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## Pressure effects on the structure of carbons produced from anthracene

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**Abstract.** A study is reported of the thermal conversion of anthracene to carbonaceous solids at temperatures between 450–2800°C and pressures between 0.34–2.07 kbar. Structures of the carbonized solid products are characterized by a highly anisotropic mesophase whose morphologies change from vesicular to mixed and then to spherical with increasing reaction pressure. This change has been considered in the light of homogeneous nucleation theory. Pressures above 1 kbar ensure the formation of the spherical mesophase but prevent its coalescence leading to the formation of a mosaic solid. Possible factors preventing coalescence are considered. Upon heat treatment of the carbonized products at 2000°C and above, the morphologies of the carbon remain basically the same, but with some modifications resulting in a folded, oblate, or delaminated structure depending upon the previous carbonization pressure.

### 1 Introduction

It has been recognized that the formation of liquid crystal structures, namely mesophase, during carbonization of certain organic substances is directly related to the structures of the resulting carbons. Mesophase is the intermediate phase formed when an isotropic organic liquid is converted into a mosaic carbonaceous solid. Nematic mesophases have been considered by Brooks and Taylor (1968), Dubois *et al.* (1970), Honda *et al.* (1970), and Marsh *et al.* (1971) in their studies on carbon production. This phase is distinguished in that upon carbonization it separates from the isotropic liquid as anisotropic spherical droplets, which tend to coalesce under certain pressure/temperature conditions to give a nematic texture. The discovery of conditions for the formation of the spherical mesophase has received the greatest attention.

From a thermodynamic standpoint, the effect of pressure is often competitive with that of temperature. In general, an increase in temperature tends to melt a solid and produce a less ordered system, while an increase in pressure tends to maintain an ordered phase. This creates the possibility that an isotropic liquid phase of a carbonizing system may be favorably transformed, under pressure, into an optically anisotropic liquid crystal. This study describes the effect of pressure on carbonization and its relationship to the graphitizability of the resulting carbon.

### 2 Experimental

#### 2.1 Materials

Anthracene manufactured by Aldrich Chemical Company was used in this study. It had a purity greater than 99.9% and a melting point at atmospheric pressure of 215–217°C. Gold tubes of purity greater than 99.994% and palladium–silver alloy tubes from Matthey Bishop Company were used as sample containers during carbonization.

#### 2.2 Carbonization procedure

Cylindrical pellets of anthracene were sealed in gold tubes under nitrogen and carbonized in a hydrothermal pressure vessel. Details of this procedure are given elsewhere (Whang *et al.*, 1974). Selected runs were also made in palladium–silver tubes.

### 2.3 Graphitization procedure

The carbonized samples were given a further heat treatment at elevated temperatures of 2000 and 2800°C. Heating was performed under helium in a graphite resistance furnace.

### 2.4 Microscopic examination

The surface features and morphology of the carbonized and graphitized samples were examined using a JEOL (Japan Electron Optics Laboratory Co., Ltd.) Model JSM-2 scanning electron microscope. Internal fine structures and selected area diffraction patterns of some samples, carbonized or graphitized, were obtained with the aid of the Philips EM-300 electron microscope. Thin specimens for transmission electron microscopy were prepared by cutting with a glass knife equipped with an ultramicrotome or by scraping the samples against a clean metal plate.

### 2.5 Infrared absorption analyses

Infrared spectra of carbonized solid products were obtained on a Perkin-Elmer 621 grating infrared spectrophotometer by established procedures with KBr pellets containing 0.2 wt.% of the sample.

### 2.6 x-Ray diffraction analyses

x-Ray diffraction data were obtained with the aid of a Norelco x-ray diffractometer, with Ni-filtered Cu K $\alpha$  radiation. Interlayer spacings and average crystallite heights were obtained with the use of the Bragg and Scherrer equations, respectively, from (004) diffraction profiles. Sodium chloride was added as an internal standard, by the procedure described by Klug and Alexander (1970).

