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PRECURSOR STATES FOR THE GRAPHITIZATION OF NAPHTHALENE, ANTHRACENE, PHENANTHRENE AND CHRYSENE

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ABSTRACT

During carbonization, graphitizable aromatic organic compounds such as naphthalene, anthracene, phenanthrene and chrysene pass through a liquid or plastic-state mesophase of optical anisotropy, the lifetime of which is limited by its hardening to a semi-coke. Reflected polarized-light micrography, using cross polarizers with a gypsum plate, has been employed to characterize the carbonaceous mesophases of the different samples.

INTRODUCTION

Organic materials, which ultimately give rise to graphitizing carbons, pass through a fusion stage during carbonization, which generally occurs in the temperature range 350–600°C. This is one, but not the only, necessary condition for graphitizable organic materials. Recent studies by several groups [1–5] on the structural conditions for graphitizability have demonstrated the significance of the mesophase transformation which takes place as a precursor to graphitization. This transformation is a liquid-state structural transition in which the large planar aromatic molecules formed by the reactions of thermal cracking and aromatic polymerization become aligned in a parallel array to form an optically anisotropic liquid crystal. In the initial stages of nucleation and growth, the carbonaceous mesophase appears as small spherules suspended in the optically isotropic matrix with a simple structure [1]. The layer planes of the simple spherules are stacked perpendic-

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ularly to the polar diameter, and curve to meet the interface of the isotropic phase normally. As carbonization progresses with increasing temperature and duration of heat-treatment, the growing mesophase spherules, which are more dense than the isotropic parent phase, sink to the bottom of the container. When spherules meet, coalescence occurs to produce larger droplets, eventually leading to a bulk mesophase. When viewed microscopically with cross-polarizers, the bulk mesophase displays a complex ensemble of extinction contours. The polarized-light extinction contours display nodes and the characteristic Maltese-cross patterns.

The processes of formation, coalescence and deformation of the plastic mesophase establish the basic elements of the graphite microstructure and so mesophase formation is essentially a precursor state for the graphitization of organic compounds.

The present work has been undertaken in an attempt to gain information on the structures formed during the relatively short lifetime of the plastic mesophase developed during the pyrolysis of some simple aromatic organic compounds, such as naphthalene, anthracene, phenanthrene and chrysene.

EXPERIMENTAL

Micrographic preparation of samples for mesophase observation

The sample (~ 0.8 g) was heated in a sealed tube for carbonization at a fixed temperature for a fixed duration. The sample was then allowed to cool and when cold the sealed tube was opened inside a safety box. The sample was then separated from the tube, dried and embedded in a cold-setting mounting resin.

When set the mounted sample was then ground on progressively finer grades of waterproof silicon carbide paper (120 to 600 grit). Subsequent polishing was done with Hyprez diamond lapping compounds (6 μm followed by 1 μm) on a wet polishing silk cloth. Final polishing of the sample was carried out with high-purity Linde α-alumina powder. Final polishing resulted in a highly polished surface with a bright lustre, characteristic of the carbonaceous mesophase which proved suitable for observation by polarized-light microscopy.

Polarized-light micrography

Samples prepared in the above manner were observed and photographed with a Reichert "Metabert" polarizing microscope using reflected polarized-light. Colour photographs of the mesophase spheres and of subsequent heat-treated samples were obtained using Kodak High Speed Ektachrome E.T. 135-20, 35 mm film. The coloured mesophase spheres were produced by the insertion of a gypsum plate inclined to the analyser at an angle of 45° and placed between the analyser itself and the sample under observation. The analyser and polarizer remained crossed with respect to each other. This is the so-called sensitive tint technique [3].

RESULTS AND DISCUSSION

Polarized-light photomicrographs of selected mesophase spheres and of subsequent heat-treated samples are presented in Figs. 1–12, of which Figs. 1–3 are of naphthalene, 4–6 are of anthracene, 7–9 are of phenanthrene and 10–12 are of chrysene. Typical mesophase spherules for naphthalene are

Fig. 1. Mesophase spherules in naphthalene heat-treated to 538°C for 5 h.

