Electron microscopic study on graphitization of bulk mesophases

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Two kinds of bulk mesophases separated by quinoline from polyvinylchloride (PVC) pitch and from 3, 5-xylenol-formaldehyde resin (XF) pitch were studied by high resolution electron microscopy. The ease of graphitization of both bulk mesophases has been examined by heat-treating them up to 1080 and 2600° C. PVC bulk mesophase mostly shows preferred long range orientation (aromatic carbon layers roughly parallel to each other), but also contains minor components where the molecular orientation occurs only over small distances, or not at all. When heat-treated at high temperature PVC bulk mesophase changes mainly into highly graphitized lamellar crystals. Similarly treated XF bulk mesophase does not show any preferred orientation and leads to porous non-graphitizable material.

1. Introduction

Poorly crystallized materials may be observed on a very small scale by high resolution electron microscopy techniques [1, 2]. They have been applied to carbonaceous products at very early stages of carbonization whether natural [3] or not [4, 5]. Size and shape of their elementary units have been determined as well as their textures.

Mesophase is known to be formed [6, 7] as an anisotropic phase issued from some pitch matrices during pyrolysis between about 350 and 500° C. In general coke is the solid obtained by heating organic matters at about 1000° C in an inert atmosphere, and carbon is obtained above 2000° C.

It has also been shown [8, 9] that the mosophase chemical composition strongly influences the degree of graphitization of the subsequent carbons. It is important from scientific and industrial points of view to determine microtexture during both carbonization and graphitization. There have, however, been few investigations using techniques of modern microscopy on heat-treated mesophases [10–12]. The present paper deals with two kinds of bulk mesphases separated from pitches and heat-treated at 1080 and 2600° C for determining their textural changes.

2. Experimental
2.1. Samples

Two kinds of bulk mesophases were used in this study. Starting materials are an industrial polyvinylchloride (PVC), and 3, 5-xylenol-formaldehyde resin (XF), synthesized in the laboratory from 1 mol of 3, 5-xylenol and 1 mol of formaline by using NH_4OH as a catalyst in air. PVC was heated to 430° C and kept at this temperature for 4 h (PVC4) and for 24 h (PVC24). XF was heated to 370° C and maintained at this temperature for 21 h (XF21). Heat-treatment was carried out in a nitrogen stream. Bulk mesophases were separated from these carbonized pitches with hot quinoline using glass filters. The yields of bulk mesophase were 95% for PVC4, 100% for PVC24 and 94% for XF21. It has been found from polarized light microscope observation that original PVC carbonized pitch shows coalesced mesophase spherules (coarse mosaic texture) in early residence times and that they develop to mainly fibrous texture with increase in residence time. PVC4 shows both coarse mosaic and fibrous textures, and PVC24 almost fibrous texture. On the other hand XF21 does not show any optical anisotropy. A scanning electron microscope study shows that XF meso-

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phases consist of small coalesced spherules ($<1\,\mu m$). XF has been reported to present a small mosaic texture under a polarized light microscope [13]. Small mosaic texture was, in fact, observed when XF was heated to 520 and 900° C.

The bulk mesophases were heated up to 1080° C at a rate of 4° C min^{-1} in a nitrogen atmosphere, then up to 2600° C at a rate of about 16° C min^{-1} in an argon stream.

2.2. Electron microscope techniques

Samples of bulk mesophases were ground in liquid nitrogen to avoid artefacts which could occur due to the plasticity of material. The other samples were ground at room temperature. Most of samples were deposited on carbon micro-grids. A Philips EM300 electron microscope was used at 100 kV. Before studying the samples it was verified from the following observation that no transformations of bulk mesophases occurred under the 100 kV electron beam in the time range of these observations: the same area in PVC4 mesophase was observed over the duration of 2 h under normal conditions, but no change of lattice-image and of dot size of the dark-field image were found. Electron microscope techniques [1, 16] such as selected area electron diffraction (SAD), bright- and dark-field and lattice-imaging were applied to the samples. The diameter of the aperture for bright- and dark-field was 0.17 Å^{-1}, allowing a resolution better than 8 Å.

3. Results

3.1. Bulk mesophases

The samples studied here are not homogeneous since the extent of the parallel orientation of the carbon layers varies from place to place. In some parts molecular orientation is long range, in others it occurs only over small distances, or not at all. In PVC samples large zones of preferred orientation are predominant, while in XF the lack of orientation prevails.