## 3 Results

### 3.1 Structures and morphologies of the pressure-carbonized products

Figure 1 summarizes the behavior of anthracene under various pressure/temperature conditions for a heating rate of 85 K min<sup>-1</sup> and zero soak time at maximum temperature. This rapid heating rate was used in order to perform 'isothermal' carbonizations. Curve A gives the lowest temperatures at which free-standing spherical mesophase was first encountered as pressure was varied from 0.34 to 2.07 kbar. Although an upper temperature limit was not determined, spherical mesophase was obtained up to 980°C at 2.07 kbar. Because the spheres obtained along curve A are hard and well formed, it is likely that they will prevail at temperatures above this

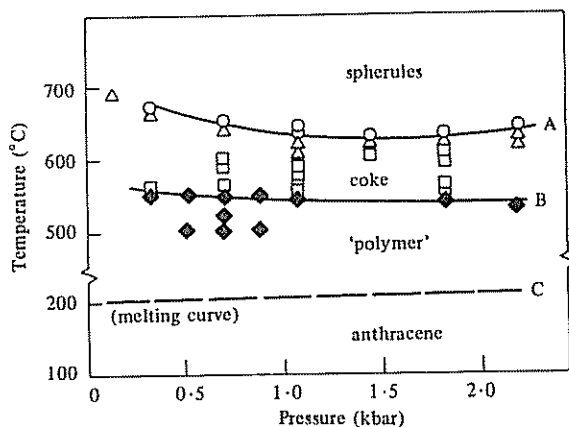


Figure 1. Carbonization products as a function of pressure/temperature conditions for a heating rate of 85 K min<sup>-1</sup> and zero soak time. ○ 100% spherules, △ mixed spherules and coke, □ 100% coke, ◆ 100% polymer.

curve. Curve B shows temperatures above which the quenched products are black in color, presumably the result of an increase in their content of conjugated double-bond systems. In the temperature interval between curves B and A, coke formation proceeded at increasing rates with increasing temperatures. At points taken  $10^{\circ}\text{C}$  below curve A, some mesophase spheres began to appear, immersed in an isotropic material. Curve C represents the melting curve of anthracene, based on observations made in a high-pressure opposed-anvil apparatus, which indicates a slope of about  $0.5\text{ K kbar}^{-1}$ . Between curves C and B, the product after quenching to room temperature was a yellow to yellowish-brown opaque solid, almost completely soluble in benzene or xylene. The products in this region consisted of a mixture of anthracene, its polymeric products, and gases which have been considered in a companion publication (Whang *et al.*, 1974).

Figure 2 shows the influence of heat treatment conditions on the first appearance of spherical mesophase. Curve D is redrawn from a part of curve A in figure 1. Curves D and E show that the lower the heating rate up to maximum temperature, the lower the temperature at which the formation of the spherical mesophase commences. Curves E and F show the influence of soak time, where an increasing soak time lowers the temperature for the formation of mesophase spheres. Figure 2 also shows the pressure/temperature conditions in which characteristic morphologies are obtained: vesicular, mixed, and spherical. At pressures below about  $0.5\text{ kbar}$  and temperatures above about  $550^{\circ}\text{C}$  an anisotropic vesicular solid is formed, when a heating rate of  $6.5\text{ K min}^{-1}$  is used. In the intermediate pressure region, from about  $0.5$  to  $0.85\text{ kbar}$ , a mixed vesicular-spherical structure is observed.

Figure 3 illustrates the major changes in x-ray diffraction profiles of the solid formed, that is from the polymer to the spherical mesophase, as temperature is increased along the  $1\text{ kbar}$  isobar. All but the strongest x-ray peak for the  $540^{\circ}\text{C}$  polymer disappears upon heat treatment to  $650^{\circ}\text{C}$ . For the  $650^{\circ}\text{C}$  spherical mesophase, all polymer peaks have disappeared and a weak (002) diffraction peak from the trigonally bonded carbon structure has appeared.

Infrared spectra in figure 4 also indicate the marked changes in chemical bonding to be found over the temperature range covering the production of chars to spheres under the  $1\text{ kbar}$  isobar. Spherical materials exhibit no detectable C-H in-plane bending, as indicated by the disappearance of the band at  $998\text{ cm}^{-1}$ . The stronger peaks indicating C-H out-of-plane bending at  $957$  and  $886\text{ cm}^{-1}$  and skeletal deformation at  $476\text{ cm}^{-1}$  are sharply reduced. Background intensities increase markedly, owing to a strong absorption throughout the entire range of wave numbers.