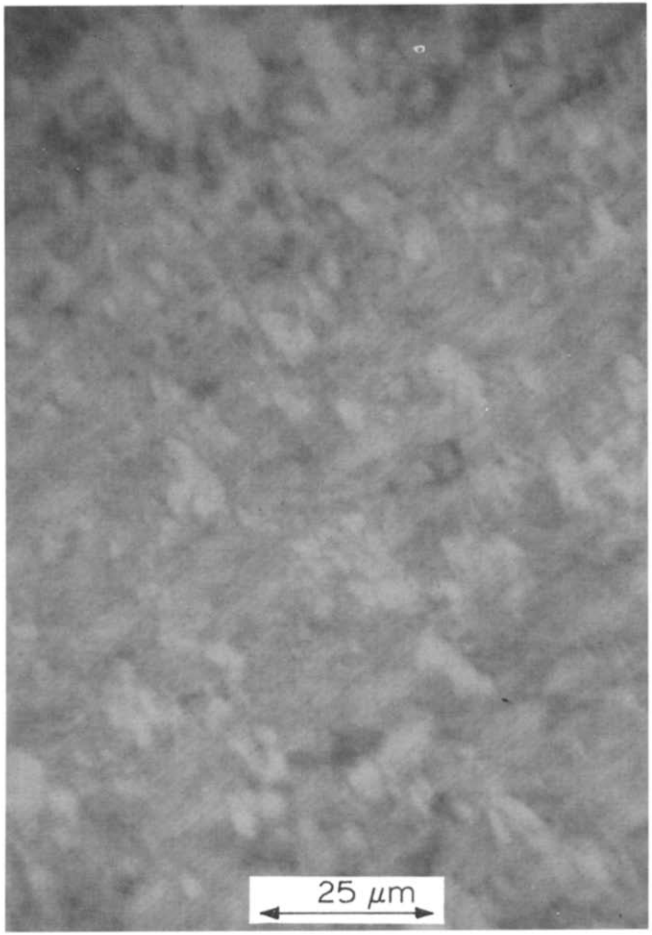

Fig. 2. Mesophase development in naphthalene heat-treated to 545 °C for 5 h.

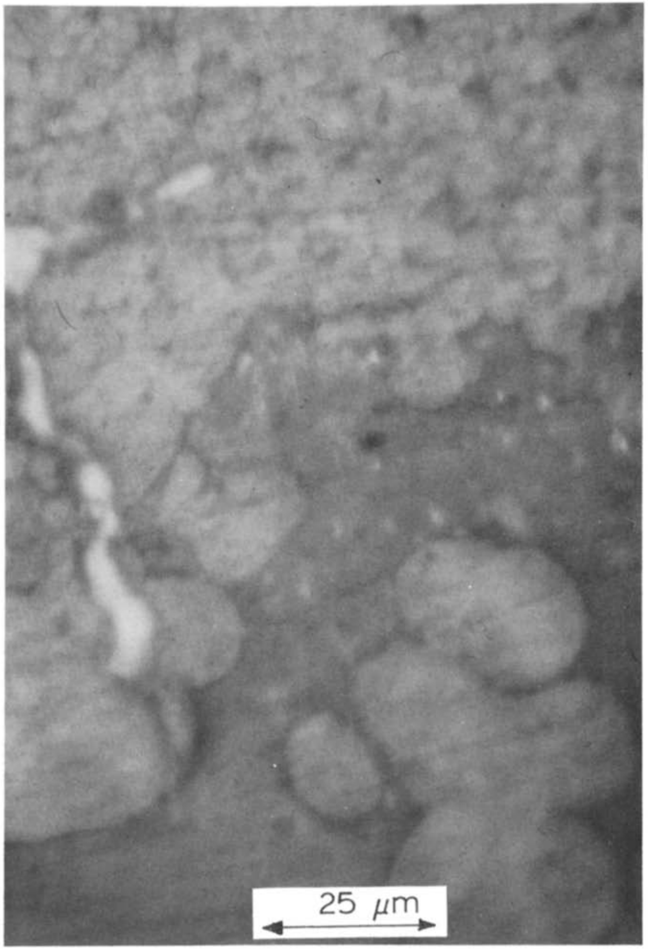

Fig. 3. Mosaic formation in napthalene heat-treated to 567 °C for 5 h.