3.1.1. PVC4

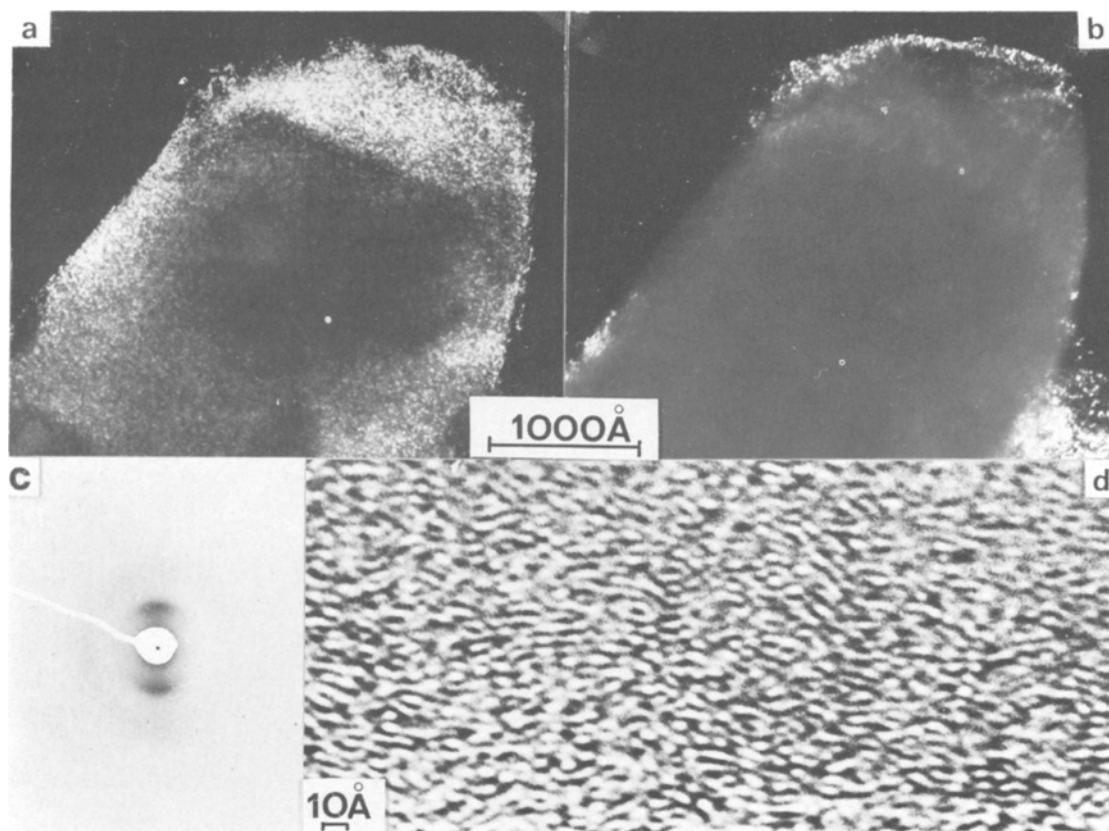In these samples the preferred orientation usually extends beyond 4000 Å. SAD patterns (Fig. 1c)

Figure 1 PVC4 bulk mesophase: (a) 0 0 2 dark-field images in the direction of preferred orientation, (b) 0 0 2 dark-field images in a 45° direction from preferred orientation, (c) SAD pattern, (d) lattice-imaging.
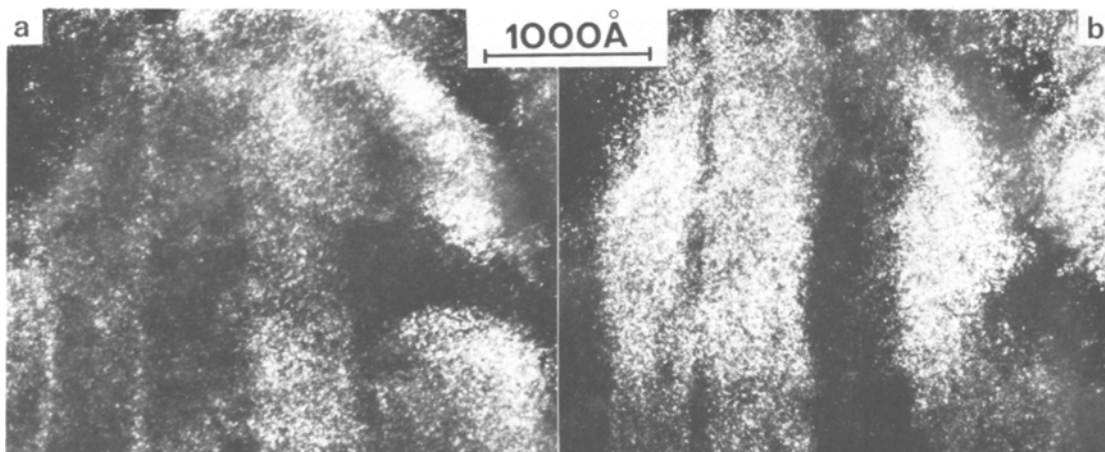
Figure 2 PVC4 bulk mesophase: 0 0 2 dark-field pictures with a 45° rotation of aperture position between (a) and (b).