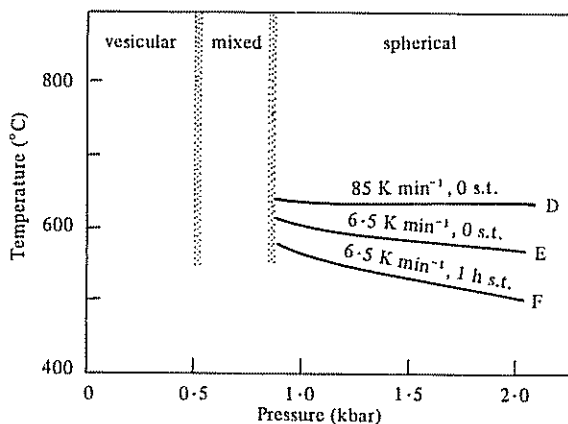


Figure 2. Influence of heating rate, soak time (s.t.), pressure, and temperature on morphology of anisotropic mesophase.

Figure 5 shows typical morphologies of pressure carbonized anthracene. The bulk vesicular sample is a continuous, hard anisotropic solid, containing numerous pores. On the other hand, the discrete spherules form an impalpable mass. The mixed morphologies, being made up of spheres variously embedded in anisotropic material, yield solids of moderate strength. Associated reaction products in each case also included small amounts of gases and volatile liquids and a thin film of brittle, glassy char formed on the surface of the gold tubing.

Figure 6 shows the rigidity of the mesophase spheres. The spheres were formed at 600°C and 2.07 kbar, at zero soak time. They were extracted with benzene, dried, and then isostatically pressed in a pliable, sealed gold tube at the same pressure/temperature conditions for 20 min. The spheres show some damage at points of contact, but there is no evidence of fusion, extensive compaction, or distortion, despite unit stresses at the points of contact being much higher than the applied pressure of 2.07 kbar.

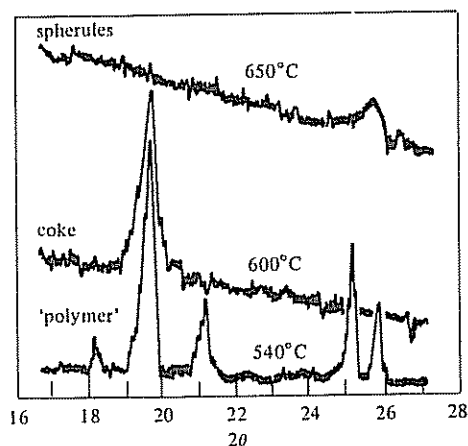


Figure 3. x-Ray diffraction profiles of products obtained by heating anthracene at temperatures between 540 and 650°C at 1 kbar and zero soak time.

