 2-BI	Flow
No. 2-BS + No. 1-BI	Mosaic
No. 2-BS + No. 2-BI	Mosaic
KP-BS + No. 1-BI	Flow
KP-BS + No. 2-BI	Flow
ET-BS + No. 1-BI	Fine mosaic
CP-BS + No. 1-BI	Flow
CP-BS + No. 2-BI	Mosaic
No. 2-HS + No. 2-BS	Fine Mosaic
No. 2-AS + No. 2-BS	Fine mosaic

*60% of BS is cocarbonized with 40% of BI material.

have termed the dominant partner effect. The amount required to
observe the effect varies according to the system under study.

      These studies of blending and cocarbonization of extracts
introduce another concept [28]. Although the formation of mesophase
is critically dependent upon a sensitive balance between chemical
reactivity (to increase molecular size) and fluidity (to allow dif-
fusion and orientation of the larger molecules) it is during the
pyrolysis process that other molecules in the system are essentially
active as a solvent (perhaps the BS fractions [28]) to the larger

more reactive molecules (BI fractions). In fact, during the forma-
tion of mesophase the solvent molecules may ultimately be entrained
within the mesophase. In this way the entire pyrolysis system is
eventually transformed into semicoke. The molecular size and molec-
ular weight measurements of Marsh and Crawford [25] and Mochida et
al. [26] suggest that this is possible.

Mochida et al. [28] also studied the effects of additions of
aluminum chloride and dicyclopentadiene (DCPD; XXXV of Figure 3)
upon the carbonization behavior of their No.1 SRC pitch and No.2 SRC
pitch. These pitches, without addition, gave either cokes with flow
structures in their optical texture (No.1 SRC pitch) or mosaic
structures (< 10 μm size optical texture; No.2 SRC pitch). The
additions improved the size of the flow-type anisotropic structures
(needle structures) from the No.1 pitch but decreased the size, sig-
nificantly, of anisotropic mosaics in cokes from No.2 pitch.
Clearly, much remains to be understood of the detailed chemistry
of formation of anisotropic carbon.

D. Influence of Free Radicals

Lewis and Kovac [30] attempted to form liquid crystal systems at
the temperatures of melting of several hydrocarbons, ranging from
about 430 K for terylene (V; eight rings, $C_{30}H_{16}$, 376 amu) to
713 K for 1,14,7,8-dibenzoperopyrene (VI; nine rings, $C_{32}H_{16}$,
400 amu). No evidence for formation of a liquid crystal phase could
be found. This is almost certainly due to the smallness of the
molecular size, molecular weights probably in excess of 1000 amu
being necessary for mesophase formation. On further heating of the
terylene (IV) to 623 K rapid formation of a liquid crystal phase
was found. However, additions of free radicals from benzanthrene
(VII) and naphthanthrene (VIII) raised the temperature of formation
of mesophase to 675 K, and according to Lewis and Kovac these could
act as radical inhibitors. However, the possibility exists that
they are simply diluents.

Lewis and Singer [31] in an earlier study of formation of meso-
phase from acenaphthylene (IV) using an ESR technique were unable
to decide if free radicals created in the fluid pitch system played
a necessary role in the process of formation of liquid crystals or
are a normal result of the polymerization reactions which occur
during the development of mesophase. However, should the formation
of mesophase *not* be sensitive to the detail of structure or compo-
sition of its constituent molecules, as suggested above, then it is
quite probable that aromatic free radicals are incorporated into
mesophase in a way which is indistinguishable from molecules, i.e.,
the second of the suggestions of Lewis and Singer [31] is more
realistic. However, once incorporated into the mesophase, this is
not to suggest that these free radicals plan an inactive role (see
References 50-52, Section V).

E. Nucleation of Mesophase

The possibility exists that the growth of mesophase is nucleated or
seeded by processes such as occur in crystallizations. The experi-
mental evidence currently available suggests otherwise (but not
unequivocally), namely, that mesophase originates by a process of
homogenous nucleation without the presence of any second phase.
Many of the industrially available pitch substances such as coal-tar
pitch contain what are termed quinoline insolubles (QI). These
have the appearance of carbon black particles and may originate as
such during the distillation of the pitch (they are then termed
natural QI). They may also originate in the hot pitch; in this
case they are termed thermal QI. These are probably small growth
units of mesophase. When considering the possibility of "seeding"
the growth of mesophase an instinctive suggestion is the use of
carbon black particles as these generally are the smallest size of
carbon which is available.

It is found, however, that additions of carbon black do not
seed the growth of mesophase in the traditional sense. The additions
interfere with the growth and coalescence processes of the mesophase

[1,32]. The carbon black particles tend to be "absorbed" onto the
surfaces of the growth units of mesophase (generally spheres).
Thus, when the growth units have enlarged sufficiently such that on
contact they would have coalesced to form larger spheres and domains,
the presence of this carbon black hinders this coalescence, and the
spheres, etc., retain their original shape and size. This effect
has been utilized by Tillmanns [33] who, with controlled additions
of carbon black to a coal-tar pitch, followed by carbonization, pro-
duced a graphite, isotropic in bulk properties (because the coales-
cence which introduces bulk anisotropy was prevented) with interest-
ing mechanical properties.

Thus, generally, additions of carbon black appear not to enhance
the growth of mesophase but to exert an influence at a later stage
in the process. If the added carbon black is of the thermal variety,
i.e., small growth units, then other effects may be noted. Mesophase,
if of relatively low viscosity, will tend to flow over surfaces
with which it comes in contact. It will flow over graphite flakes
or surfaces of silica. It could likewise flow over spherulitic
surfaces and in so doing create an enlarged sphere, the orientation
of the contained molecules being circumferential rather than lying
on equatorial planes as is usually observed in mesophase spheres [1].
Such mechanisms are these, i.e., variations in growth procedures
rather than nucleation processes, may account for unusual structures
seen in mesophase by Matsumoto et al. [34]. These authors report
that two carbon blacks (GPF and APF) uniquely influenced the growth
of mesophase spheres to create structures different from that of the
equatorial stacking, reported by Brooks and Taylor [1]. This is
attributed to adsorption of the carbon black particles on established
spheres of mesophase and to the fine crystal faces existing on the
surfaces of the carbon black particles.

The presence of carbon blacks in carbonization systems appar-
ently may do two things. It can influence (usually degrades) the
growth and coalescence behavior of spherules of mesophase. It is
also reported to accelerate the rate of formation of mesophase [1].

It is the experience of Marsh (unpublished work) that extraction
procedures (used to measure extents of formation of mesophase) using
pyridine or quinoline may not be thorough enough. Examination of
polished sections by polarized light optical microscopy of material
thought to be exhaustively extracted, can reveal unpyrolyzed pitch
trapped within agglomerates of carbon black. This artifact would
be interpreted as too high an extent of conversion of pitch to
mesophase, and would give a false impression of accelerated growth.
(See also References 41 and 42 and Section IV.A.)