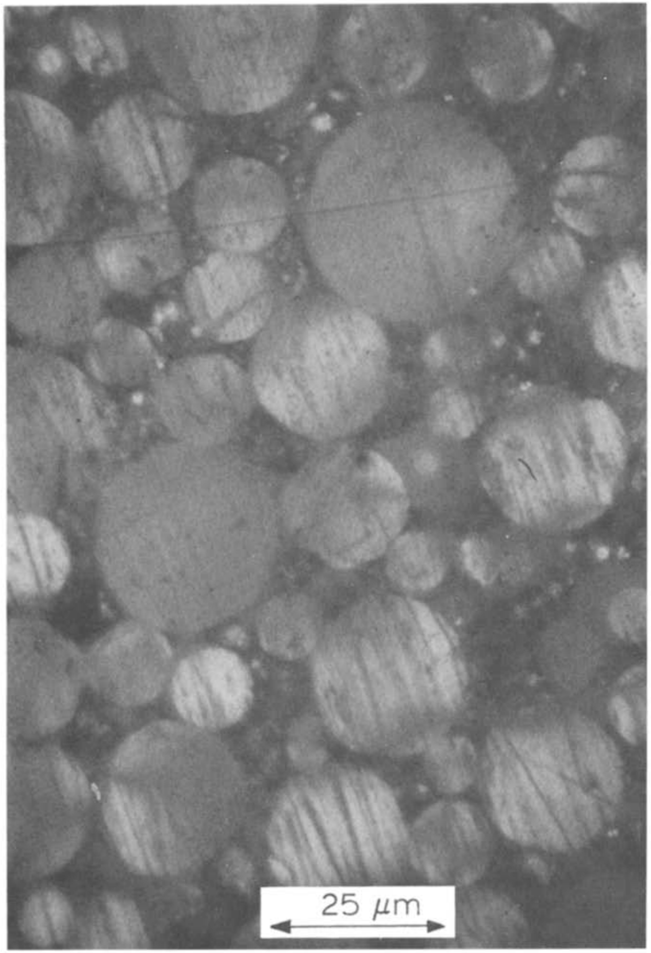

Fig. 4. Mesophase spherules in anthracene heat-treated to 460 °C for 2 h.

Fig. 5. Mesophase development in anthracene heat-treated to 480 °C for 2 h.