therefore show strong 0 0 2 arcs corresponding to an about 60° angle. 0 0 2 dark-field images (Fig. 1a) obtained with the aperture centred on this arc present a high concentration of homogeneously distributed bright dots. These bright dots originate from the regions where the Bragg condition for the 0 0 2 reflection is fulfilled in a mesophase particle, i.e. where carbon layers are edge-on relative to the observation plane. Therefore, the size of the elementary diffracting regions can be directly obtained from the size of the bright dots, and their distribution from the rotation of the aperture on the 0 0 2 arc or ring. Their average size is usually below 10 Å. These dots entirely disappear as the aperature is moved along the 0 0 2 ring with a 45° rotation angle from the first position. The image then remains dark for any other aperture position such as 90° (Fig. 1b)* and 135°. Although misoriented (±30°) the carbon layer stacks represented by the bright dots have a strong preferred orientation which covers, for instance, the whole fragment seen in Fig. 1a. There are no carbon layer
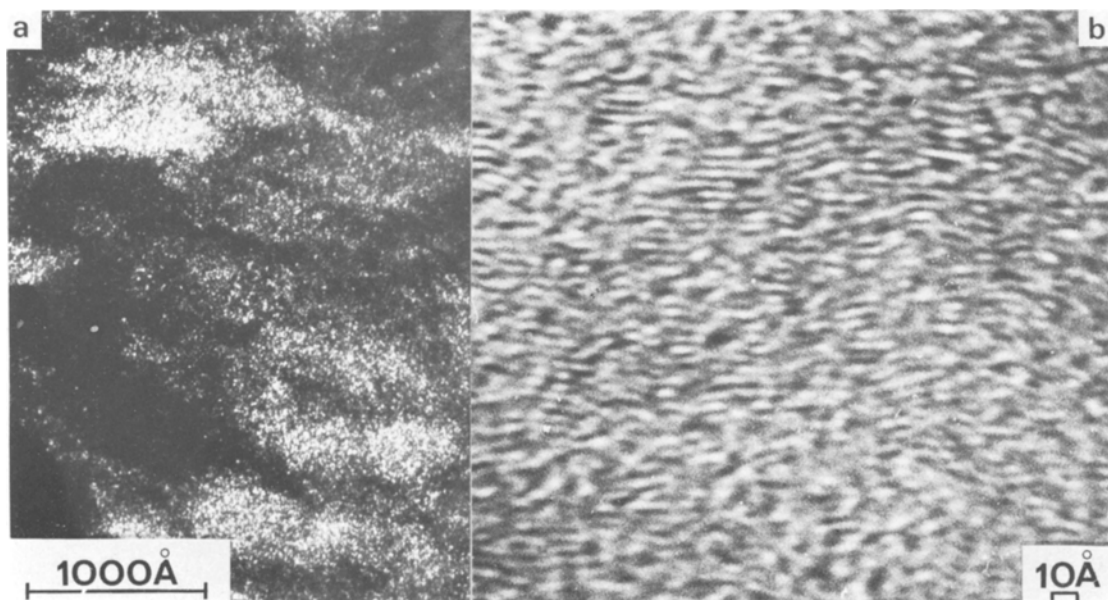

Figure 3 PVC4 bulk mesophase: elongated clusters of bright dots in 0 0 2 dark-field images, (b) PVC4 bulk mesophase: lattice-imaging corresponding to Fig. 3a.

*It should be noticed that bright dots appear along the edges of the broken fragment, corresponding to a carbon layer orientation parallel to the external surface. This is a common feature, often shown by lattice-imaging as well. It can be due either to a parasitic secondary nucleation of carbon or to a grinding effect during sample preparation.

stacks distributed at random in the particle since no bright dots are visible in Fig. 1b. Lattice-imaging illustrates these results well (Fig. 1d). It shows groups of 2 or 3 parallel fringes the length of which are under 10 Å. Although two successive stacks of fringes are 20 to 25° misoriented, they remain almost parallel over a very long range (4000 Å). Figs. 2a and b correspond to aperture positions rotated by 45° showing alternate parallel bands. By comparing the cluster positions in the two micrographs a regular arrangements of regions of molecular orientation is demonstrated. They are made of parallel bands with an alternate 45° preferred orientation change. Such a texture is often encountered in liquid crystals, but seldom in this type of bulk mesophase.

Nevertheless the sample is not homogeneous. It contains fairly well represented parts where the molecular orientation extends over distances so small that the SAD patterns show continuous 0 0 2 rings (the selector aperture limiting a field about 1 µm in diameter, the size of the area with the preferred molecular orientation, if any, is much smaller than 1 µm). As a matter of fact, in 0 0 2 dark-field images, bright dots are visible as elongated clusters about 500 Å in width and 1000 Å in length (Fig. 3a). Inside each cluster carbon layers are approximately parallel, but the misorientation among clusters is larger than the angular range of the aperture opening. Bright dot clusters are usually distributed at random in the particle since their position changes as the aperture moves along the 0 0 2 ring. Each bright dot is below 10 Å in size and is similar to those described

above. Lattice-imaging (Fig. 3b) shows a more striking misorientation among the successive groups of fringes than in Fig. 1d corresponding to the largest molecular orientation.

Finally, some regions of the sample do not show any orientation at all since the bright dots are homogeneously distributed for all the aperture positions on the 0 0 2 ring. This texture is not going to be described here (see Section 3.1.3) since it is a minor phase.

