

STRUCTURAL ASPECTS OF MESOPHASE
MATERIALS FROM PETROLEUM, COAL AND OIL SHALE

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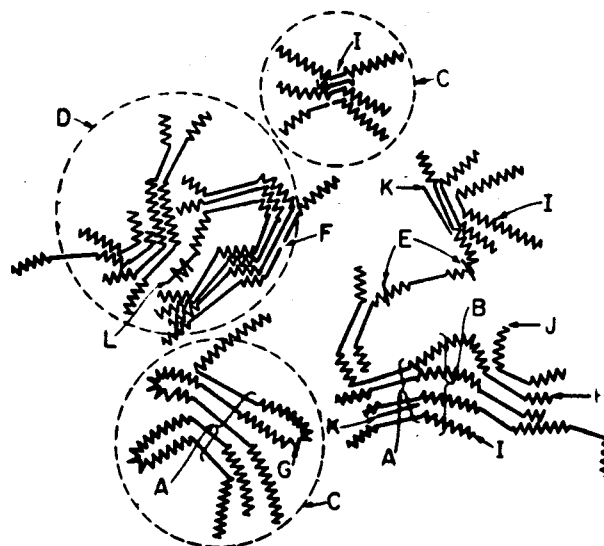
Petroleum pitch and semicoke have been used in the specialty graphite area as high quality carbon precursors for graphites and carbon fibers. The performance of these finished materials depends on the characteristics of their starting feedstock supply. However, in recent years the impact due to the shortage of petroleum, as well as the improvement of refining technology, forces one to look for other alternative energy sources, such as coal and oil shales. These materials will become important in the next decade as they are inevitably to be developed as substitutions for petroleum during the interim period until ultimate energy sources, such as solar energy and fusion are technologically demonstrated.

Coal and oil shale, as well as petroleum, are all fossil fuels. The pathways of their diagenesis and source materials are entirely different. Therefore, it is expected that there be differences in the structures of their asphaltic (carbonaceous) bitumens. These bitumens are important in that they are the precursors leading to the mesophase formation under carbonization. Within the macrostructure of bitumens, sufficient embryonic nematic crystals may be the nucleus to control the mesophase.

Macrostructure of Asphaltic Bitumen

Naturally-occurring bitumen is not entirely isotropic in its structure. It is a mesomorphic liquid, i.e., many individually-oriented clusters are suspended and randomly distributed within their lower molecular weight homologs. The individually oriented clusters consist of a number of planar aromatic molecules stacked vertically in layers due to the π - π association. The side substituents of these aromatic systems are zig-zag chains due to the requirement of succession of the tetrahedrally-linked carbon atoms. These chains act as a "shock absorber" in a sea of floating "islands."

Fig. 1 depicts the general macrostructure of asphaltic bitumen (1). The association of the π -systems actually gives interlayer distance of ca. 3.5 Å which yields (002) peak under x-ray diffraction. This type of association is equivalent to the layered structure of graphite which is termed crystallite (A). The zig-zag chain can orient in a bundle-like fashion (B) depending on the torsional angle when propagation of sp^2 -bonded orbital takes place. These island-like stacks are termed particles (C). Usually particles can further associate into micelles (D), the peripheral groups are polar. There are a number of weak links (E) along the chain configuration, some of these are ether, thioether or even hydrogen bonds, which can undertake cleavage. There are imperfections in the aromatic systems with di- or trivalent heteroatoms such as nitrogen, sulfur or oxygen. Clusters may



Macrostructure of Asphaltics

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|----------------|-----------------|
| A. Crystallite | B. Chain Bundle |
| C. Particle | D. Micelle |
| E. Weak Link | F. Gap and Hole |
| G. Intracuster | H. Intercluster |
| I. Resin | J. Single Layer |
| K. Petrophyrin | L. Metal |

also be linked either by folding the chains--intracluster (G); or by bridging through weak links--intercluster (H). The resin (I) is a small homolog of asphaltene which is larger and the molecular weight is higher. Simple layer (J) of the stacked clusters can be formed by disassociation, provided that conditions do not favor the reassociation. Petrophyrins (K) is a single layer containing extended conjugation of pyrroles. The metal (L) can be a center of coordination for several clusters.

The schematic illustration is useful for the structural change during heat treatment. In general, aromaticity increases upon the application of heat. The conversion of asphaltene into carbenes and carbenes into carboids is such an example. The average number of effective layers (Me) increases from a value of 5 to a larger value of 15. For petroleum coke the value can raise up to 35 (2). Under heat, more hydroaromatic structures can become aromatic. Hence the increase is not only along the z-axis, but also an anticipated growth in the x, y-plane, that is, an increase in layer diameter.

Prediction of Coal and Shale Oil as Mesophase Sources

The development of the oriented areas of mozaics and domains under carbonization is important. The growth of such anisotropy during graphitization

is also important. What will be discussed here is the constituents of different bitumens for this type of study. The stacking defects will be caused by the extent of heteroatoms as well as metals. Table I is a brief summary of the constituents in petroleum-, coal-, and shale-derived asphaltenes. The predominant type of heteroatoms is different in various asphaltenes, e.g., in each molecule of petroleum-derived asphaltene, there are 2 or 3 sulfur atoms; in each of the oil shale-derived asphaltene, there are 2 or 3 nitrogen atoms; and in each of the coal-derived asphaltene, there are about 2 or 5 oxygen atoms.

Table I. Composition of Different Asphaltenes

	<u>Petroleum</u>	<u>Shale</u>	<u>Coal</u>
Metals	V, Ni	Fe, Ni	Ge, Mo
Major Hetero-atoms(N, O, S)	S	N	O
Aromatics	peri	kata or link	kata

Table II. Structural Parameter of Various Asphaltenes

	<u>Petroleum</u>	<u>Shale</u>	<u>Coal</u>
f_a	0.2-0.5	0.4	0.6-0.7
L_a (A)	10-15	7-12	7-14
L_c (A)	20	15	10
σ	0.5-0.7	0.5-0.6	0.3-0.5
H_I/C_A	0.3-0.5	0.8-0.9	0.6-0.8
n	4-6	2-3	1-2

states exist with the bituminous aromatic sheets (3). The thermal excitation is attributed to the propagation of Wannier excitons. As graphitization occurs, the Wannier spins act as independent mobile or delocalized excitons. The odd electrons eventually become charge carriers and can be degenerated to certain extent as in a metal. All those depend on the J-value (singlet-triplet energy) and $\Delta\epsilon$ (conduction energy gap) of the mesophase source material. To summarize, it is not only the chemical composition of parent substances that determines mesophase growth, but the macrostructure of the parent source material also plays an important role.

References

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- (2). T.F. Yen, "Chemistry of Asphaltene in Coal Chemistry," Preprints, Workshop on Coal Chemistry, Stanford Research Institute, pp. 144-164 (1976).
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Table II lists different parameters as measured by NMR and X-ray diffraction. The higher aromaticity (f_a) of coal and coal-derived products may be important for the graphitization process, but the drawback may be that coal is kata-condensed systems. The fact that coal-derived asphaltene has shorter substitution (n) and lower extent of substitution (σ) may not be the most desirable parent substance. The longer chain and the excessive amount of substitution may have the "buttressing" effect for aromatization. Another consideration is that in trace metals, e.g., alkali metal may catalyze polycondensation. In this manner, the prediction of the application of shale-derived asphaltene to mesophase formation is in between that of petroleum-derived product and that of the coal-derived product.

Finally, the spin correlation studies indicate that both singlet-triplet transitions and doublet