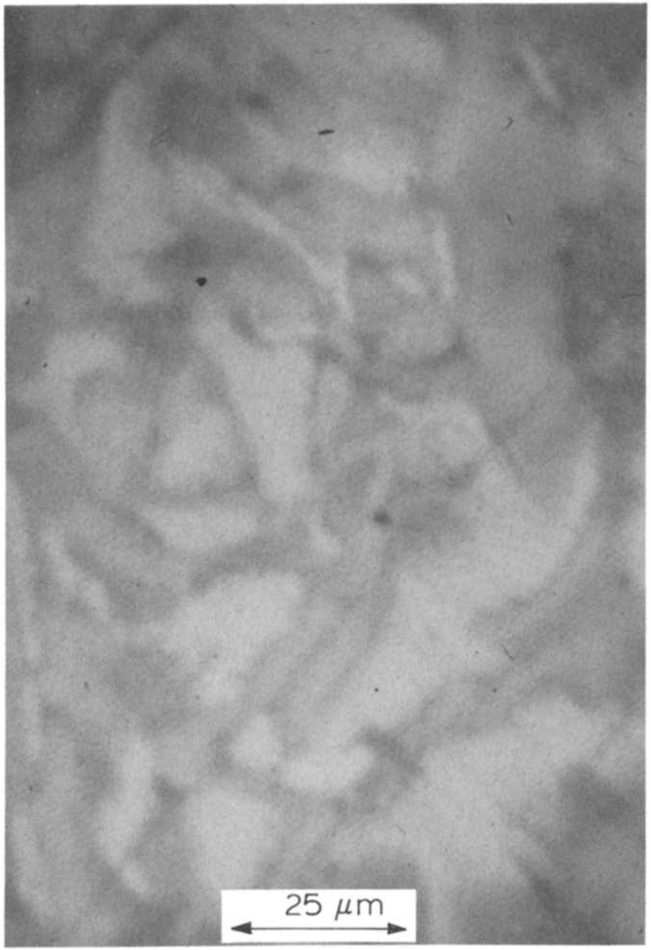

Fig. 6. Mosaic formation in anthracene heat-treated to 531°C for 4 h.

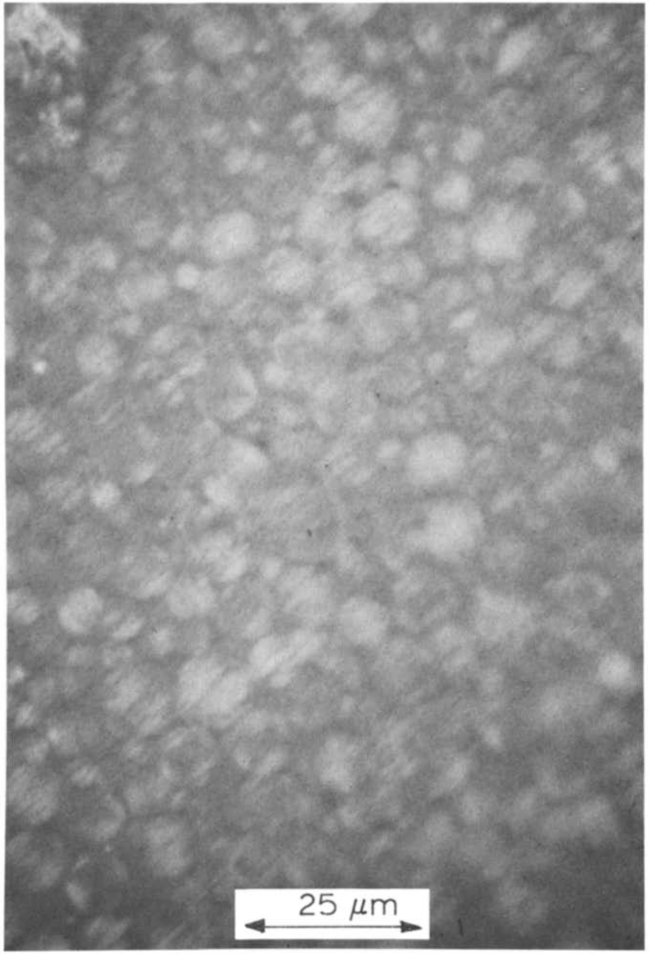

Fig. 7. Mesophase spherules in phenanthrene heat-treated to 530°C for 5 h.