3.1.2. PVC24

In this sample the major phase also has a long range molecular orientation, but the two other components are no longer well represented. Nevertheless the size of the elementary units as well as the characteristic features of the sample are the same as for PVC4.

3.1.3. XF21

These samples are more homogeneous than PVC4 since they are almost wholly formed of fragments without any preferred orientation. In SAD patterns (Fig. 4b) the 0 0 2 reflections are almost invisible and the 10 and 11 bands also are very faint. In the 0 0 2 dark-field image the bright dots present a uniform dispersion for every aperture position (Figs. 4a and c). Their size is in the same range as above (<10 Å). Lattice-fringes are not usually observed (except along the edges of some particles) which has been attributed to the effect described in the footnote on page 704. From these data we conclude that the degree of ordering is very low and that there is no molecular orientation.
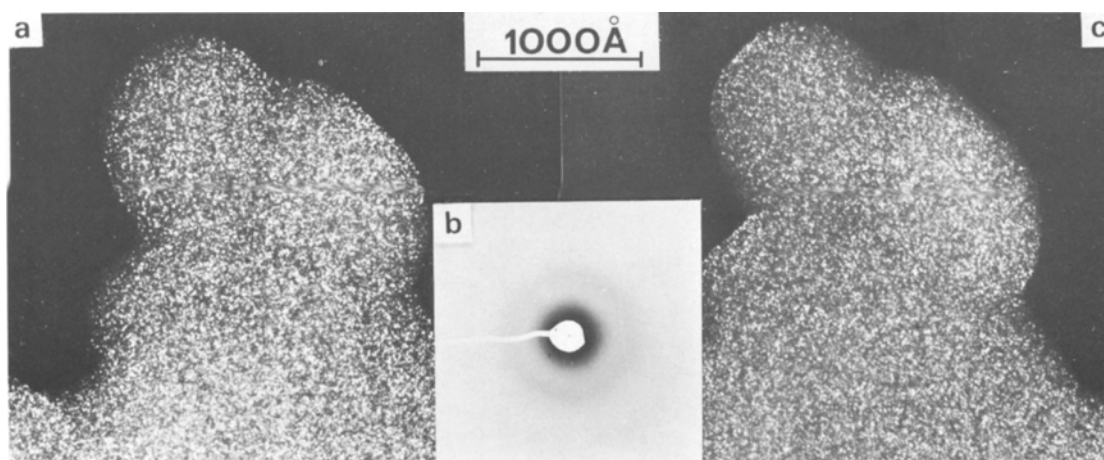

Figure 4 XF21 bulk mesophase: (a) and (c) 0 0 2 dark-field pictures with a 90° relative rotation of the aperture positions, (b) SAD pattern.
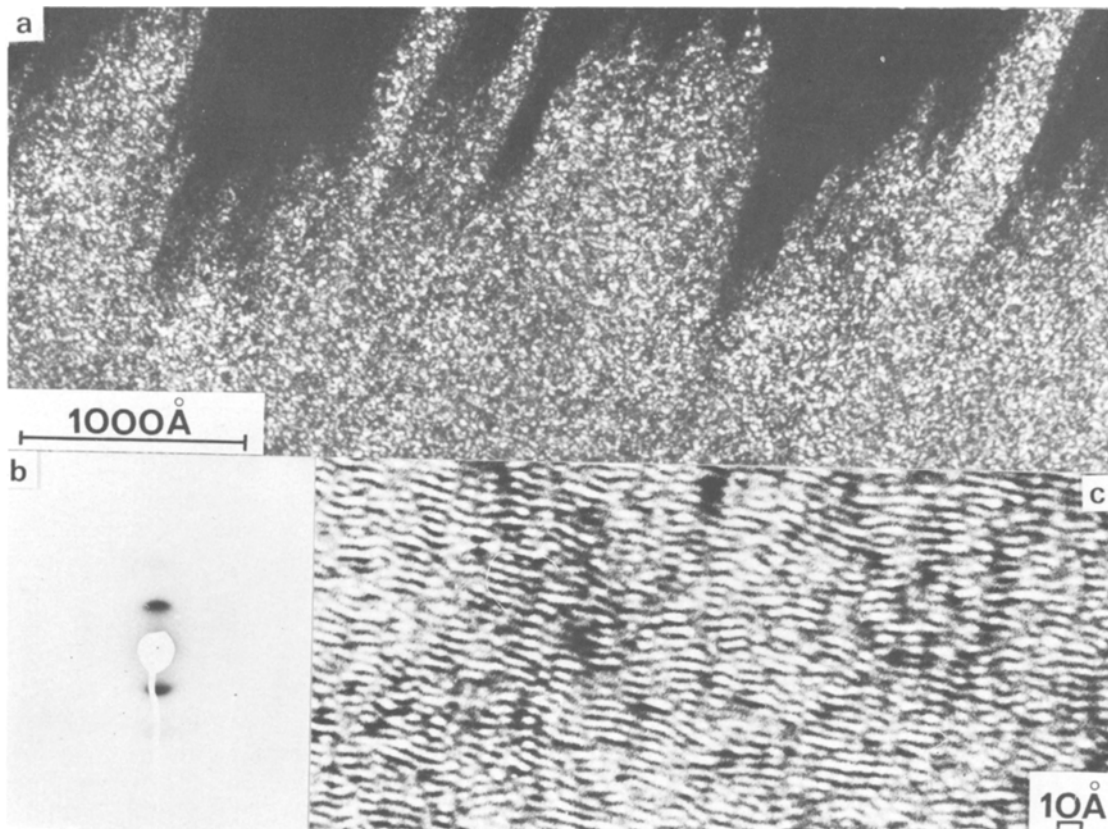
Figure 5 PVC coke: (a) 0 0 2 dark-field image, (b) SAD pattern, (c) lattice-imaging.