    There is a further interesting facet to this aspect of homo-
geneous nucleation. If two pitch materials are compared, one of
which gives a coke of large domains and the second of small domains
or mosaics, then during the carbonization process it is usual to
observe in the first type of pitch a smaller number of growth units
of larger size when compared with the second pitch (larger number
of smaller units). This may be associated with the ease with which
the constituent molecules can form liquid crystals and mesophase.
Of relevance here is a high-resolution phase-contrast electron mi-
croscopy study by Marsh et al. [35] and a study by Forrest [93]
based on quantitative reflectance microscopy. Results from these
studies suggest that the molecular size and stacking order is lower
in the smaller sized mosaic growth units. This factor of smaller
size and perhaps a more irregular molecular shape [35] may tend to
delay somewhat the origins of liquid crystals and hence give rise
to some degree of supersaturation of molecules which form mesophase.
Supersaturation would tend to give a larger number of smaller sized
growth units because with growth from the "critical" or "saturated"
solution, the removal of molecules to the mesophase is rapid enough
to equal the rate of formation of suitable molecules from the pitch
substance.

IV.   KINETICS OF FORMATION OF MESOPHASE

A.   Reaction Sequences

It is possible to summarize (rather inadequately) the above discussions on mechanism of formation of mesophase as follows:

$$Mp \rightarrow Mv \tag{1}$$

$$Mp \rightarrow M_I + M_{R_1} \tag{2}$$

$$M_I + M_{R_1} \rightarrow M_L + M_{R_2} \tag{3}$$

$$M_L + M_{R_2} \rightarrow \text{Mesophase} \tag{4}$$

where

Mp = molecules of pitch substance

Mv = molecules of volatiles

M_I = molecules of intermediate compounds

M_{R_1}, M_{R_2} = molecular free radicals formed during pyrolysis

M_L = molecules, large in size, of about 1400 amu

Some molecules of pitch substance decompose on pyrolysis to produce volatile material [Equation (1)] which is lost in nonpressurized systems. Other molecules of pitch substance, in a multiplicity of processes, polymerize or undergo rearrangements followed by polymerization to produce intermediate compounds and molecular free radicals [Equation (2)]. These intermediate compounds and radicals further polymerize to produce molecules and radicals large enough in size to form the lamellar nematic liquid crystal [Equation (3)]. Finally, formation of mesophase occurs via these large molecules and radicals [Equation (4)].

In measuring and interpreting activation energies for the for-
mation of mesophase as well as the kinetics of the process, it is
relevant to have a knowledge of the rate-controlling step. It is
not clearly understood whether a single step acts as a rate-
controlling stage in the formation of mesophase. Currently, the
processes grouped under Equation (2) are thought (not established)
to be rate controlling.

It is possible (but not established) that the growth of meso-
phase occurs over a significant period of the pyrolysis reaction
from a low, constant, standing concentration of larger molecules
(M_L). The rate-controlling process could then be their rate of
formation [Equation (3)]. But, it is also possible that Equation (3)
is relatively fast compared with Equation (2), in which case the
rate of pyrolysis of initial molecules of pitch is rate controlling.

Physical factors may be rate controlling. There exists the
possibility that rates of diffusion of the M_L systems through the
isotropic pitch to the spherules of mesophase may be rate controlling.
The possibility also exists that it is the actual assimilation, or
adsorption, or incorporation of the M_L systems into the spherules
of mesophase which may be the rate-controlling step.

Makebe et al. [36] suggest two mechanisms for the establishmer
of critical concentrations of molecules (M_L) capable of forming
mesophase. The concentrations could be established either by a
growth in the number of molecules (and concentration) via mechanisms
suggested in Equations (1) to (3), or by an increase in the concen-
tration (at almost constant number) caused by loss of material of
low molecular weight as volatiles during pyrolysis. To distinguish
between these two mechanisms, Makebe et al. [36] accordingly examined
the optical textures of material prepared by carbonizing a pitch
(from the thermal decomposition of naphtha) at 643 and 673 K,
residence times of up to 35 h, at 0.1 MPa (atmospheric) pressure
of nitrogen and at 0.27 kPa (2 mm Hg) of residual pressure. The
latter experiment was intended to accentuate the removal of volatile
material.

These authors found that mesophase formation was established in identical kinetic conditions in both experiments, indicating that differences of concentration of M_L created by the different experimental approaches were not significant and that molecules such as M_L were formed from molecules of pitch substance (Mp) by pyrolysis [Equations (1) to (3)]. However, although the mesophase was formed under identical kinetic conditions, the resultant materials did not have similar optical textures. That material formed at atmospheric pressure possessed large domains and flow-type anisotropy (100–200 µm) while that formed at 0.27 kPa pressure was of much smaller texture (> 20 µm). Makebe et al. [36] associated these differences in optical texture with differences in fluidity of the two systems, the loss of volatile matter at 0.27 kPa pressure essentially removing low molecular weight material which remains as a liquid at atmospheric pressure. The softening point of material heated at 643 K was raised from 513 to 573 K by vacuum treatment at 643 K. These ideas fit in well with the theories relating to size of optical texture as expressed above.

The study of Makebe et al. suggests, on the other hand, that carbonization at pressures well above atmospheric pressure could further augment the size of optical textures in resultant cokes. This is reported by Huttinger and Rosenblatt [37] who carbonized extracted coal-tar pitch (CTP) and a petroleum pitch (PP) to temperatures between 573 and 873 K under nitrogen pressures from 0.2 to 15 MPa. They confirmed earlier work of Fitzer and Terweisch [38] which indicated that maximum coke yields are obtained at pressures of about 10 MPa at 823 K and that carbonizations under pressure increase the graphitizability of resultant carbons as previously reported by Marsh et al. [15]. Pressure also lowers the temperature at which pyrolyses are complete, there being a significant difference in this respect between the CTP and the PP. Whereas for the CTP the weight losses decreased by 41% from 58% to 17%, on increasing the pressure from 0.2 to 15 MPa at 873 K, for the PP the weight loss decreased by only 28% (68–40%). For the PP most of the weight

loss occurred below 773 K. On preheating the CTP and PP at 673 K
and 15 MPa, and then carbonizing to 873 K at the lower pressure of
0.1 MPa, the weight loss remained unchanged at 58% for the CTP but
decreased from 68-50% for the PP. Huttinger and Rosenblatt consider
that this is due to the effect of pressure which enhances, for PP,
the retention of low molecular weight reactive species which can un-
dergo condensation reactions. The CTP with its higher concentration
of less reactive polynuclear and nonvolatile aromatics is less sus-
ceptible to the effects of pressure.