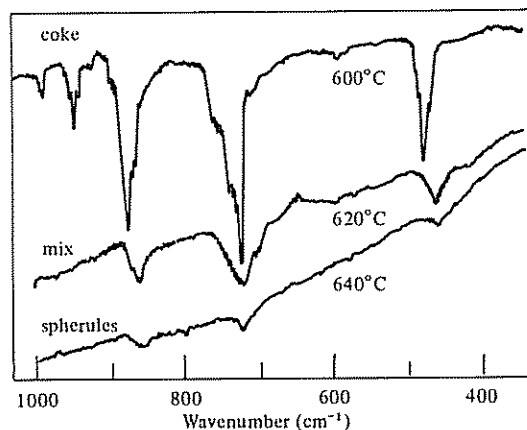
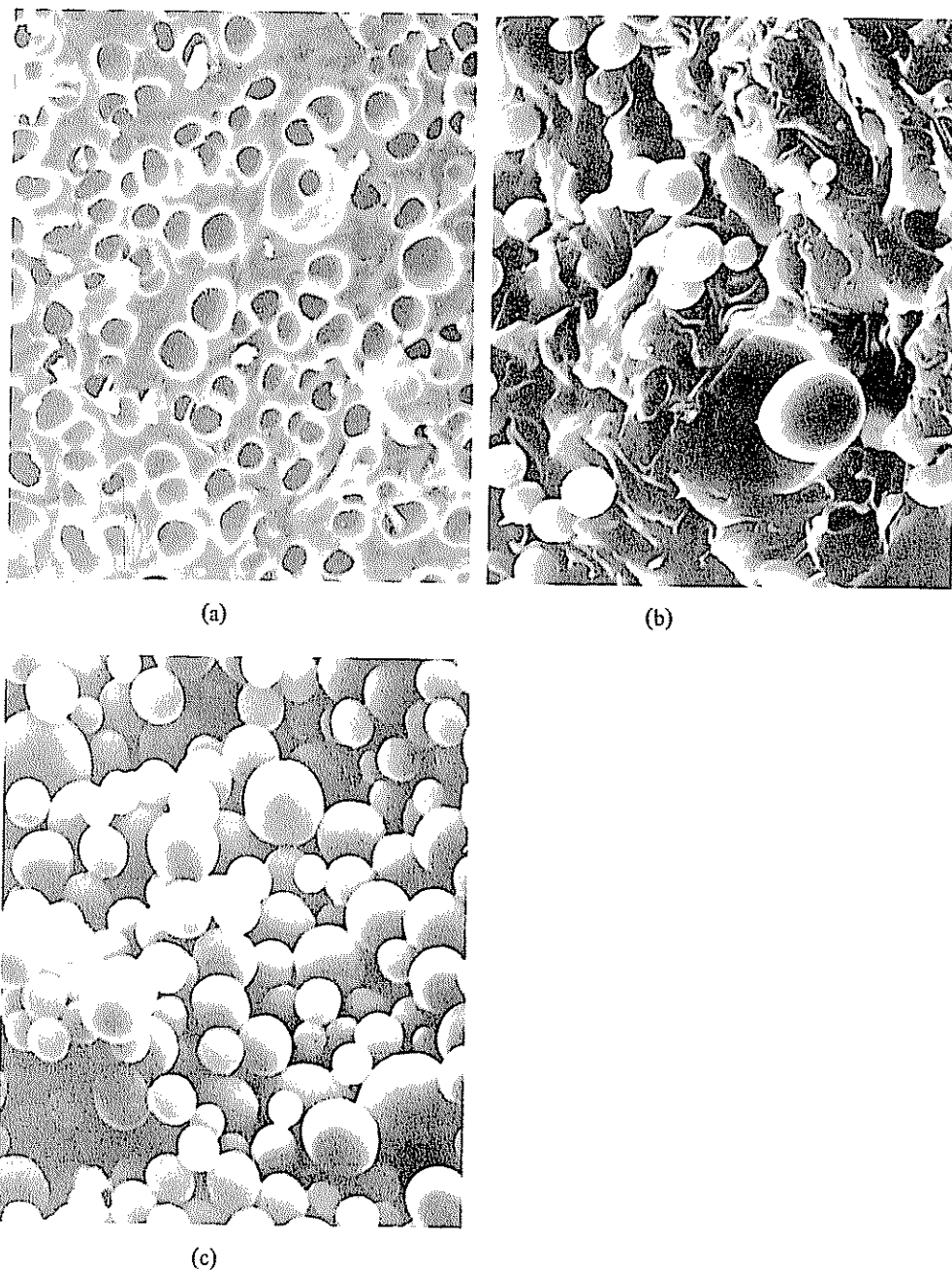


Figure 4. Infrared spectra of products obtained by heating anthracene at temperatures between 600 and 640°C at 1 kbar and zero soak time.



**Figure 5.** Scanning electron micrographs ( $\times 10^3$ ) showing typical morphologies of solids produced by the pressure carbonization of anthracene at  $6.5 \text{ K min}^{-1}$  and 1 h soak time. (a) Vesicular (0.5 kbar and  $550^\circ\text{C}$ ), (b) mixed (0.7 kbar and  $600^\circ\text{C}$ ), (c) spherical (2.0 kbar and  $600^\circ\text{C}$ ).