A molecular orientation restricted to very small regions (100 to 150 Å) appear in very few particles and will be described later on.

3.2. Cokes
3.2.1. PVC
Both PVC4 and PVC24 almost always show long range order. The SAD patterns show 0 0 2 arcs similar to the bulk mesophase ones, but 0 0 4 arcs now also appear (Fig. 5b). This corresponds to less distortion, i.e. an improvement of layer parallelism. The 0 0 l arc spreading is considerably less, which indicates a decrease in the misorientation from 60° to 35°. The width of the 0 0 l reflections is not changed and they are still very diffuse, the number of layers per stack should thus remain small. This phenomenon has been also observed in anthracene coke [14]. 0 0 2 dark-field pictures (Fig. 5a) correspondingly show bright dots approximately similar in size to those observed in bulk mesophases (their size is about 15 Å), but their intensity is much higher (improvement on layer parallelism). Lattice-imaging (Fig. 5c) agrees well with dark-field since fringes are parallel over

large regions (>1 μm). The number of fringes per stack is commonly 4 to 5.

The two minor textures shown in bulk mesophase (regions without preferred orientation, and molecular orientation extended over 500 to 1000 Å) have both disappeared. Few fragments containing very small clusters of bright dots (100 to 150 Å) may be found. They will also be described below.

3.2.2. XF21
Most of the samples consist of very small regions (100 to 150 Å) where molecular orientation appear. SAD patterns thus show continuous 0 0 2 rings (Fig. 6c), while 0 0 2 dark-field pictures show very small clusters of bright dots which, since their positions in the particle change as the aperture is moved around the 0 0 2 ring (Figs. 6a and b), must be distributed at random in the fragments.

3.3. Carbons
3.3.1. PVC
It has been found by X-ray diffraction that the interlayer spacing of this carbon is 3.37 Å and that
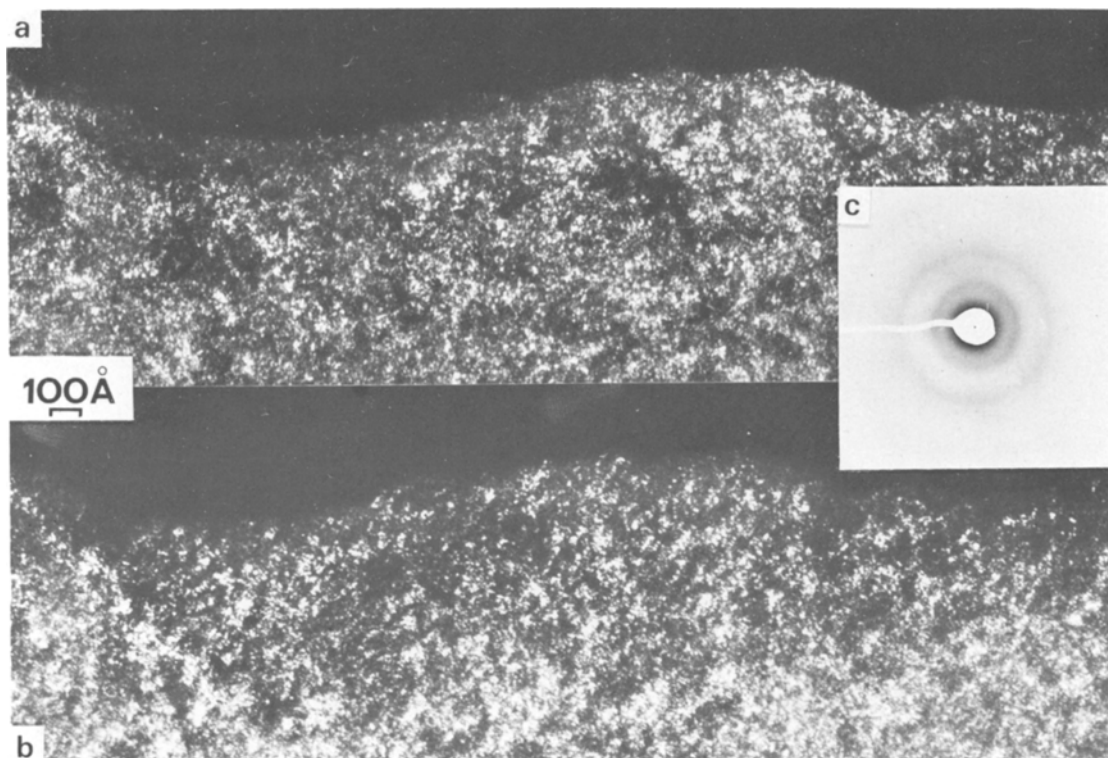
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Figure 6 XF coke: (a) and (b) 0 0 2 dark-field pictures with a 90° relative rotation of the aperture positions, (c) SAD pattern.