Optical microscopy reveals that the domain size in the optical
texture of resultant material is enhanced by carbonization at 15 MPa
pressure, e.g., from 5-50 μm to 100-200 μm (CTP) and from 10-100 μm
to 100-300 μm for PP. This is attributed to the enhanced fluidity
of the system caused by the presence of smaller molecules which
would otherwise be lost as volatiles (the same explanation as that
of Makebe et al. [36]). X-Ray analyses of carbons (preheated to
873 K, 5 MPa) heated to 3073 K show that CTP carbon has c/2 (inter-
layer spacing) of 0.3369 nm and a mean defect-free distance ($\bar{L}$) of
52.8 nm compared with 0.3352 nm and 23.7 nm for PP carbon. Although
the CTP is more graphitizable in terms of $\bar{L}$ values, it is less so
in terms of c/2 despite the larger optical domains (see also dis-
cussion of References 61 and 62).

Effects similar to those caused by carbonizing at reduced pres-
sures (enhanced loss of volatiles) can be observed by decreasing the
rates of carbonization. With coals of several ranks [20] and a
relatively paraffinic pitch [24] a decrease in rate of carbonization
brought about a decrease in the size of the optical texture. This
is caused by greater losses of volatiles during the slow carboniza-
tions. (Compare with study of Honda et al. [18], p. 241).

B. Kinetic Parameters: Rate, Order,
     and Activation Energy

Specific interpretations of kinetic data are difficult because the
pyrolytic reactions do not proceed from a homogeneous system. The
molecular components of pitch(es) themselves react at different

rates such that the detail of the chemistry at the beginning and end
of a reaction is different. The measured activation energy may then
not describe even a single step of events, but may be a complex
function of a multiplicity of reactions in each reactive step, the
activation energies of which are not significantly different from
each other.

Studies involving mass spectrometry [17] and chemical studies
of model systems [39] and pitches [40] show that polymerization
processes referred to above are mostly dehydrogenative aromatic
condensation reactions leading to the formation of mesophase.
Lewis and Singer [31] prepared mesophase from acenaphthylene pitch
between 673 and 703 K and estimated the contents of mesophase in
reaction products by Soxhlet extraction using pyridine. They con-
cluded that the rate of formation of material (insoluble in pyridine)
showed first-order kinetic behavior and that the activation energy
for its (mesophase) formation was 185 kJ mol^{-1}. In a similar study,
Honda et al. [18] using a coal-tar pitch also found first-order
kinetic behavior and an activation energy of 164 kJ mol^{-1}.

Yamada et al. [41] studied the influence of natural QI (believed
to be the metaphase of Yamada et al. [41]) and carbon blacks upon
the kinetics of formation of mesophase from a coal-tar pitch.
First-order kinetics were again reported, the rate constant at 673 K
increasing from 3.8 to 7.8 × 10^{-6} sec^{-1} with increasing amount of
metaphase and carbon black. The activation energy for formation of
mesophase was found to decrease (250–170 kJ mol^{-1}) with increasing
amounts of metaphase and carbon black. Yamada et al. [41] consider
that the rate-determining step in the formation of mesophase is
radical formation [Equation (2)] because of the similarity in values
of rate constants and activation energies for radical formation by
fission of C-C bonds between aromatic and aliphatic carbon atoms.
The lowering of the activation energy by addition of metaphase and
carbon black is attributed to the change in mechanism of growth of
mesophase from the direct growth of spherules in the pitch to the
growth of layers of mesophase on the surfaces of the additive. Thus,
it would appear that there are differing viewpoints regarding the

effects of addition of carbon black to mesophase systems, the study
of Yamada et al. [41] raising interesting possibilities which may
be applicable to other systems. (See Section III.E.)

Whittaker and Grindstaff [42] observed that rates of formation
of mesophase at 703 K vary with petroleum feedstocks (a factor of 7
is reported). They state that additions of finely divided solids to
the feedstocks prior to coking *inhibit* the growth of spherules of
mesophase and their coalescence. No kinetic data are reported. It
is further reported by Fritz et al. [43] that the presence of
micrometersized catalyst fines in slurry oils (capable of yielding
needle cokes when free from catalyst fines) resulted in isotropic
structures (fine mosaics) undesirable in needle cokes.

Whereas the kinetic studies reported above were essentially
isothermal experiments (the extents of formation of mesophase being
measured usually by solvent extraction of solid products),
Huttinger [44] studied the kinetics of the pyrolysis of pitches
[probably the reactions covered in Equations (1) and (2) rather than
that specific aspect of formation of mesophase] using a mathematical
formulation of nonisothermal kinetics. Four coal-tar pitches, with
softening points in the range 328-390 K, were carbonized at rates
of heating between 1.1 and 5.4 K min^{-1} to a maximum temperature of
about 800 K and weight losses measured with respect to time and
temperature. Calculated reaction orders and activation energies
were found to be independent of the heating rate. The reaction
orders varied from 1.4-1.8, the values increasing with lower soften-
ing point, i.e., those with a higher content of low molecular
weight compounds. Huttinger [44] considers that with the lower
order reactions (higher softening point) the rate of decomposition
reactions becomes the controlling factor; with higher order reactions
(lower softening point) the rate controlling processes are polycon-
densation reactions. The activation energies increased with soften-
ing point of the pitch from 40-52 kJ mol^{-1}. Huttinger concludes
that these kinetic parameters are related directly to the constitu-
tion of the initial material which characterizes the pyrolysis be-
havior as well as the pitch itself [44].

Whang et al. [16] studied the thermal conversion of a model organic compound, anthracene (I), to a carbonaceous solid at temperatures between 763 and 782 K at pressures between 34 and 207 MPa. The activation energy for the rate of disappearance of anthracene was evaluated as 95 kJ mol^{-1} and first-order kinetics are reported.

V. MOLECULAR REACTIVITIES

In an earlier study, Weintraub and Walker [45], reporting on a pressurized carbonization of anthracene (I), phenanthrene (III), and biphenyl (XI), commented upon a rather extensive experimental survey by Tilecheev [46] and summarized by Rosen [47]. A principal finding was the much greater reactivity of anthracene when compared with phenanthrene. Tilicheev [46] cracked hydrocarbons in an iron autoclave at 674 to 873 K under pressures of nitrogen of 15 MPa without removing the reaction products. He observed that benzene, biphenyl, naphthalene, and phenanthrene form the most stable group. Their alkyl derivatives possessed cracking velocities some 13 times faster than the unsubstituted molecules. Aliphatic compounds possessed cracking velocities some 13 times as fast again. Cracking velocities ·nd calculated times for the appearance of 1% of insoluble carbon during cracking of selected compounds at 723 K are listed in Tables 3 and 4, respectively.

