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

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Introduction. Poly(*p*-phenylene benzobisoxazole) (PBO) fibers are known to possess the highest tensile modulus and strength among all commercial synthetic polymer fibers.[1] Furthermore, PBO fibers exhibit an excellent thermal stability with a decomposition temperature of above 600 °C.[2] The general manufacturing method for PBO fibers starts with a dry-jet wet-spinning process from the polymer solution in poly(phosphoric acid) (PPA).[3−5] After spinning, the fiber is coagulated in water to remove the solvent (PPA). The coagulation process is a critical step in the PBO fiber structure formation. In a previous work, we have studied the structural changes of the PBO fiber during the spinning process by in situ synchrotron wide-angle X-ray diffraction (WAXD).[6] Our results showed that a significant molecular ordering took place after the fiber had passed through the coagulation water bath at temperatures ranging from 25 to 60 °C. Although the coagulation process was found to strongly affect the final PBO fiber structure, the evolution of the structural changes in the coagulation process had not been sufficiently investigated. In the present study, a unique modification was made to the spinning apparatus, which allowed us to probe the coagulating fiber after coagulation with a time period as short as 0.03 s. This modified spinning apparatus was used to examine the effects of the coagulation time on the structural development in the PBO fiber using the in situ synchrotron WAXD technique.

Experimental Section. The spinning experiment was carried out at the Advanced Polymers Beamline X27C of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The X-ray beam (λ = 0.137 nm) passed through a three-pinhole collimation system[7] (190 cm long) with the first and last pinhole having a diameter of 0.10 and 0.37 mm, respectively. The spinning unit was a modified version of the experimental unit constructed by the Dow Chemical Co.,[8] which had been described in detail elsewhere.[6] Compared with the previous spinning apparatus, two major modifications were made:

(1) A new spinneret was designed and manufactured (by Toyobo Inc. Japan). The exit orifice of the spinneret had a diameter of 0.3 mm and length of 0.3 mm, which was smaller and shorter than that in the previous study.[6]

(2) A new water bath was designed (Figure 1) to meet the requirements of short coagulation time. In this bath, the water stream from a circulation system (60 °C) was injected symmetrically into the bottom. The flow rate of the water stream could be controlled. A cylinder with 12.7 mm diameter was inserted into the base of the water bath to guarantee the fresh water flow around the fiber. The height of the drain tube could be adjusted to change the water level in the bath. The coagulation time was determined by the depth of the water level and the fiber wind-up velocity. The accessible range of coagulation times was 0.03−0.3 s. Using a fine stepping motor to transport the spinning rig and the rapid X-ray beam monitor system, the X-ray detection could be

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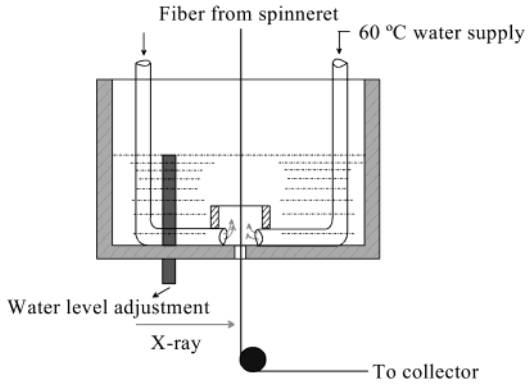

Figure 1. Side view of the new design of water bath for short time coagulation during PBO fiber spinning.

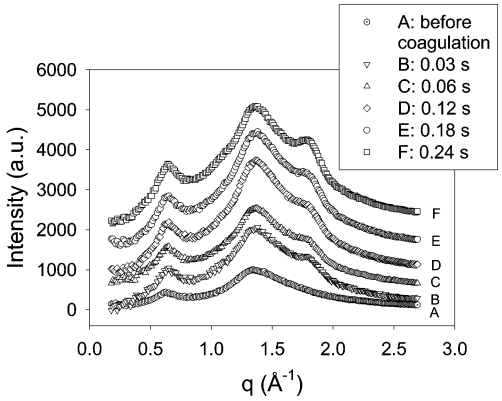

Figure 2. One-dimensional equatorial intensity profiles of PBO fiber with SDR of ~2.0 at various coagulation times (plots vertically shifted for visual separation).

switched quickly between the positions before and after coagulation.

The PBO/PPA dope with PBO molecular weight larger than 10 000 and a PBO concentration of 14 wt % in poly(phosphoric acid) (PPA) was provided by Toyobo Inc. The PBO/PPA dope was inserted into the preheated barrel having an inner diameter of 9.52 mm. The dope was kept in the barrel at 160 °C for about 50 min to reach the thermal equilibrium and was then extruded by a plunger. In the present study, the extrusion speed from the spinneret was fixed at about 64 mm/s. Two-dimensional WAXD images were recorded using a CCD X-ray detector (MARUSA) after accumulation for about 2 min. The sample-to-detector distance was 118.9 mm. The collected WAXD images were corrected for beam intensity fluctuations and sample absorption.