it is highly graphitized. Almost all the particles are lamellar and they tend to lie with their 0 0 1 plane parallel to the supporting film. Therefore, since they are thin, they are often distorted and folded, and therefore various kinds of SAD patterns are found. Some of them (particles lying flat) only show 1 0 0 and 1 1 0 rings. Other ones contain faint 0 0 2 reflections due to folds in the particle and 1 1 2 reflections coming from the distorted parts of the particle (Fig. 7b). The 1 0 1 reflection does not appear, probably because stacking faults are numerous. The rings are dotted, indicating a large diameter for crystallites. From SAD patterns it is obvious that the particles are graphitized. The 1 1 0 dark-field pictures (Fig. 7a) show a crystallite diameter larger than 3000 Å. In these pictures moirés fringes appear more or less superimposed to hexagonal shaped regions. These moirés patterns correspond to more than two superimposed crystallites, so that they cannot be used for measuring crystallite size directly. Nevertheless, the size of the region common to all the superimposed crystallites represents the minimum possible crystallite size (much smaller than the real

one). This is particularly noticeable in Fig. 7a in the region close to the arrows. The minimum size thus measured is about 3000 to 5000 Å which explains the dotted $h k 0$ diffraction rings in SAD patterns. Lattice-imaging (Fig. 7c) shows large flat unconstrained highly parallel layers.

A small number of particles have a porous texture which will be described later on.

3.3.2. XF21

Interlayer spacing as measured by X-ray diffraction is 3.45 Å and the structure is turbostratic. Sharp peaks corresponding to 3.36 Å and 3.43 Å do not appear. SAD patterns show 0 0 2 continuous diffuse bands (turbostratic structure). Some of them show either 0 0 2 arcs (Fig. 8a) or very faint 0 0 2 rings (Fig. 8b). This fact shows that a preferred orientation occurs in the material. It is not predominant, as shown by the fact that the 0 0 2 ring representing the fraction of random layer stacks (Fig. 9) clearly appears in most fractions of the material, notwithstanding its diffuseness. In bright-field images the fragments usually have the typical porous structure of hard
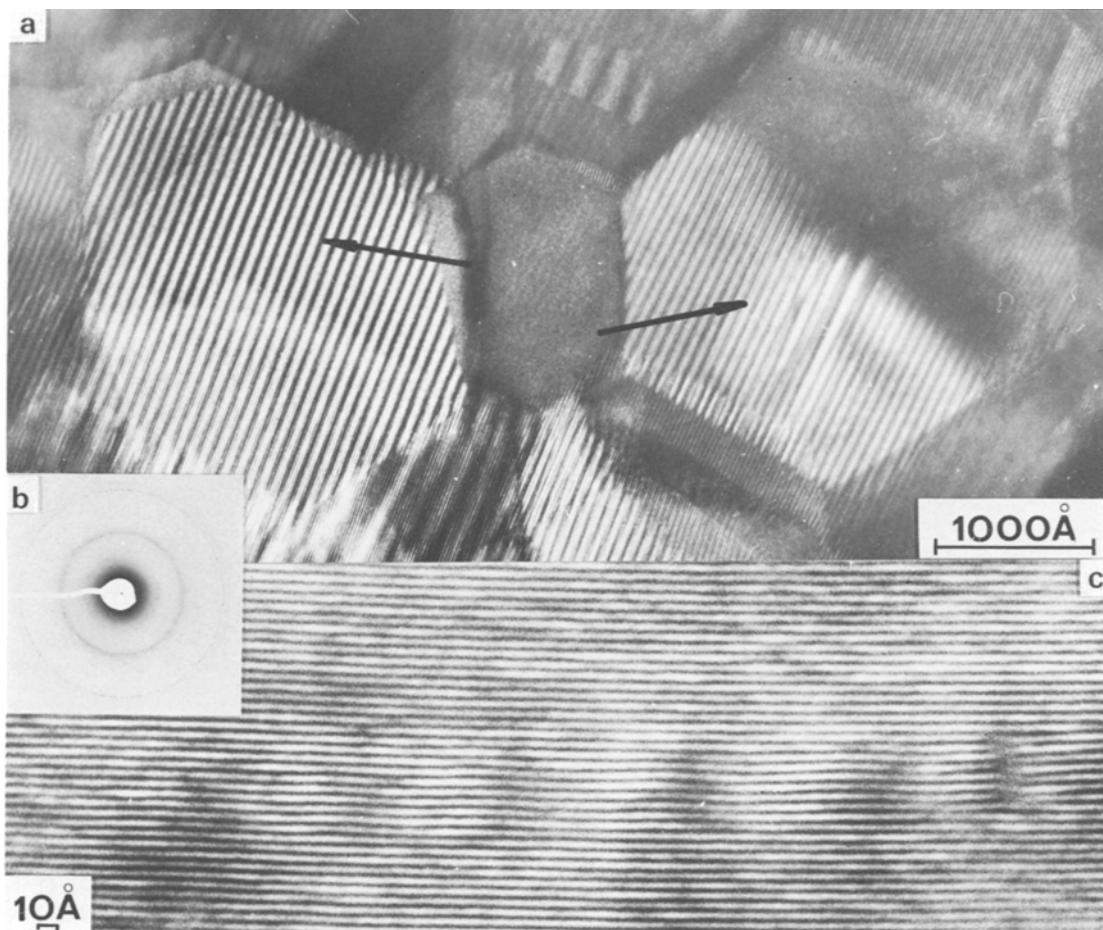
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Figure 7 PVC carbon: (a) 1 1 0 dark-field images, (b) SAD pattern, (c) lattice-imaging.
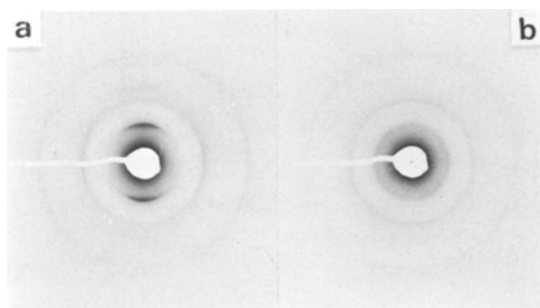