As reported by Rosen [47], Tilecheev calculated the time (in minutes) for the appearance of 1% of insoluble carbon (carboids) to appear in the reaction system at 723 K for several starting compounds, by assuming an activation energy for these processes of 252 kJ mol^{-1} (a high value compared to that for formation of mesophase). Both tables indicate that anthracene (I) is significantly more reactive than its isomer phenanthrene (III), or naphthalene (II). Heats of combustion indicate that phenanthrene (III; 7053 kJ mol^{-1}) is somewhat more "stable" than anthracene (I; 7163 kJ mol^{-1}).

These differences in the rates of cracking (or decomposition) reported by Tilecheev [46] and Rosen [47] are confirmed by

Table 3. Cracking Velocities of Organic Compounds
          in an Iron Autoclave [46,47]

Compound	Cracking velocity $(10^{-5} \ sec^{-1})$
Benzene	0.038
Naphthalene (II)	0.012
Biphenyl (IX)	0.027
Phenathrene (III)	0.087
Anthracene (I)	32.0
Diphenyl methane	0.73
Triphenyl methane	1.2
Fluorene (X)	2.3
α-methyl naphthalene (from II)	3.3
β-methyl naphthalene (from II)	0.9
1,6-dimethyl naphthalene (from II)	2.2
2,6-dimethyl naphthalene (from II)	0.65
Acenaphthylene (IV)	14.0
Dibenzyl (XI)	790.0
Phenyl cyclohexane	1.5
Decalin (XII)	2.0
Tetralin (XIII)	1.7
$C_{10}H_{22}$	40.0
Octene	100.0
Ethylene	280.0

Soloveichik et al. [48] who pyrolyzed flowing anthracene (I) and
phenanthrene (III) in quartz tubes at the higher temperatures
973-1673 K. For example, at 1273 K, the reaction products soluble in
benzene amounted to 83% when anthracene was the precursor and 95%
when phenanthrene was the precursor.

Isaacs [49] carbonized anthracene (I) and phenanthrene (III) at
873 K under an argon pressure of 4 MPa with a soak period of 1 h.
These conditions completely converted both organic compounds to

Table 4. Calculated Times for the Appearance
          of 1% of Insoluble Carbon during the
          Cracking of Organic Compounds [46,47]

Compound	Time (min)
Indene (XIV)	16
Acenaphthylene (IV)	35
Dibenzyl (XI)	66
Anthracene (1)	61
α-methyl naphthalene	400
Decalin (XII)	1650
Phenanthrene (III)	1970
Biphenyl (IX)	189,000
Naththalene (II)	670,000 (1.27 years)

graphitizable carbon. Galiakbarov and Kasatochkin [50] catalytically
dehydrogenated anthracene over Ni metal and Al-Co-Mo oxide calalysts
and obtained only a nongraphitizing carbon.

The higher reactivity of anthracene (I) is shown in another
context, i.e., that of extraction of coal. Shapiro and Gadyatskii
[51] treated a coking coal with anthracene (I), phenanthrene (III),
nd dimethyl naphthalenes (from II) at 503, 533, and 563 K. After
extraction with anthracene (I), the residual material from the coal
was deficient in coking capacity and volatile content. With the
other two extractants, the residual material was unchanged in coking
capacity and volatile content.

The purpose of the above discussion is to draw attention to
the possibility of extremes in chemical reactivity between molecular
constituents of pitch substances. The inferences, however, must not
be extrapolated too far because of uncertainties in our knowledge
of the detail of the various experimental systems reported above in
which carbon is produced, ranging from quiescent carbonization con-
ditions of a liquid pitch, at, e.g., 673 K [31], to the supercritical
conditions of Soloveicheik [48]. That the chemical state of the car-
bonization system may be important in discussions of rate phenomena

is suggested by studies of Berlin et al. [52-54]. In 1964 they
postulated that paramagnetic species, perhaps initially present in
anthracene (I) as impurities or induced during carbonization, may
serve as catalysts for the acceleration of radical polymerization.
They suggested the possibility of formation of π complexes with
diamagnetic species [52]. Later, in 1968, they confirmed these pre-
dictions, namely, that additions of a polymeric paramagnetic fraction
(obtained presumably in a prior experiment) to anthracene permits a
decrease in the temperature of thermolysis from 723 K to 633-673 K
[51]. Berlin et al. [54] then compared the polymeric fractions ob-
tained by low-temperature pyrolysis of anthracene with polymeric
fractions prepared over $AlCl_3$-$CuCl_2$, using IR, ESR, and X-ray
methods. The polymeric fractions were considered to be similar,
i.e., independent of preparation method. However, this autocatalytic
ability of polymeric paramagnetic radicals to promote the thermal
pyrolysis (thermolysis) of anthracene was not reported in the study
of similar systems by Lewis et al. [30,31] who also added free-
radicals to their carbonizations (see Section III.D).

A. Catalysis of Formation of Mesophase
   by Aluminum Chloride and Metals

It should be possible to modify, chemically, for a given pitch, the
process of polymerization to give large lamellar molecules and, by so
doing, to modify the optical texture of resultant cokes. From this
viewpoint, additions of aluminum chloride and metals are reported to
produce catalytic effects. The use of aluminum chloride in organic
reactions (molten solvents) has recently been reviewed by Jones and
Osteryoung [55].

Oi et al. [56,57] studied the influence of sulfur and metals, in
a coal-tar pitch and cracked oil, upon the resultant optical tex-
tures of cokes prepared from these parent materials. As found by
Marsh et al. [58] for anthracene (I), the additions of iron [as
ferrocene (XV)] reduced the unit size of the optical texture in the
cokes from the coal-tar pitch [56]. Additions of 1200 ppm of nickel

and 800 ppm of vanadium to cracked oil (from Khafji asphalt), when
subsequently carbonized at 693 K, brought about significant change
in the optical texture, the coke containing the vanadium having a
mosaic texture (2 μm) compared with a domain texture (200 μm) in
cokes from the cracked oil despite about 6% of sulfur in the cracked
oil. This effect could be brought about by the metals acting as de-
hydrogenation catalysts and creating reactive species in concentra-
tions much higher than found in the noncatalyzed reaction. The
addition of vanadium, as well as changing the optical texture of
resultant cokes, also increased the rate of formation of mesophase
at 693 K by a factor of about 9. The resultant effect is one of
formation of mesophase at an earlier stage in the reaction, the
enhanced reactivity promoting further dehydrogenative condensation
reactions within the mesophase. Consequently, the viscosity now
becomes too high and growth and coalescence are severely restricted.