Results and Discussion. In the present study, the smaller spinneret orifice (0.3 mm) yielded a good quality PBO filament in terms of smoothness. The coagulation process was more uniform (although not yet necessarily complete) throughout the fiber due to the much smaller fiber diameter when compared with that obtained in the previous experiment.[6] This point is very important for studying the coagulation process, especially when the coagulation times are as short as 0.03 s. However, the thin diameter of the fiber also incurred some difficulties during the measurement, such as fiber alignment in the X-ray beam and much weaker scattered intensity from the fiber.

Figure 2 shows the one-dimensional equatorial scattering profiles, obtained by averaging ±5° sectors on the equator of 2D scattering patterns showing no off-axes reflections,[6] of PBO filament with a spin draw ratio (SDR) of ~2.0 before coagulation and at different coagulation times. It was found that there were two scattering peaks on the equator before coagulation (Figure 2A) (at $q = 0.65$ and 1.41 Å^{-1}, corresponding to d-spacings of 9.67 and 4.45 Å, respectively). These two peaks are related to the extruded PBO/PPA dope structure, possessing lyotropic liquid-crystalline characteristics with short-range order only in the cross section. The 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. In the previous study,[6] we attributed this structure to a "biaxial nematic" order, where the mesogenic unit was a well-defined complex between PBO and PPA molecules, similar to the 3D crystalline one reported by Cohen et al.[9] This structure can also be referred to as the "sanidic" phase,[10] which was first noted by Ringsdorf et al. in the liquid-crystalline system of plank-shape molecules.[11,12] After the fiber passed through the water bath, even if the coagulation time was as short as 0.03 s (Figure 2B), an additional peak at $q = 1.87$ Å^{-1} ($d = 3.36$ 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 beginning of the coagulation process, probably forming a skin-core morphology with the coagulation starting near the fiber surface. With increasing coagulation time, this peak became stronger, indicating that more PPA-free PBO regions had been formed as more PPA molecules were hydrolyzed and washed away during coagulation.

We did not, however, observe the appearance of the 200 reflection of the final PBO crystal ($q = 1.15$ Å^{-1} and $d = 5.46$ Å) after this short time coagulation (up to 0.24 s). This result confirms that the first step of coagulation during PBO fiber spinning is the formation of face-to-face stacks of PBO molecules on top of each other separated by a 3.36 Å spacing (corresponding to $q = 1.87$ Å^{-1}). There is no significant lateral packing order between these stacks yet at this early stage of the coagulation (as there is no evidence of the 200 reflection). 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 $(2\bar{1}0)$ reflection will be observed,[6] 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. When the two broad equatorial peaks corresponding to the PBO/PPA complex have totally disappeared, the completion of coagulation is achieved.

The equatorial intensity profiles (I vs q) from the coagulating fiber in Figure 2 can be separated into four peaks by using a Gaussian peak fit routine, including two PBO/PPA complex peaks, the PBO (010) peak, and a broad halo due to the PPA solvent. After subtraction of the PPA halo, the integrated area below the (010) peak in the Lorentz-corrected intensity profile ($Iq^2 \sim q$) could be used to approximately estimate the amount of PPA-free PBO domains formed at that stage of the coagulation. Figure 3 shows the fraction of these pure PBO domains during the coagulation as a function of

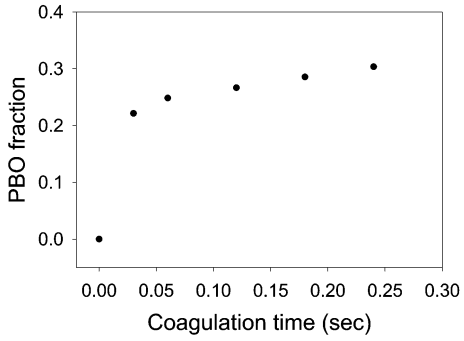

Figure 3. Fraction of PPA-free PBO as a function of the coagulation time.

coagulation time. As expected, the PBO content was an increasing function of the coagulation time. The coagulation speed was very fast at the beginning but subsequently slowed down. The PPA-free PBO fraction reached about 30% after 0.24 s of coagulation.

Conclusion. A water bath optimized for fast coagulation studies was designed and constructed to evaluate the structural development at the early stages of the coagulation process during PBO fiber spinning by using synchrotron wide-angle X-ray diffraction. The results showed that PBO started to segregate into PPA-free PBO domains immediately when the fiber reached the water bath, even when the coagulation time was as short as 0.03 s. The eventual PBO 010 reflection was found to be formed ahead of the 200 reflection, which confirmed the concept that the first step of the coagulation was the formation of pure PBO stacks, with interstack order being formed later. The fraction of PPA-free PBO was found to reach almost 30% after 0.24 s of coagulation.

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