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A Synchrotron WAXD Study on the Early Stages of Coagulation During PBO Fiber Spinning

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The structural development at the very early stages of the coagulation process during PBO fiber spinning was investigated by using synchrotron wide angle X-ray diffraction (WAXD). PBO was found to segregate into the PPA-free domains immediately upon the contact with water. Our results confirmed the hypothesis that the first step of coagulation process during spinning was the formation of pure PBO stacks, with interstack order being formed later.

Poly(*p*-phenylene benzobisoxazole) (PBO) fiber is known to be the strongest commercial synthetic polymer fiber. Its excellent mechanical properties and superb thermal stability make PBO the optimum material for high performance applications like lightweight bulletproof vests, helmets and fire-resistant suits. The manufacturing process for PBO fibers involves dry-jet wet-spinning from a polymer solution in poly(phosphoric acid) (PPA). After spinning, the fiber is coagulated in water to remove the PPA component. Although the coagulation process was found to strongly affect the final PBO fiber properties, the structural evolution during the coagulation process had never been fully understood. In this work, a gel spinning apparatus was modified to study the fiber during coagulation with time resolution as short as 0.03 sec. The PBO/PPA dope was spun at 160 ºC. Two-dimensional wide angle X-ray diffraction (WAXD) images were recorded using a CCD X-ray detector at the beamline X27C.

Figure 1 shows the one-dimensional equatorial scattering profiles of the PBO filament before coagulation and at different coagulation times. Two scattering peaks were found on the equator before coagulation (**Figure 1A**), corresponding to *d*-spacings of 9.67 Å and 4.45 Å, respectively. These two equatorial peaks suggest that the molten dope structure is not simply nematic. The second peak was much stronger than the first one, excluding the possibility of a hexagonal-like disordered close packing. We attributed this structure to a "biaxial nematic" order, where the mesogenic unit was a well-defined complex between PBO and PPA molecules. After the fiber passed through the water bath, even if the coagulation time was as short as 0.03 sec (**Figure 1B**), an additional peak at d = 3.36 Å appeared, which corresponded to the eventual 010 reflection of the final PBO crystal structure, implying that PPA-free stacks of flat PBO molecules had been formed immediately at the very beginning (~0.03 sec) of the coagulation process. With increasing coagulation time, this peak became stronger, indicating that more PPA-free PBO regions had been formed.

We did not, however, observe the appearance of the 200 reflection of the final PBO crystal (d = 5.46 Å), even after the short time coagulation of 0.3 sec. This result confirms that the first step of coagulation is the formation of face-to-face stacks of PBO molecules on top of each other separated by a 3.36 Å spacing. There is no significant lateral packing order between these stacks

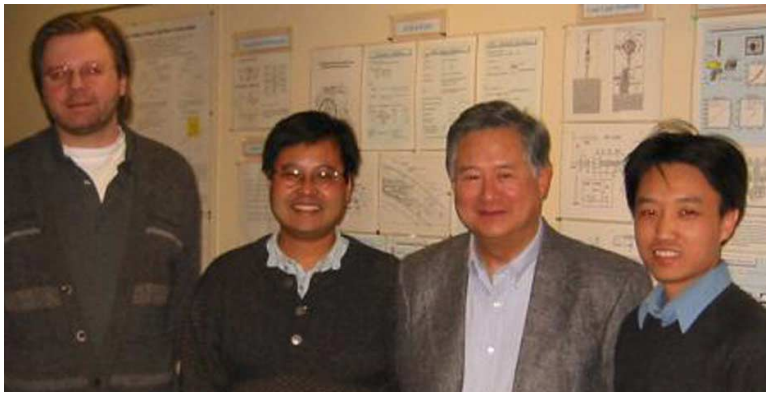

Photo: (from left) Christian Burger, Benjamin S. Hsiao, Benjamin Chu and Shaofeng Ran

at this early stage of the coagulation, as shown schematically in **Figure 2A**. We assume that, after the PBO stacks accumulate to a certain critical fraction, the lateral packing ordering between the stacks would be formed, resulting in the appearance of the 200 reflection. When coagulation time is long enough, such that all of the PPA solvent is washed away, a (2-10) reflection will be observed, indicating that the order in the fiber cross section is no longer of short range nature only, but that a two-dimensional lattice with a certain degree of long-range order has been formed, **Figure 2B**.