Mochida et al. [59-62] made a more extensive study of catalytic
formation of mesophase using aluminum chloride and alkali metals.
Without the presence of a catalyst it is impossible to carbonize
materials such as anthracene (I), naphthalene (II), and chrysene (XVI)
in open boats at atmospheric pressure. Some form of sealed tube
xperimentation is necessary [15,16]. However, when carbonized in
the presence of aluminum chloride (0.1 mole ratio) Mochida et al.
found for these and other hydrocarbons [except pyrene (XVII)] that
high coke yields were obtained at 653 K. The cokes possess an
optical texture made up of large orientated domains and flow-type
anisotropy. The carbonization yield (measured as percent benzene
insolubles) increased with increasing mole ratio of aluminum
chloride to about 0.1, while further additions produced little
additional effect [for chrysene (XVI) the yield was about 82%].
With addition of 0.1 mole ratio of aluminum chloride to pyrene
(XVII), the resultant coke was isotropic up to 673 K. However, on
heating to 683 K the resultant coke became anisotropic (small do-
mains, 5-10 μm). No spherules of mesophase were observed. By
reducing the mole ratio of added aluminum chloride to 0.05 in the

pyrene (XVII), spherules of mesophase were now observed on carboniza-
tion, these coalescing to give domain and flow-type anisotropy.
Mochida et al. [59] considered at that time that extents of graphiti-
zation (graphitizability) of these carbons are independent of size of
domain and mosaic. However, further unpublished results indicate
a more complex situation requiring further work.

There appears to be some uncertainty in the detailed corre-
lations of optical texture with graphitizability. Matsuo et al. [63]
prepared cokes by heating anthracene (I), naphthalene (II), and
phenanthrene (III) to 973 K at pressures not exceeding 10 MPa,
under identical conditions. The size of the mosaics as seen in
polished sections of resultant carbons, by optical microscopy, in-
creased in the order phenanthrene (III) to anthracene (I). In
this context it is reported by Isaacs [49] that cokes derived from
anthracene (I) are more graphitizable than cokes from phenanthrene
(III).

The experiments of Mochida et al. [59] illustrate the delicate
balance which exists between the rate of formation of large lamellar
molecules capable of forming mesophase, the rate of formation of
mesophase itself, and the fluidity of the carbonization system.
Should the reactivity be accelerated disproportionally [as with
pyrene (XVII)] at temperatures where the fluidity of these aromatic
systems is too low, then extensive condensation prior to orientation
occurs and a resultant mosaic carbon is formed. It may be inferred,
therefore, for mesophase growth as spherules from a liquid phase,
that the rate of formation of the larger lamellar intermediate
molecules is the rate-controlling step [Equation (2)].

Mochida et al. [60] further found that isotropic carbon, in
high yield, resulted from the cocarbonizations of aromatic hydro-
carbons [anthracene (I) and pyrene (XVII)] with the alkali metals,
lithium, sodium, and potassium. The type of carbon produced was
independent of the alkali metal, starting materials, and heating
rates. The isotropic carbons (HTT 773 K) had properties, i.e.,
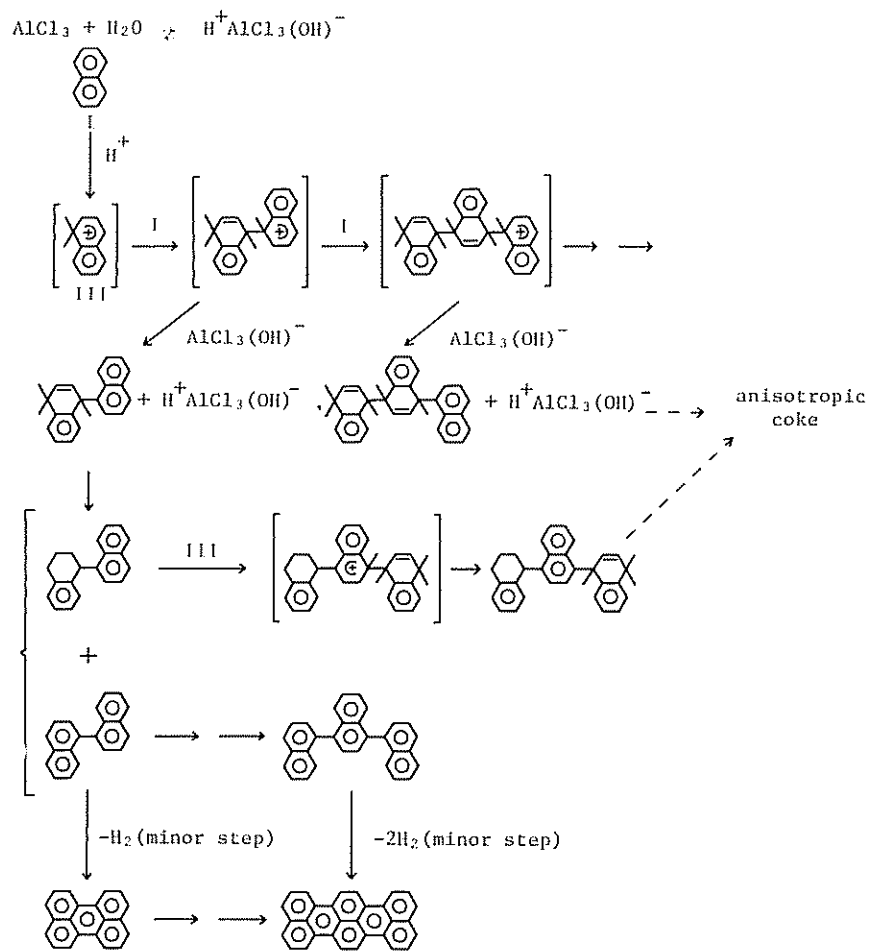surface area (10 m^2 g^{-1}) in pores 10-50 μm diameter, crystallite

size (HTT 2773 K, 3 nm), and specific gravity (xylene immersion
1.43 g cm^{-3}), comparable to glassy carbon. Carbonization of anthra-
cene (I) with aluminum chloride (mole ratio of 1:1) gave the aniso-
tropic graphitizing carbon. This material (HTT 773 K) is reported
to have a surface area of 450 m^2 g^{-1} in micropores less than 10 nm
in diameter, a crystallite size (HTT 2773 K, 65.7 nm), and a specific
gravity (xylene immersion) of 2.1 g cm^{-3}. Evidently, the isotropic
carbon possesses considerable closed porosity. A surface area of
450 m^2 g^{-1}, measured by nitrogen adsorption at 77 K, for an aniso-
tropic graphitizing carbon is unusually large. Marsh and Wynne-
Jones [64], for carbons prepared from vinylchloride, found surface
areas less than 5 m^2 g^{-1}. The influence of the use of aluminum
chloride in preparing graphitizing carbons may introduce new possi-
bilities with regard to surface area and surface properties.