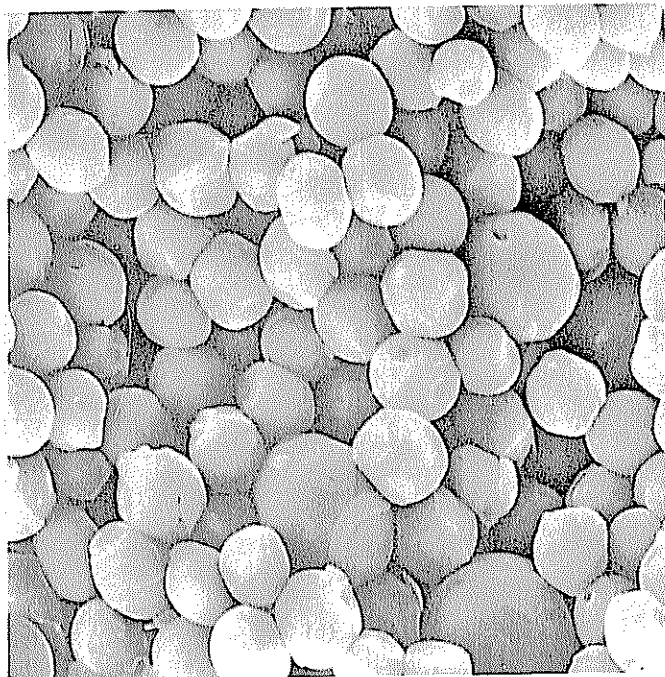


Figure 6. Scanning electron micrograph ( $\times 10^3$ ) of mesophase spheres resulting from recarbonization at  $600^\circ\text{C}$  and 2.07 kbar for 20 min of spheres originally formed at  $600^\circ\text{C}$  and 2.07 kbar at zero soak time. Heating rate was  $3.5\text{ K min}^{-1}$ . Capsule opened and spheres washed in benzene between runs.

### 3.2 Structures and morphologies of the graphitized products

A series of samples carbonized at  $600^\circ\text{C}$  for 1 h at various carbonization pressures was subsequently heat treated at  $2000^\circ\text{C}$  for 3 h and at  $2800^\circ\text{C}$  for 10 min under 1 atm of helium. The variation, with carbonization pressure, of crystallite height,  $L_c$ , and interlayer spacing,  $d$ , both calculated from (004) x-ray diffraction peaks, is shown in figure 7. Samples heated at  $2800^\circ\text{C}$  show a maximum crystallite size after carbonization at about 0.68 kbar. The average interlayer spacing is  $3.359\text{ \AA}$ , which is found to be lower than those obtained without the application of pressure by Weintraub and Walker (1971) and Isaacs (1970). Their values were  $3.363$  and  $3.365\text{ \AA}$ , respectively, after heating to  $2800^\circ\text{C}$ . Samples heat treated at  $2000^\circ\text{C}$

