MAGNETIC ORIENTATION STUDIES OF SYNTHETIC MESOPHASE PITCHES

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I. Introduction

Previous work by Singer and Lewis[1] has shown that carbonaceous mesophase spherules with the familiar Brooks-and-Taylor structure align in a magnetic field with their c-axes (optical axes) perpendicular to the magnetic field direction. Mesophase spheres with unusual optical properties have been reported by Honda, et al.[2], for pitches to which carbon black has been added. These authors proposed a very different structure from that described by Brooks and Taylor[3].

We have also observed unusual optical effects in spheres contained in mesophase pitches made from model compounds with anhydrous aluminum chloride. To further investigate these effects, we have studied these materials using polarized light and sensitive tint optical microscopy and magnetic field orientation.

II. Experimental

The synthetic pitches which were studied were made from the pure compounds naphthalene and anthracene by reaction with anhydrous aluminum chloride at temperatures from 160-300°C. Residual inorganic material remaining in the pitches after reaction was removed by acid hydrolysis. These pitches were then examined by conventional polarized light microscopy techniques.

Magnetic orientation of these materials was done using the apparatus and sample preparation techniques described previously by Singer and Lewis[1]. A magnetic field of 10 Kgauss was used. Samples were heated in the magnet gap to temperatures between 300°C and 400°C and were held in the field at these temperatures for 1/2 hour. Experiments were done with each material both with and without rotation of the sample tubes around an axis perpendicular to the field.

After cooling to room temperature in the field, the oriented samples were sectioned for microscopy to give both transverse and longitudinal views. Transverse views contained a plane of section parallel to the magnetic field and, for rotated samples, perpendicular to the rotation axis. Longitudinal views contained a plane of section perpendicular to the magnetic field. Optical evaluation of the samples was done using polarized light and sensitive tint microscopy.

III. Results and Discussion

The pitches prepared using $AlCl_3$ contained from 10-60% mesophase. Microscopy of the unoriented samples showed the mesophase to be present in the form of spheres as well as large coalesced regions. Spheres which exhibited rotating cross extinction patterns appeared quite similar to typical Brooks-and-Taylor spheres in polarized light. However, in sensitive tint, the quadrants showed exactly opposite color configurations to those which were observed for "normal" spheres. To further investigate this apparent anomalous behavior, magnetic orientation experiments were performed.

As Singer et al.[4] have demonstrated, mesophase from plate-like aromatic molecules will orient in a magnetic field with the optic axis perpendicular to the field direction, whereas conventional liquid crystals from rod-like molecules will orient with the optic axis parallel to the field direction. Examination by polarized light microscopy of the longitudinal views of the samples not rotated in the field showed spheres having no apparent orientation with respect to one another. However, the transverse views of the magnetically oriented, rotated samples showed spheres that were all of uniform darkness (complete extinction), which did not change upon stage rotation. This result implies that the direction of view is parallel to the optic axis of the oriented mesophase, i.e., the optic axis is aligned parallel to the rotation axis and perpendicular to the field. These observations are consistent with the conclusion that the mesophase in these unusual spheres consists of flat, disc-like molecules, not rod- or lath-like molecules, and that the optical sign of the mesophase is negative, as is observed in other carbonaceous mesophase systems.

Examination of the longitudinal sections of the rotated samples showed that the spheres present were all well-oriented by the field. In polarized light observation, these spheres appear to have extinction patterns similar to those observed for spheres with Brooks-and-Taylor type structure. As is observed with Brooks-and-Taylor spheres, the magnetic field also orients the spheres internally and curvature can be observed only in a thin shell near the sphere surface. On examination with a sensitive tint plate, the regions of curvature in the outer shell showed an opposite color configuration from that observed for "normal" spheres. That is, the areas which would appear blue in a "normal" sphere, appear yellow, and vice versa. Also, it was observed that while the extinction brushes in the Maltese cross of a normal sphere emanate from the poles, in these unusual spheres the brushes emanate from the equator.

These results suggest the new structure (II) for these spheres which is shown in Figure 1 together with the standard Brooks-and-Taylor structure (I). The three-dimensional structures of the spheres are given by a body of rotation around the perpendicular axis shown. The internal orientation of the spheres is lamellar, just as in the Brooks-and-Taylor sphere. However, near the surface, the layers orient themselves parallel to the sphere surface and not perpendicular as is observed for a Brooks-and-Taylor sphere. The new structure has a belt-like singularity around the equator rather than the two single poles that occur in a "normal" sphere.

In conclusion, the mesophase spheres observed in pitches made from model compounds with $AlCl_3$ show a difference in structure from that of spheres produced in normal pitch materials. This structural difference is believed to arise from interactions at the interface of the mesophase and isotropic phase, which give rise to a change in orientation at the surfaces of spheres. Such unique surface effects may be tied to chemical differences in the mesophase from these model systems.

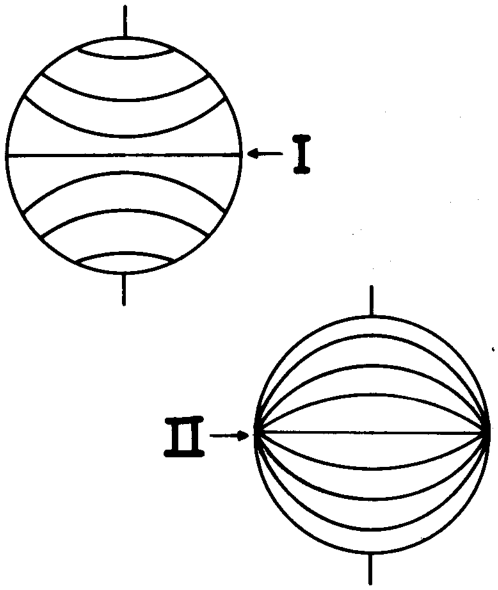

Figure 1. Mesophase Sphere Structures: (I) Standard Brooks-and-Taylor Structure, (II) Proposed Structure for Mesophase Spherules in Synthetic Model Pitches.

References

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