Figure 8 XF carbon: (a) and (b) SAD patterns.

carbons (Fig. 9) with pore walls distributed at random. They are roughly parallel in the particles which leads to such SAD pattern as Fig. 8a (Figs. 10a and b). Such particles have been observed in very small amounts [14] in other hard carbons (saccharose carbons, cellulose and so on), and they formed the whole samples in anthracites heat-treated at 2000° C [15, 16]. Occurrence of a preferred orientation has been explained by the effect of local shear stresses which tend to flatten the pores. In the present work many fragments present such an orientation, but their occurrence cannot be related to any particular preparation feature.

4. Discussion
4.1. PVC
The present work has shown that at the early stages of carbonization the PVC samples, although separated by quinoline from the pitch, are comparable to soft carbon precursors [1, 16] since they are mainly made of fragments with a long range preferred orientation. As soft carbons do when heat-treated, they lead to highly graphitized lamellae. Therefore an early quinoline insoluble (PVC4) separates into 3 phases which only differ in their preferred orientation extension (long range:
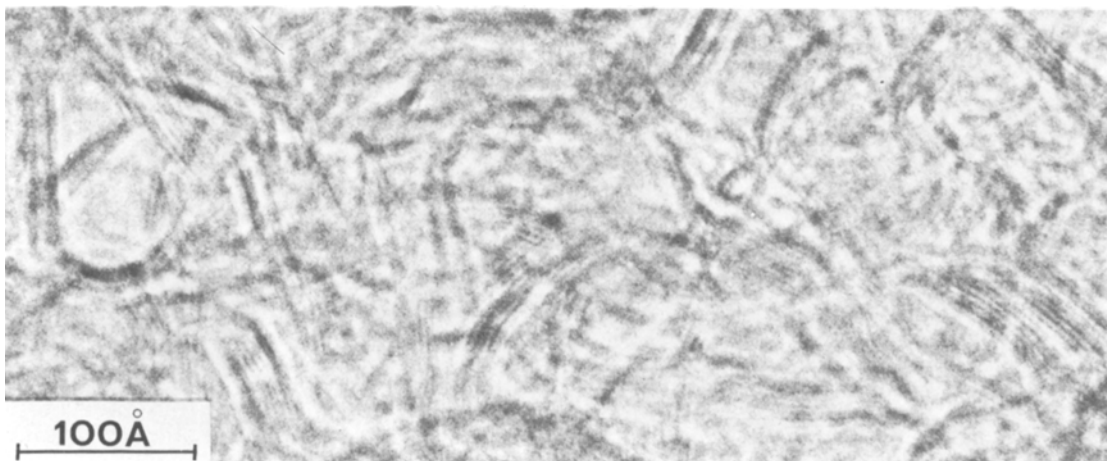
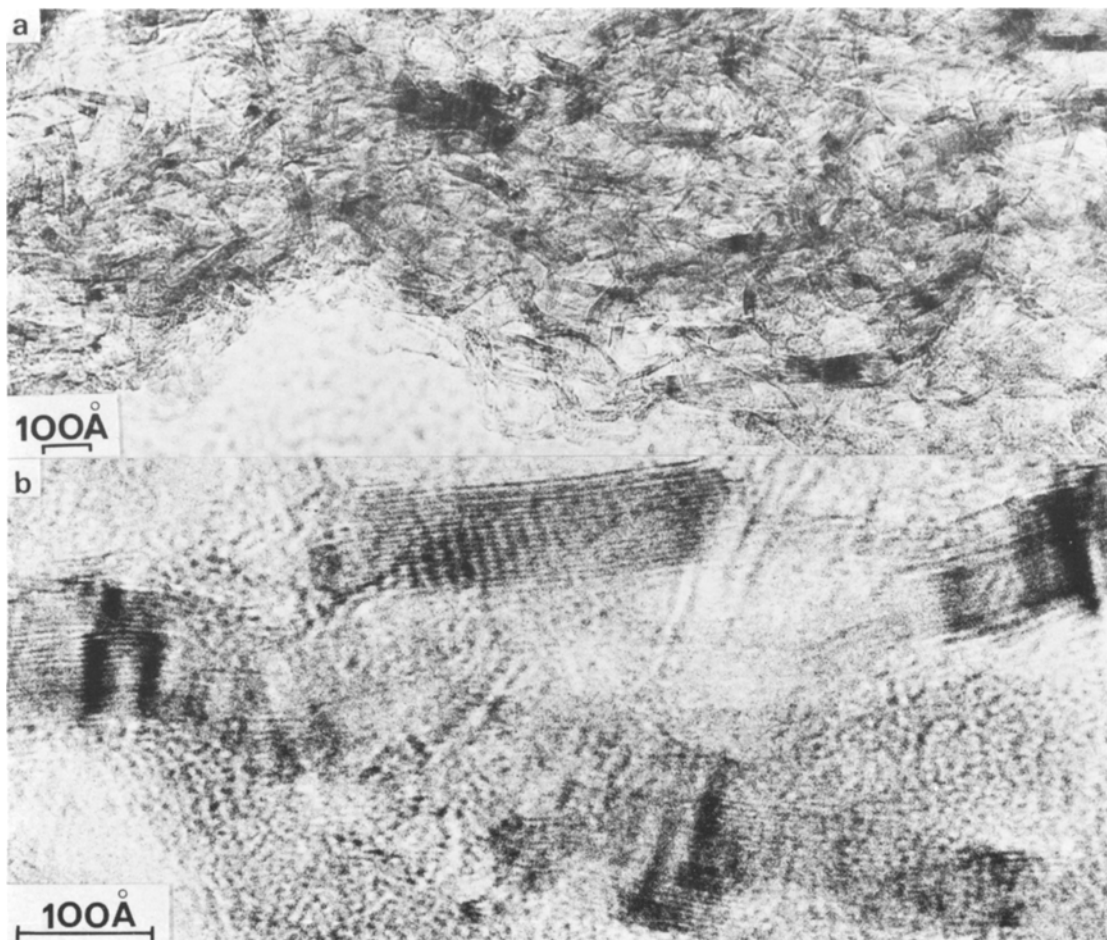*Figure 9* XF carbon: bright-field picture of porous structure.

Figure 10 XF carbon: (a) and (b) bright-field pictures corresponding to Fig. 8a.

>4000 Å, medium range: ≃500 to 1000 Å, no orientation). The medium range molecular orientation can be transformed into the long range one and disappear as the bulk mesophase is heat-treated at 1080° C. A further heat-treatment leads to graphitized lamellae. On the other hand, the particles without any preferred orientation evolve as typical hard carbons [1, 5, 14] since at 1080° C a very small range molecular orientation appears (100 to 150 Å) as a porous structure preventing graphitization.