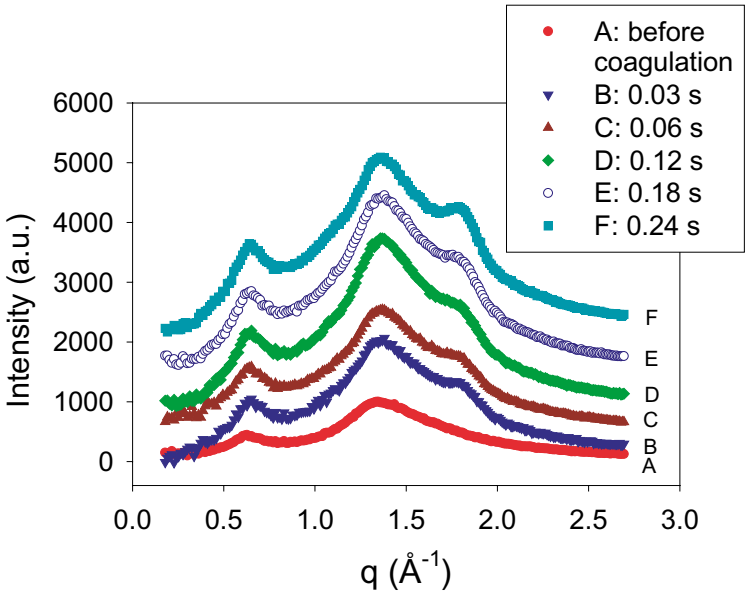

Figure 1. *One-dimensional equatorial intensity profiles of PBO fiber at various coagulation times.*

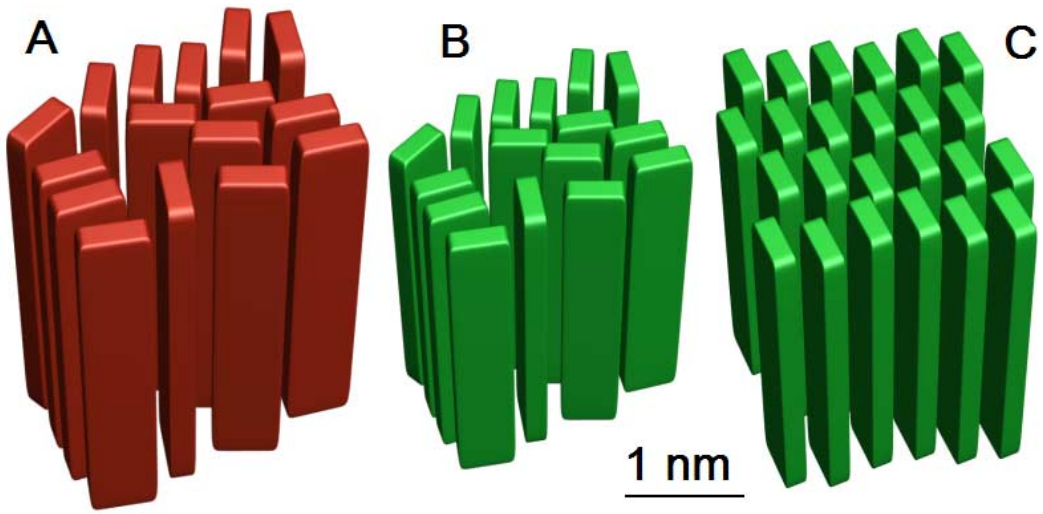

Figure 2. *Schematic representation of sanidic or biaxial nematic packings: PBO-PPA solvate complexes* ***(A)*** *and pure PBO molecules* ***(B)****, respectively, are represented by plank-shaped units with appropriately scaled cross-sections. The heights of these units are actually much larger than shown in the figure. The WAXD equator will show strong (0k0), weak (h00), and no mixed (hk0).* ***(C)*** *Two-dimensional long-range order in the cross-section (mixed (hk0) reflections) with translational disorder in the fiber direction (no mixed (hkl) reflections).*