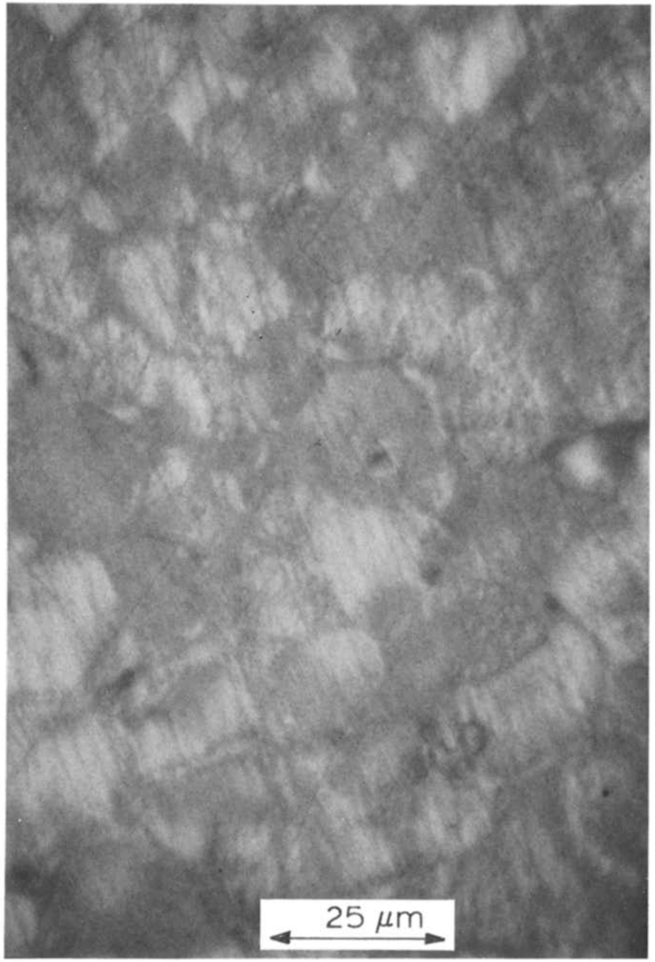

Fig. 8. Mesophase development in phenthrene heat-treated to 542° C for 5 h.

Fig. 9. Mosaic formation in phenanthrene heat-treated to 550° C for 5 h.

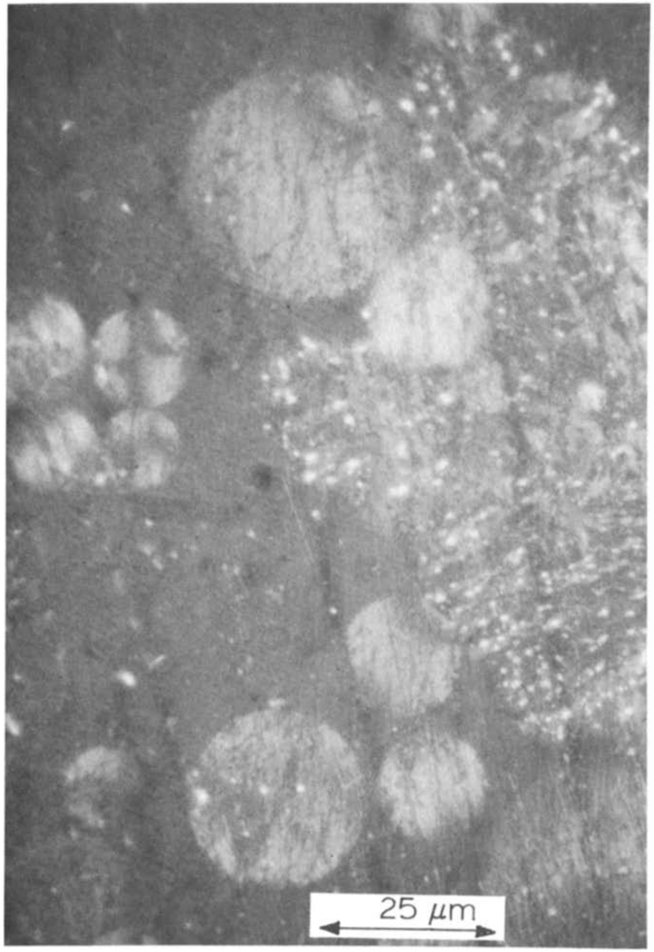

Fig. 10. Mesophase spherules in chrysene heat-treated to 510°C for 5 h.

Fig. 11. Mesophase development in chrysene heat-treated to 515°C for 5 h.