Such "parasitic" phases are infrequent in PVC24, which indicates their tendency to disappear during the mesophase ageing which precedes quinoline treatment.

4.2. XF

XF samples act as hard carbons, a fact which is not clearly understood at present. Rigidity of its precursor polymer may have been increased by oxidation (reticulation) since XF resin was sythesized in air for a long time (7 h at 110 to 120° C, then 24 h at 130 to 160° C) and preserved in air, and then the oxidized precursor polymer was separated by quinoline. It should be noticed that XF resin synthesized in nitrogen is comparable to PVC when heat-treated and leads to graphitized lamellae [17]. In the same way XF synthesized in nitrogen normally shows optical anisotropy [18] as well as high graphitizability [19].

5. Conclusion

Although the yield of bulk mesophase from XF pitch is about the same (94%) as for PVC4 (95%), the two bulk mesophases obviously are entirely different. PVC bulk mesophases mostly showed preferred long range orientation (since poorly oriented phases contained in PVC4 disappear diring heat-treatment). Mesophase spherules separated by quinoline from coal-tar and asphalt pitch matrices are known to show the same degree of graphitization as untreated ones [20]. PVC bulk mesophases used in this experiment also follow this rule and change primarily into highly graphitized lamellar crystals. However, XF just represents the opposite since it is not graphitizable at all.

In all the samples precursors are made of small elementary units [1, 5, 16, 21] formed by 2 or 3 parallel aromatic layers, the diameter of which is less than 10 Å. These results confirm a general rule, i.e. the ease of graphitization is mainly dependent on the extent of the molecular orientation occurring in the early stages of carbonization.

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