The isotropic structure of carbons obtained using the alkali
metals is assumed to be due to the extensive dehydrogenation of in-
termediates brought about by the metal. The intermediates created
by reaction of naphthalene (II) with alkali metals had relatively
low contents of aliphatic hydrogen; those created by the aluminum
chloride had relatively high contents of aliphatic hydrogen, this
`indicating a clear difference in the mechanism of catalysis of poly-
ᴤerization.

Mochida et al. [61] discuss in detail two schemes (Figure 6)
describing the sequence of reactions leading to isotropic and aniso-
tropic coke. The further suggestion is made that oxidants such as
ferric, molybdenum (V), and cupric chlorides may similarly promote
dehydrogenation reactions to give isotropic coke.

B. Carbonization of Heterocyclic and Other Model Compounds

Mochida et al. [62] continue this study by carbonizing heterocyclic
aromatic compounds (containing sulfur, nitrogen, and oxygen) with
aluminum chloride. Some hydrocarbons [phenazine (XVIII) and
diphenylsulfide (XIX) as do anthracene (I) and fluorene (X)]

Scheme 1

Fig. 6. Possible sequences of reactions leading to mesophase from naphthalene (II) using alkali metals (Scheme 1) and aluminum chloride (Scheme 2) [61].

$$AlCl_3 + H_2O \;\rightleftharpoons\; H^+AlCl_3(OH)^-$$

Scheme 2

Fig. 6 (continued).

gave flow-type anisotropy in resultant cokes. Others [benzoquinolene
(XX), acridine (XXI), carbazole (XXII),thioxanthene (XXIII)] gave
fine mosaics; 1,10-phenanthroline (XXIV) gave a superfine mosaic,
and xanthene (XXV) gave an isotropic carbon. With carbazole (XXII),
the resultant carbon had an optical texture dependent upon the
quantity of aluminum chloride added. The carbons were isotropic
(0.1 mole ratio), flow-type (0.5 mole ratio), mosaic (1.0 mole ratio),
and isotropic (2.0 mole ratio). This further illustrates how the
reactivity of molecules in the carbonizing system can be promoted
from too low a value (0.1 mole ratio with aluminum chloride) to
that necessary for needle coke to form and exceed (2.0 mole ratio)
to form an isotropic material. There was a decreasing tendency for
needle coke formation for heteroatoms in the order of sulfur, nitro-
gen, and oxygen. Marsh et al. [65] in pressurized carbonizations of
heterocyclic compounds containing sulfur, nitrogen, and oxygen
reached an essentially similar conclusion. They also undertook a
number of cocarbonizations leading to several examples of unpre-
dicted behavior, i.e., additions of oxygen-containing compounds,
e.g., naphthoic acids (XXVI) and phthalic anhydride (XXVII),
increased the domain size in resultant cokes.

It would appear that predictions of effects of heteroatoms
and side groups in parent substances upon the optical texture of
resultant cokes are not easy to make. This is because it is very
difficult to quantify, precisely, for such many and diverse systems
that are carbonized, the balance which has to be maintained between
the reactivity of components of carbonizing systems (to increase the
average size of constituent molecules) and the fluidity of the
resultant pitch necessary for the movement and orientation of these
larger molecules to adopt the structure of the lamellar nematic
liquid crystal. Too high a reactivity or too low a mobility both
result in the formation of isotropic coke.

VI. CHARACTERIZATION OF INDUSTRIAL FEEDSTOCKS

Attempts are being made to correlate the carbonization characteristics
of industrial feedstocks with their chemical properties. (See
also Section III.C, Reference 28.) Recently, Kakuta et al. [66]
attempted a detailed NMR analysis (based upon the methods of Yamada
et al. [67]) of Sumatran light vacuum residue, Sumatran light vacuum
distillate, and decant oil from a catalytic cracking process. From
physicochemical examinations of saturates, aromatics, resins, and
asphaltenes derived from these source materials and a comparison
with the graphitizability of resultant cokes, it was generally found
that the smaller the value of the number of aromatic rings in the
parent molecules, or the smaller the number of alkyl side chains, the
more graphitizable was the resultant carbon. It is suggested that
if an aromatic ring has too many alkyl side chains during condensa-
tion polymerizations then the product becomes cross-linked, rather
than stacked, to form mesophase, the cross-linkage resulting in poor
graphitizability. This study of Kakuta et al. [66] confirms essen-
tially similar findings reported earlier by Mochida et al. [68,69]
although the context of the experimentation is somewhat different.
Mochida et al. attempted to modify, chemically, the QI components
of pitches in order to solubilize them, to introduce fluidity, and
hence to produce needle coke material. Generally, it was found
that alkylation of the QI introduced some solubility (in benzene)
but the resultant pitchlike material produced only an isotropic
coke. Ethyl additions were less stable than methyl additions.
Hydrogenation (probably extensive) of the QI produced a soluble
fraction capable of forming anisotropic coke. These findings of
Kakuta et al. [66] and Mochida et al. are thus in broad agreement
(in a limited context) with the reactivity data of compounds summa-
rized by Rosen [47] where alkylation of naphthalene (II) to
1,6-dimethyl naphthalene [from (II)] increases the cracking velocity
from 0.012 $\times$ 10^{-4} sec^{-1} to 2.2 $\times$ 10^{-5} sec^{-1} at 723 K.

In an analysis similar to that of Kakuta et al. [66], Tillmanns
and Pietzka [70] examined cokes prepared from a new type of parent
material, i.e., a reactive tar from a pressurized coal vaporization
(gasification) process (CPV). This tar was heated to almost 1275 K
at heating rates of 2.5 K h^{-1} and 25 K h^{-1} (623-723 K). Resultant
cokes were found to have isotropic properties. These are attributed
to a high inherent reactivity resulting in three-dimensional cross-
linkage being established at an early stage of carbonization. This
CPV tar, when compared with traditional coal-tar pitch, has a lower
aromatic content. The pyridine-soluble material has a higher average
molecular weight. An NMR analysis of the toluene-soluble material
in CPV shows a larger content of reactive aliphatic and naphthenic
(saturated alicyclic hydrocarbons) groups to be present in the CPV.