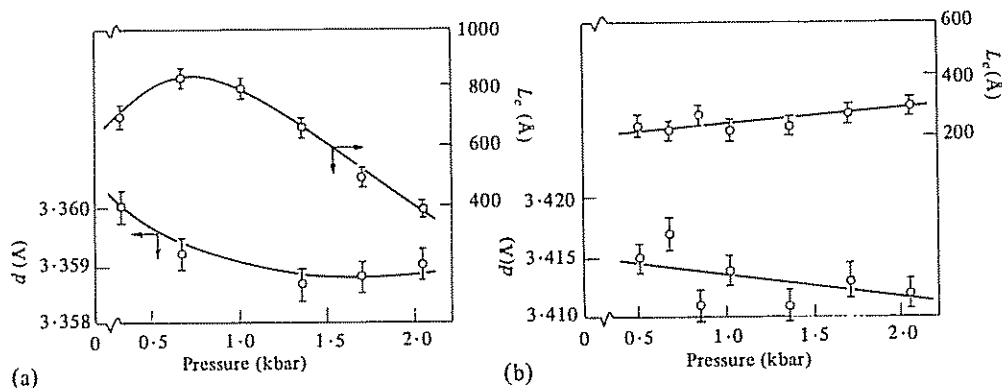
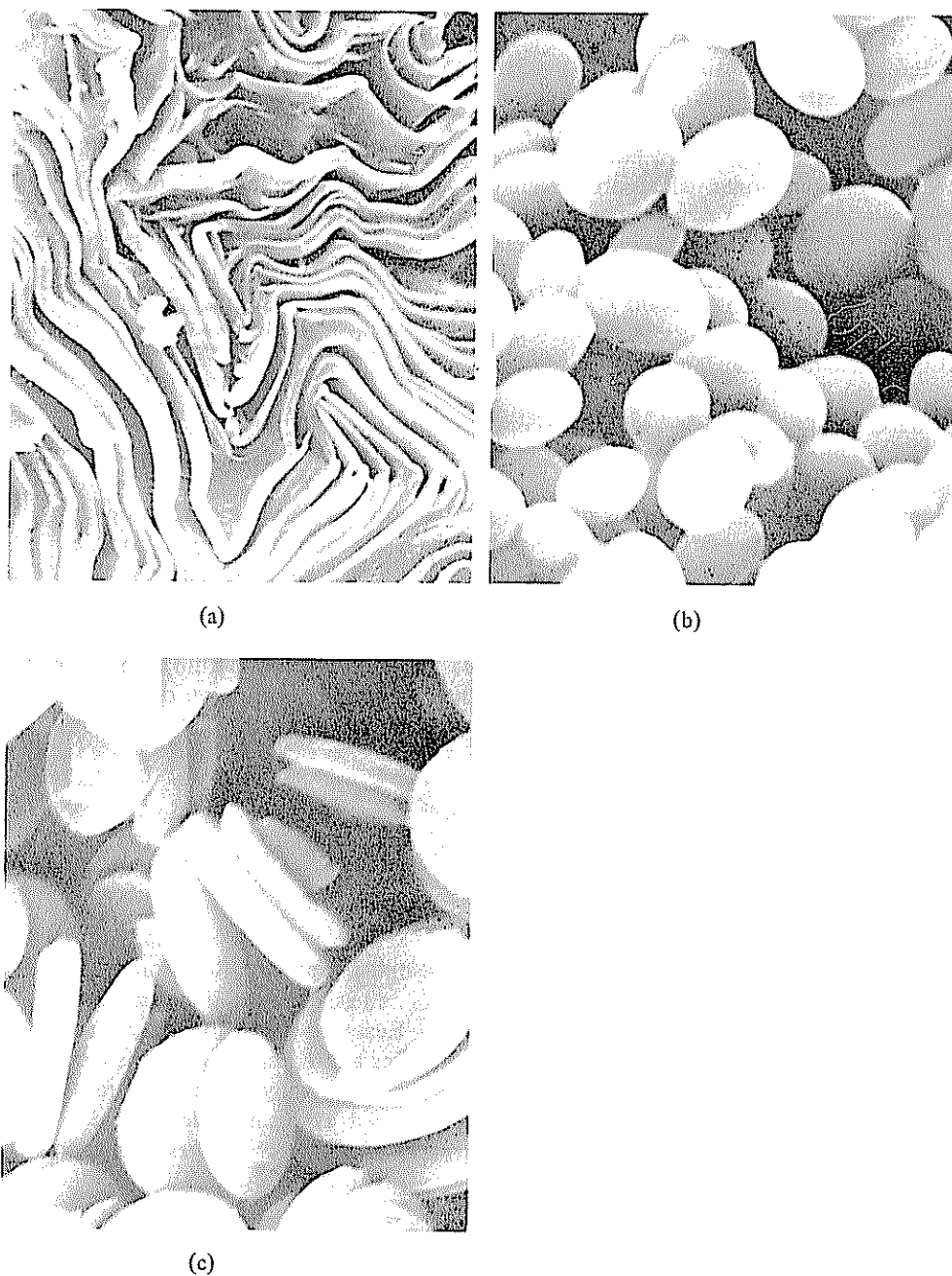


Figure 7. Average crystallite height,  $L_c$ , and interlayer spacing,  $d$ , of (a)  $2800^\circ\text{C}$  and (b)  $2000^\circ\text{C}$  carbons prepared from mesophase formed at  $600^\circ\text{C}$  under various pressures and a 1 h soak time.



**Figure 8.** Scanning electron micrographs ( $\times 10^4$ ) showing morphologies of carbons produced by heat treatment of carbonization products of anthracene at  $2000^\circ\text{C}$ . Carbonization conditions:  $6.5 \text{ K min}^{-1}$  and 1 h soak time. (a) Folded structure (carbonized at  $0.5 \text{ kbar}$  and  $650^\circ\text{C}$ ), (b) oblate structure (carbonized at  $1 \text{ kbar}$  and  $600^\circ\text{C}$ ), (c) delaminated structure (carbonized at  $2 \text{ kbar}$  and  $650^\circ\text{C}$ ).

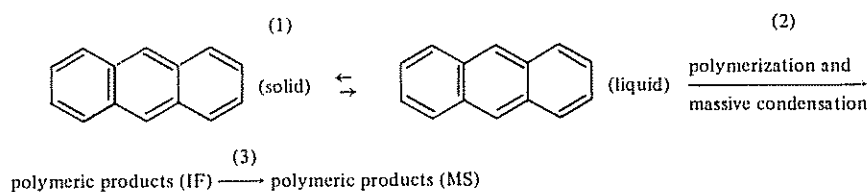
have interlayer spacings between 3.41 and 3.42 Å, which are less than the spacing for an ideally turbostratic structure, 3.44 Å. Bright field electron micrographs and selected area diffraction indicate the presence of some graphitic crystallites and a preferred orientation.

