SELF-ASSEMBLED CARBON SURFACES BY LIQUID CRYSTAL ANCHORING OF MESOPHASE PITCH

Dan Tuhus-Dubrow, Hong-Shig Shim, Zelalem Asmamov,
Ying Hu, Gregory Crawford, and Robert Hurt
Division of Engineering, Brown University
Providence, RI 02912

Introduction

Both rod-like and disk-like liquid crystals exhibit preferred molecular orientations in the vicinity of interfaces, the phenomenon of "surface anchoring" [1]. In pitch-derived carbon materials, the anchoring direction can determine the ultimate graphene layer orientations in interfacial zones, such as the fiber/matrix boundary, the external surface, or the inner surfaces of solidified bubble cavities. Anchoring also determines the proper orientational boundary condition for mesophase flow problems that govern the texture of carbon fibers or tapes. Finally, it may be possible to use surface anchoring strategically to assemble carbon materials with preprogrammed surface orientation and properties. While anchoring angles have been measured for many conventional liquid crystals in contact with a variety of technologically important surfaces, there has been little systematic study of mesophase pitch.

Experimental

This study employed samples of naphthalene-derived AR mesophase pitch supplied by Mitsubishi Gas Chemical and by Professor Dan Edie at Clemson University. Selected experiments were also performed with a mesophase sample obtained by solvent fractionation of petroleum pitch by Thies and coworkers [2].

The pitches were made fluid by heating to 400 ºC in inert gas and spread onto substrates by one of three techniques: (a) hot rolling with coating rods, (b) hot pressing between two substrate sheets, or (c) self (unassisted) spreading onto horizontal substrates. The substrates examined are shown in Table 1. After cooling, the interfacial zones were viewed under polarized light by one or more of three techniques: (a) direct observation of the interfacial plane (used for the gas interfaces and for transparent substrates such as PTFE film and inorganic oxides) (b) direct observation after removal of the substrate by dissolution in acid (for metal foils) or by simple physical removal, and (c) observation of interfacial zone in cross-section after epoxy mounting and fine polishing.

Results and Discussion

The gas/pitch interface usually quenches with liquid-like (optically smooth) texture and can be viewed without preparation (see Fig. 1). It always shows 100% anisotropy with very distinct disclinations indicating edge-on orientation as reported in our earlier study [3] and originally by White and coworkers [4].

Figure 1. Quenched free surface of AR mesophase pitch, viewed under polarized light without sample preparation.

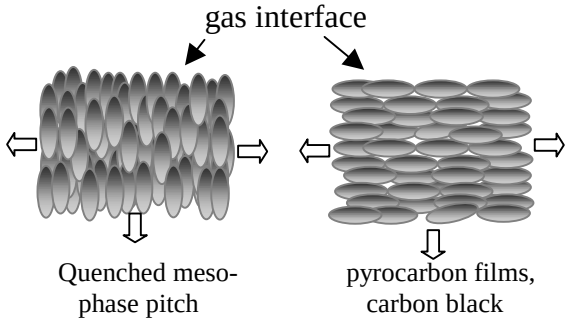

Figure 2. Structures observed at the gas interface for quenched mesophase pitch and selected carbon materials. These structures indicate a dominant face-to-face assembly process for pitch (left) and edge-to-edge assembly process for pyrocarbon and carbon black.

The edge-on orientation at the gas interface is confirmed by examination of polished cross-sections — experiment (c) above. The edge-on orientation at the gas/pitch interface is consistent with molecular modeling studies that predict the dominant interaction between polyaromatic molecules to be face-to-face association [5]. The edge-on orientation creates the lowest energy surface because it preserves all the face-to-face interactions within the pitch (see left-hand image in Fig. 2).

The experiments on solid substrates were all of type (a) and (b), which do not reveal precise anchoring angles, but do clearly show whether the interfacial plane is optically active (indicating edge-on orientation, either strictly perpendicular or with tilt) or isotropic (indicating strict face-on orientation). The results of all experiments are summarized in Table 1.

Table 1. Summary of Anchoring Results

Substrate	Anchoring (of AR)
gas phase	edge-on
glass	edge-on
quartz	edge-on
sapphire	edge-on
ITO	edge-on
PTFE	edge-on
aluminum	edge-on
stainless steel	edge-on
graphite (HOPG basal)	planar (face-on)

Selected experiments were also carried out with petroleum mesophase pitch on HOPG basal surfaces, glass, and at gas interfaces. In each of these cases the anchoring was observed to be the same as that for AR pitch as reported in Table 1.

The results in Table 1 show that anchoring is dependent on the nature of the substrate, as is well known from other liquid crystalline systems [1]. Mesophase exhibits edge-on anchoring on both low energy surfaces (e.g. PTFE) and high energy surfaces (inorganic oxides, metals). Face-on orientation is observed only on the HOPG basal surface. We do not currently have a unifying explanation for this set of results, but it is worth noting that in each case the interfacial zone is configured to maximize the total extent of π–π bonding in the system (i.e. the pitch molecules give up their internal π–π bonds only with when they can be replaced by new interfacial π–π bonds, such as with basal graphite).

A special issue arises in mesophase anchoring regarding the thermal stability of the edge-on structures. Since further heating eventually promotes polymerization by edge-to-edge coalescence, at high temperatures a driving force must develop for the formation of the face-on structure (Fig. 2, right). This likely explains the parallel graphene layers seen by TEM in the interfacial zones of many carbon materials. In general, however, the switch from edge-on to face-on configuration may or may not occur depending on rearrangement kinetics. We have observed the preservation of optical activity (edge-on anchoring) during high temperature heat treatment on some of our free surfaces, but more work is needed to precisely identify the conditions under which the edge-on anchoring is thermally stable.

Finally, we believe there is potential to use surface anchoring strategically in the design of new carbon materials. Using the proper template, all-edge or all-face surfaces can be self-assembled, which, after template removal, possible oxidative stabilization, and carbonization, become all-edge or all-basal surfaces, as desired.

References

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