BORON NITRIDE BULK MESOPHASE

Patrick PUJOL, Marc BIROT*, Jean-Paul PILLOT*, Xavier BOURRAT, Olivier MANFE*, René PAILLER, Roger NASLAIN and Jacques DUNOGUES*

LCTS, Laboratoire des Composites Thermostructuraux Université Bordeaux 1, 3 Allée de la Boétie F-33 600 Pessac
**LCOO, Laboratoire de Chimie Organique et Organometallique, Université Bordeaux 1, 351 Cours de la Libération, F-33 405 Talence cedex*

Introduction

The first observation of a liquid crystal occurrence in a BN polymer was reported by Kim and Economy [1] but the evidences were faint and mesophase formation never controlled. No further report on BN mesophase was published till that time in the literature, as far as we know.

BN bulk mesophase synthesis

Our two groups in Bordeaux have produced quantitatively an instant bulk mesophase [2]. This mesophase is based on the synthesis of a polyborazylene obtained by the direct polymerization of borazine. Borazine is represented below with its charge density in the plane : Fig.1.

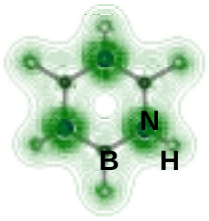

Figure 1. Borazine (mineral benzene) (charge density in the plane).

First, the borazine was processed as shown in Fig. 2 starting with sodium borohydride and ammonium sulfate.

Then, the borazine was polymerized in bulk, with pressure being allowed to increase in a stainless steel autoclave at a temperature of about 70°C for about 50hours. Under these conditions the borazine polycondenses to generate a low molecular polymer (oligomer) consisting of planar polycondensed molecules of borazine rings. The pressure within the autoclave is due mainly to the progressive release of dihydrogen (dehydrogenation/condensation reaction).

Finally, the mesophase was obtained by mixing an equivalent amount of borazine (or aromatic solvent), as an additive to the polyborazylene oligomer. A bulk mesophase was obtained instantaneously.

Liquid crystal characterization

Characterization was first conducted by means of optical microscopy. Under cross polars the transmitted light shows that this liquid reacts as a crystal. The light split in the birefringent liquid and propagated in two orthogonal directions with different velocities. In the analyzer, these two beams recombined to create an interference color distinctive of the phase shift between the two beams. The liquid oligomer is a bulk mesophase as shown in Fig.3.

Transmission electron microscopy shows the evidence of (10) and (11) broad bands related to [100] and [110] rows of atoms of the condensed polyborazylene liquid molecules (electron diffraction mode). By electron energy loss spectroscopy it is possible to point out a N/B ratio close to 1, hexagonal fine structures at the boron K threshold as well as interband excitations at E=8eV corresponding to the $\pi \rightarrow \pi^*$ transitions.

Conclusion

A bulk BN mesophase was produced quantitatively and in a controlled manner from a polyborazylen precursor.
The BN mesophase can be processed to make fibers, matrices or even thin films to act as interphase. By heat treatment this mesophase transforms to BN and “graphitizes” at approximately 1500°C to give hexagonal BN.

References

[1] D.Kim & J. Economy, Chem. Mater., 1994, 6, 395-400
[2] P. Pujol, Précurseurs mésogéniques de BN hexagonal, Thèse (PhD) de l'Université de Bordeaux 1, 0A 2222 (2000).

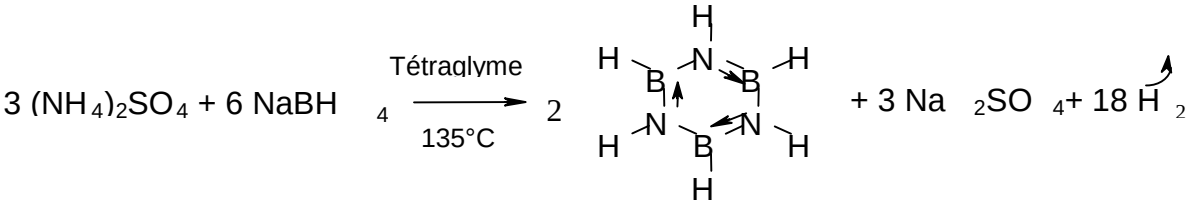

Figure 2. Global reaction for borazine synthesis

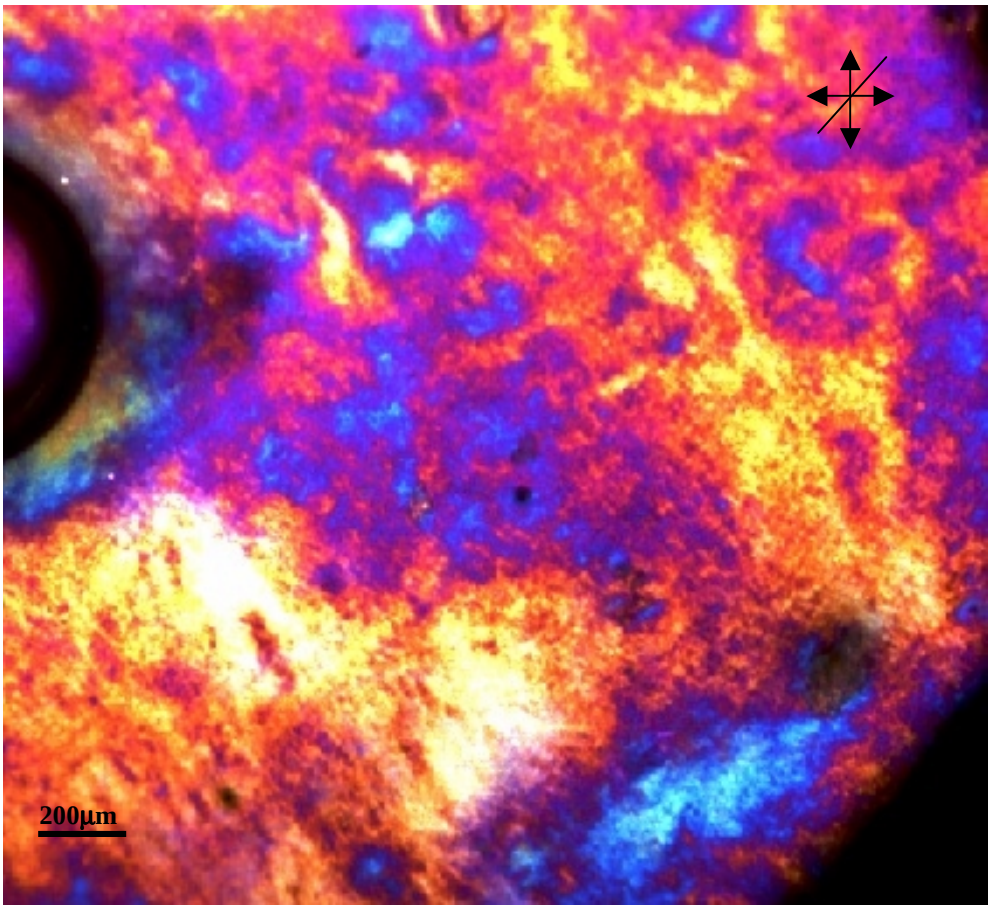

Figure 3. BN Bulk mesophase : transmitted light under cross polars with λ-plate