Morphologies of carbons heat treated at 2000°C remain basically the same as those for carbonized samples, but with some modifications. In figure 8 three distinct morphologies are shown, which are designated as folded, oblate, and delaminated structures. The folded structure resulted from heat treatment of vesicular mesophase, while the oblate and delaminated structures resulted from heat treatment of spherical mesophases, which were prepared by carbonization at 1 and 2.07 kbar, respectively. Further heat treatment to 2800°C produced no major changes in morphology over the 2000°C heat treatment. Delamination cracks did begin to appear in sample (b) and more delaminations appeared in sample (c).

#### 4 Discussion

As mentioned earlier, an understanding of conditions for the formation of spherical mesophase is of considerable importance, because the mesophase predetermines the ultimate structures and properties of the resulting carbon. The initial stages of mesophase sphere formation can be envisaged as a nucleation step in which nuclei begin to appear homogeneously from the isotropic phase.

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



where IF denotes an isotropic fluid, and MS a mesophase sphere. Reaction step (1) is not expected to be influenced significantly by pressure levels used in this study because of the small value of  $dT/dP$  (see figure 1, line C). Reaction (2) is obviously affected through the influence of pressure on chemical kinetics and equilibrium. It is evident that the compositions of the polymeric products are remarkably different in reactions under pressure (Whang *et al.*, 1974) than those obtained by Evans (1969) for carbonization of anthracene without the application of pressure. However, reaction (3) is considered more important than the other steps insofar as nucleation of mesophase spheres is concerned.

It is assumed that the composition of the IF and MS phases are not much different when nuclei of MS begin to appear, but MS is certainly more ordered than IF. When transformation takes place, stable nuclei of the new phase, MS, first form and then grow into the parent phase, IF. On the basis of the similarity of the IF  $\rightarrow$  MS transformation to the melting-freezing phenomenon, free energy versus pressure in the IF  $\rightarrow$  MS transformation can qualitatively be sketched as shown in figure 9. Here, MS is stable at pressures greater than  $P_{eq}$ , which is the pressure of the equilibrium state ( $\Delta G = 0$ ). On the other hand, at pressures below  $P_{eq}$  IF is more stable than MS. However, this chemical free energy is not the only criterion for determining the final stable phase. Interfacial energy between the phases also contributes to the overall energy changes in the IF  $\rightarrow$  MS transformation. The



homogeneous nucleation theory (Chalmers, 1964) can be used to show (Whang, 1973) that there may be a pressure,  $P_n$ , along the curve of overall free energy change,  $\Delta G_r$ , at which the free energy of nucleation is obtained upon the carbonization of anthracene under particular temperature/pressure conditions. On the basis of this study,  $P_n$  may be in the pressure range 0.68–0.83 kbar (680–816 atm) at about 600°C; it is probably located in the pressure region where  $\Delta G_r$  is at a maximum. For some pressure range the corresponding critical radii of nucleation fall in the region where rapid growth of discrete spheres can occur. At pressures in the region of nucleation it is not certain whether the morphologies are vesicular or spherical; that is mixed morphologies are often found. On the lower-pressure side the surface free energy predominates, while the chemical free energy is more influential on the higher-pressure side. It is reasonable that in a high-energy system the substance tends to form spheres in order to lower the energy.

From a thermodynamic point of view, coalescence of spheres is obviously a stabilizing process because of a reduction in surface area and of a consequent lowering of surface energy. Despite the favorable energy situation produced by coalescence, coalescence was hardly observed in this study of pressure carbonization. The number of collisions of particles per unit time has been calculated (Bikerman, 1958) from the theory of Brownian movement as

$$-\frac{dn}{dt} = \frac{4kTn^2}{3\eta} \quad (1)$$

where  $n$  is the number of spheres in  $1 \text{ cm}^3$ ,  $t$  time in s,  $k$  the Boltzmann constant,  $T$  the absolute temperature, and  $\eta$  the viscosity of the gas phase. At constant temperature and constant number of spheres the rate of coalescence,  $-dn/dt$ , is inversely proportional to  $\eta$ . For gases at ordinary temperatures and pressures the viscosity is independent of pressure and increases with temperature. However, as a gas is compressed, its behavior more resembles that of a liquid; viscosity increases with increasing pressure and decreases with increasing temperature (Hamann, 1957). Thus, it is to be expected that increasing pressure would decrease the frequency of coalescence.