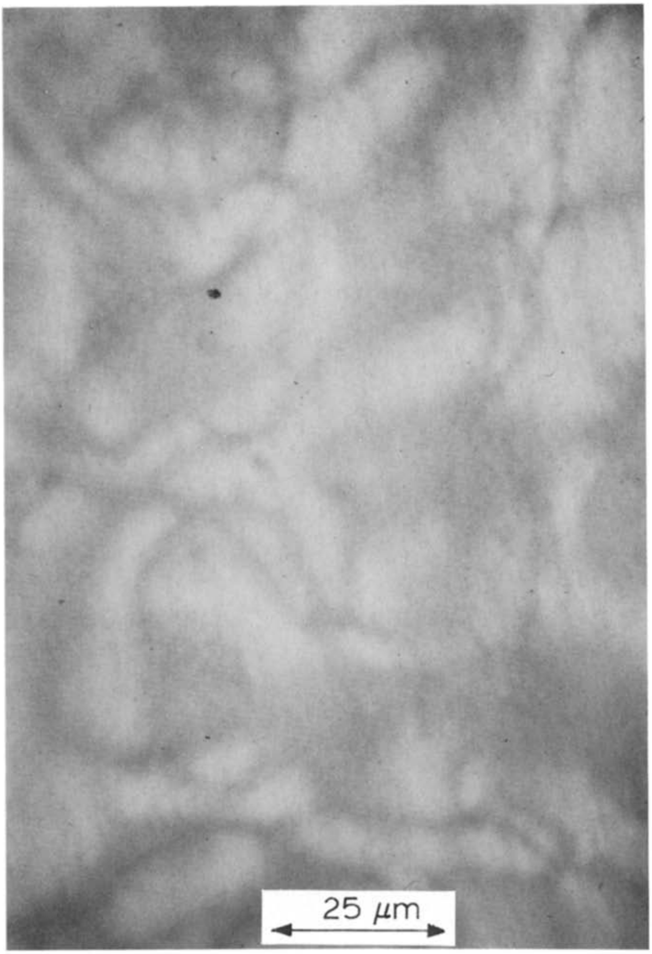

Fig. 12. Mosaic formation in chrysene heat-treated to 530°C for 5 h.

found to be present at 538°C (Fig. 1). These spherules coalesce to produce a bulk mesophase consisting of larger spherules at 545°C (Fig. 2). Finally, complete coalescence takes place to form a mosaic at 567°C (Fig. 3). The spherules appear to link up to form branch-like chains. This may arise from different surface tension–viscosity effects. From the typical coalesced mesophase of naphthalene, it is presumed that very minute spheres appear in this case during heat-treatment, but the characteristic Maltese crosses are not observed so distinctly. However, when they grow in size on coalescence at a higher temperature, the crosses become comparatively clear. Typical mesophase spherules for anthracene showing the characteristic Maltese-cross patterns are present at 460°C (Fig. 4). Coalescence occurs to give larger spherules at 480°C (Fig. 5). In this case, complete coalescence, forming a mosaic, occurs at 531°C (Fig. 6). In the case of phenanthrene, mesophase spherules just start to appear at a temperature of 530 °C (Fig. 7). Thereafter they start to coalesce, forming larger spherules. Figure 8 shows the picture of such a coalescence at 542°C. Figure 9 shows that complete coalescence, giving rise to a mosaic, takes place at 550 °C in the case of phenanthrene. Figures 10–12 are the polarized-light photomicrographs of chrysene at different heat-treatment temperatures. Figure 10 indicates that the spherules just appear at 510 °C. Figure 11 refers to the growth of the spherules at 515 °C as a result of coalescence. Finally, formation of mosaic on complete coalescence at 530 °C is presented in Fig. 12. The Maltese-cross pattern is markedly displayed in the case of chrysene.

CONCLUSIONS

The polarized-light photomicrographs (Figs. 1–12) obtained for naphthalene, anthracene, phenanthrene and chrysene at different heat-treatment temperatures and durations indicate that all the samples satisfy the most important criterion of the graphitizable organic compounds, i.e. the compounds pass through the carbonaceous mesophase transformation, fulfilling the general features of a mesophase and hence they are all graphitizable. Again, the DTA traces obtained earlier for the compounds under study [6] clearly indicate that endothermal processes of decomposition in the initial portions of the curves, a second criterion for a graphitizable organic compound, are typical in all samples and they are again all graphitizable.

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