Smith [10,71] made a similar NMR analysis of a commercially
available petroleum pitch (Ashland A170) and its precursor, the
pitch being characterized by Newman [10,72]. The A170 pitch has a
composition of 92.4% C, 5.7% H, 1.3% S (total, 99.4%) and a sta-
tistical formula, derived from the NMR analysis, of
$C_{27.3}H_{12.7}(C_{1.4}H_{3.7})_{3.3}$, with possible structural formulae of
the type:
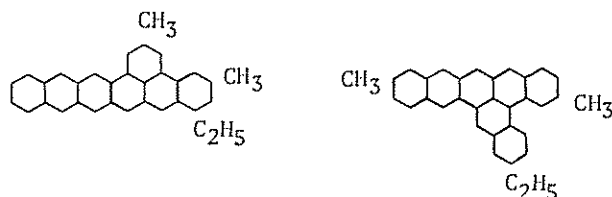
Newman [72] considers that reactive sites can be formed during
pyrolysis by the dissociation of methyl groups or hydrogen from the
rings. If such structures polymerize without excessive ring cleavage
then the resultant molecular weights can increase in stages from 365
to 730, 1095, and 1460. These larger molecules [M_L of Equation (4)]
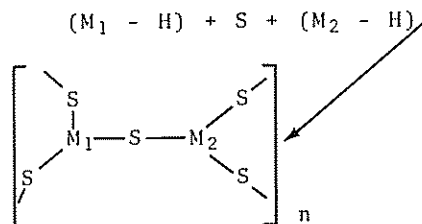can then form mesophase directly. But the reactivity of the

precursor molecules must not be so high that polymerization occurs
at too low a temperature

A.   Influence of Additions of Sulfur

The effects upon chemical reactivities, and hence upon carbonization
behavior, of additions of sulfur to aromatic hydrocarbons (acenaph-
thylene, anthracene) and coal-tar pitch have been investigated by
Fitzer et al. [73-75]. Basically, two principal effects were ob-
served. First, with additions of sulfur restricted to less than
5.0 atom percent (relative to hydrogen content) there resulted a
drastic increase in coke yield without any significant decrease in
the graphitizability of the resultant anisotropic coke. Second,
with increasing quantities of added sulfur the graphitizability
decreased until at additions of 10.0 atom percent a nongraphitizable
isotropic glassy carbon results. Fitzer et al. [73-75] analyze for
evolution of H_2S during carbonizations and for the percentage of
sulfur remaining within resultant cokes. The two effects described
above are interpreted in terms of two modifications to the chemical
reactivities of the carbonizing system. With small additions of
sulfur a process of dehydrogenation occurs between constituent
olecules, H_2S being evolved with the two molecules combining:

$$M_1-H + M_2-H + S \rightarrow M_1-M_2 + H_2S$$
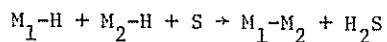
M_1 and M_2 would otherwise have been lost as volatile material. Now,
the product M_1-M_2 remains within the carbonizing system and further
polymerizes to establish M_L which ultimately forms the mesophase.
Hence, a higher yield of graphitizable material is realized. How-
ever, with larger additions of sulfur there are established thio-
bridges with resultant retention of sulfur in a nonfluid carbonizing
system, these thiobridges occurring extensively and randomly to
create an isotropic carbon.

$$(M_1 - H) + S + (M_2 - H)$$

$$\left[\begin{array}{c} \begin{array}{c} S \\ | \\ M_1 \end{array} - S - \begin{array}{c} S \\ / \\ M_2 \\ \backslash \\ S \end{array} \end{array} \right]_n$$

B. Blending and Graphitizability

The progressive decrease in graphitizability (or anisotropic optical
texture) created by blending or mixing procedures (with a component
which does not form anisotropic carbon) is a fairly general phenom-
enon. Weintraub and Walker [45] noted that additions of biphenyl
(IX) to anthracene (I) had a similar effect. Marsh et al. [65]
observed a progressive decrease in anisotropic optical texture of
resultant carbons by additions of sulfur heterocyclics to aromatic
hydrocarbons. Even polymeric systems can interact in a similar way.
Horne [76] cocarbonized blends of furfurylideneidene (XXVIII;
FAI, a thermosetting compound giving isotropic carbon) and
cinnamylideneindene (XXIX; CFI, a thermoplastic compound giving
anisotropic carbon) and noted a nonlinear decrease in graphitizabil·'
with increasing FAI content, the decrease being measured in crystal-
lite height, L_c (nm) of samples HTT 3073 K. Small additions of FAI
were disproportionally more effective in reducing graphitizability.

Yamashita and Ouchi [77] modified several pitches by additions
of polyvinylidene chloride and polyvinylchloride prior to carboniza-
tion. The effects of additions of polyvinylidene chloride were
progressively to destroy the graphitizability of resultant carbons.
Marsh and Everett [78] noted that additions of polyvinylchloride
to coal-tar pitch modified the optical texture of resultant cokes
but did not destroy graphitizability (see Section III.C).

VII. THEORETICAL ASPECTS

It will probably never be possible to know, in detail, all of the
inter- and intramolecular rearrangements undergone during pyrolysis
by each chemical species present in parent pitch substances. In-
stead, use will no doubt be made of modern methods of separation
and analysis including high-pressure liquid chromatography, gel
permeation chromatography, mass spectrometry, and $[^{13}C]$ – and $[^{1}H]$
– NMR. The differences in chemical reactivities of pitches (these
reactivities controlling to a significant extent the optical texture,
graphitizability, and physical properties of resultant cokes) will
become understood at the same time as chemical compositions of
pitches are elucidated.

The final analysis of the origins of the specific reactivity
of a chemical compound is the province of the theoretical chemist.
Essential guidelines into this area are provided by Pullman [79]
and Salem [80]. Generally, the reactivity toward substitution reac-
tions and bond additions of an aromatic molecule increases with its
size. Clar [81] comments extensively upon the stability of the
larger highly condensed aromatic molecules. Reactivity is localized
to the periphery of highly condensed molecules. Considerations of
the reactivity of such molecules should be restricted to that of the
circular peripheral chain which corresponds in reactivity, to that
of the acene series, anthracene (I), naphthacene (XXX), pentacene
(XXXI), etc. The chemical reactivity of these compounds is deter-
mined not so much by the mean values of bond orders or free
valencies but by the maximum values of these indices. Although
for the acene series the mean values decrease with increasing molec-
ular size, the maximum values of these indices are found to increase.
These considerations have relevance to the sequence of reactions
as shown in Equations (1) to (4). As the sizes of the aromatic
molecules increase following the dehydrogenation condensation
polymerizations, so their reactivity also increases, suggesting
that the reactions grouped under Equation (3) are probably faster
than those grouped under Equations (1) and (2). That further

polymeric reactions continue to occur within the mesophase and
semicoke is shown in studies of Jackson and Wynne Jones [82] and
Patrick   [83] by ESR measurements which indicate a maximum
in free-radical concentration at about an HTT of 870 K (from model
organic compounds), i.e., in the semicoke material.