In this carbonization system, the principal gaseous product was methane (Whang *et al.*, 1974). Let us consider a system of methane (80%)–propane (20%) as an approximate model phase in this carbonization system. On the basis of the data listed by Lee (1965), the viscosity of the mixture is estimated as approximately 700  $\mu\text{P}$  at carbonization conditions of 500°C and 1.7 kbar. This value of viscosity for the layer around each sphere can reduce the speed and closeness of their mutual approach and thus inhibit coalescence.

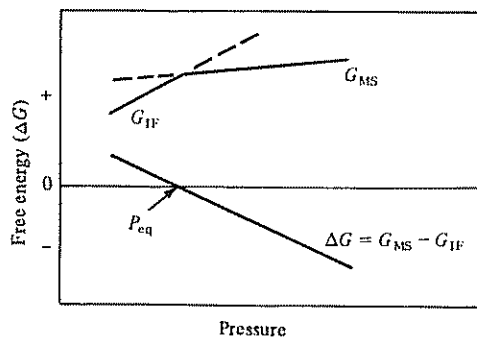


Figure 9. Free energy versus pressure in the region of a first order transformation.

In an attempt to vary the viscosity of the gaseous phase, palladium-silver alloy tubes were used as sample containers. At carbonization conditions these tubes are permeable to hydrogen, as confirmed by Hirano *et al.* (1973). The release of hydrogen would be expected to increase the average viscosity of the continuous phase, thus making this phase even more effective at preventing particle coalescence. Indeed, under these conditions negligible particle coalescence was found. However, a significant effect of carbonization in palladium-silver tubes was found: the average size of the individual mesophase spheres was larger than that found when carbonization was conducted in gold tubes. This suggests that removal of hydrogen decreases the effective number of nucleation centers in the system.

Another possible explanation for the formation of individual spheres can be drawn from emulsion theory. Here the system consists of a continuous phase as a dispersion medium, spheres as a dispersed phase, and some particular species in the gas phase as an emulsifier. The functions of the emulsifier are to facilitate emulsification and to promote emulsion stability. The emulsifying agent forms an adsorbed film around the dispersed spheres which tends to prevent their coalescence. Also there may be electrostatic charges around the spheres which induce an electrical double layer. If the electrical double layer repulsion is greater than the London-van der Waals attractive forces between spheres, coalescence of the spheres will not take place.

In an attempt to substantiate the above explanation, a re-carbonization was carried out after removal of the gas phase and the adsorbed layers from spheres by extraction in benzene. Figure 6 shows many indented spheres. Indentation obviously results from compression, which is possible because all the volatile components of the original charge were removed. Despite the intense pressure, the spheres were not deformed greatly or fused in any way. This indicates that the spheres have considerable mechanical strength.

The morphologies of the spheres during carbonization substantially determined the morphologies of the final graphitized carbons. The structure inside the spheres, however, undergoes changes toward more ordered stacking arrangement of the layers as graphitization proceeds at temperatures above 2000°C. During this process the morphologies are modified to become folded, oblate, or delaminated, depending on the pressure applied during carbonization. The folded structures might result from bulk displacement or deformation due to collapse and shrinkage of pores, while the oblate structures result from an increasing anisotropic character as the development of order and approach to the interlayer spacing of perfect graphite are established upon heat treatment. Whether the particles delaminate upon heat treatment is thought to depend primarily on the extent of crystallite alignment. The greater the crystallite alignment, the greater the stresses which are set up in the particle upon cooling, because of the major differences in the thermal expansion coefficient in the *a* axis and *c* axis directions in the graphite crystallite. Stresses are relieved by the formation of delamination cracks running in a direction perpendicular to the *c* axis of the carbon crystallites.

## 5 Conclusions

The morphology of the carbonaceous solids formed upon the carbonization of anthracene is markedly affected by pressure. At pressures above ~1 kbar spherical particles in the 3–10 μm diameter range can be formed. The temperature at which spherical particle formation is observed depends upon the heating rate, soak time, and pressure level; it is as low as 500°C for a pressure of 2.0 kbar, a heating rate of 6.5 K min<sup>-1</sup>, and a soak time of 1 h. Prevention of coalescence of the mesophase spheres is attributed to the presence of a viscous layer of reaction products (primarily methane) surrounding each sphere. The morphology of the carbons produced upon

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heat treatment of the carbonized products to temperatures of 2000°C and above depends strikingly upon the morphology of the carbonized solid.

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