Anthracene (I) owes its exceptionally high reactivity [com-
pared with naphthalene (II) and phenanthrene (III)] to being essen-
tially the smallest member of the acene series of linearly annulated
polycyclic aromatic compounds. Such compounds, again unlike naph-
thalene (II) and phenanthrene (III), possess only two double bonds
in the end ring structure. This is to say that the atomic and
molecular orbital description of anthracene (I) and phenanthrene
(III) can also be seen to be different. In addition, the spectro-
scopic properties and excitation characteristics of these acenes
will differ from naphthalene (II) and phenanthrene (III). Whang
et al. [16] discuss this aspect and contrast the rates of conversion
of anthracene (I) and phenanthrene (III) to carbon.

Various approaches have been published which discuss aspects of
the chemical reactivity of anthracene (I) and other aromatic poly-
cyclic molecules. Poole and Griffith [84] observe a general agree-
ment between the experimental ESR hyperfine coupling constants and
the observed order in reactivities of various sites in naphthalene
(II), anthracene (I), phenanthrene (III), pyrene (XVII), chrysene
(XVI), 1,2-benzanthracene (XXXII), 3,4-benzpyrene (XXXIII), and
perylene (XXXIV). Kutham [85], studying NMR proton chemical shifts
of alternant hydrocarbons and Hueckel molecular orbital (HMO)
chemical reactivity indices, attempted to classify hydrogen atoms
into angular and nonangular ones and the order of positions in which
chemical reactions should occur according to the chemical reactivity
indices. Dewar and Trinajstic [86] describe an extension of a
semiempirical treatment of ground states of conjugated molecules,
based on the Hueckel σ, π approximations, to the lowest singlet
and triplet excited state of aromatic compounds. Klopman and
Hudson [87] consider that correlations of a particular molecular
orbital with molecular reactivity do not take into consideration

changes in the relative reactivity of the several positions in a
conjugated electron donor system with the nature of the electro-
philic reagent. They regarded the formation of the transition state
as a mutual perturbation of the molecular orbitals of both reactants.
The relative reactivities of reaction sites were shown to vary with
the magnitude of this perturbation. The treatment outlines the
conditions under which the frontier orbitals may control the course
of a reaction. The importance of electrostatic interactors is
stressed. This approach is applied by Yanez and Fernandez-Alonso
[88] to, inter alia, anthracene (I) and phenanthrene (III) and their
nucleophilic substitution by OH^-, BH_4^-, or CN^-. Experimental data
agree with theoretical predictions. The inversion of the position
of maximum reactivity was satisfactorily predicted. Herndon [89]
created an algorithm (the logarithm of the number of Kekule struc-
tures) which gives resonance energies for benzenial hydrocarbons.
These resonance energies were equivalent to results of highly
parameterized SCF-LCAO-MO calculations. This relation was also
found to hold for odd alternant cationic and anionic species.
Reactivity indices based on the structure count algorithm correlate
with various types of experimental reactivity data.

A stumbling block which one encounters when attempting to
correlate the chemistry of formation of mesophase with theoretical
and preparative organic chemistry is the magnitude of the problem
created by the complexity of the pyrolyzing systems. Basic texts
in aromatic chemistry [81,90,91] usually are not interested in the
larger aromatic molecules created during pyrolysis (of amu > 500).
One is then tempted to look into aromatic polymeric systems, and
although this field is reported to be vast and complex [92], one
cannot help feeling that it is very well ordered and understood
when compared with pitch systems. It is proving very difficult to
change the ethics of the manufacture of baked carbon and graphite
from that of a black art to a basic science.

VIII. SUMMARIZING DISCUSSION

Anisotropic carbons, prepared from pitch materials, are conveniently
studied in polished sections, by polarized light optical microscopy.
The surface of the carbon contains areas (optical texture) of optical
activity of different sizes, varying from < 0.5 μm to about 500 μm,
these areas indicating a degree of invariance of angle of projection
of the lamellar constituents of the carbon toward the light beam.
The anisotropic carbon initially grows from within the pitch
pyrolysis system as a lamellar nematic liquid crystal. This growth
is, at its onset, reversible with respect to the isotropic liquid
pitch. The liquid crystal is composed of large lamellar (approxi-
mately 50) aromatic molecules, the growth process *not* being unduly
sensitive to the detail of molecular size or composition. This
liquid crystal quickly undergoes internal polymeric reactions to
produce mesophase (insoluble in quinoline and unable to dissociate
back into the liquid pitch) which will eventually harden to form
semicoke.

The major requirements for mesophase development are that the
chemical reactivity of constituent molecules must not be so high
that extensive polymerization has occurred at a temperature so low
that the system does not have the necessary fluidity to enable the
constituent molecules to orientate to form the liquid crystal.
Otherwise, at worst, an isotropic carbon results; or anisotropic
carbons result with small optical textures (< 1.0 μm) compared with
the optimum conditions leading to flow-type anisotropy (∿ 500 μm).
It is the chemical reactivity of the system, more than any other
variable parameter, which controls the resultant optical texture
in carbons. There is evidence, still to be confirmed, that free
radicals in the carbonizing system may have an autocatalytic role.

The origin of these liquid crystals from within the isotropic
pitch is probably by a process of homogeneous nucleation. The evi-
dence for nucleation and enhanced growth rates of mesophase by
additions of carbon black to the pitch is rather contradictory.
Certainly, carbon blacks and other finely divided solids will cause

the disappearance of flow-type anisotropy to be replaced by mosaics. Kinetic studies are rather limited, the formation of mesophase being considered to be first order with an activation energy of about 170 kJ mol^{-1}. Probably, the rate-controlling stage is the initial pyrolysis of constituent molecules rather than reactions involving larger polymeric molecules.

The optical texture of carbons can be modified by additions of suitable catalysts, e.g., alkali metals or aluminum chloride to parent materials. These basically modify the balance of chemical reactivity with respect to the fluidity of the system. The alkali metals initiate reaction at a low temperature, and this results in the formation of isotropic (nongraphitizing) carbon. Although systems which give needle coke can easily be degraded to give small mosaics or even isotropic carbon, the converse, unfortunately, does not readily occur.

Industrial processes are currently being modified to upgrade the quality of pitch toward needle coke formation (with flow-type anisotropy). Characterization of pitch by elemental analysis, [^{1}H] – NMR and [^{13}C] – NMR, although giving broad guidelines toward suitability, may not be sufficient for precise predictions. The problem remains of knowing the range of chemical reactivity of the large spectrum of molecular species found in pitch substances. Semiempirical approaches to modify optical texture (usually one of degradation) include additions of sulfur, of thermoplastic, and thermosetting resins, as well as cocarbonization with other pitches of different properties.

ACKNOWLEDGMENTS

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