Preferential Orientations of Molecular Planes of Rigid-Rod Polymers along the Radial Direction Normal to the Fiber Axis

Tooru Kitagawa （北河 享）

TOYOBO (SHANGHAI) CO., LTD. (东洋纺上海有限公司)
Email: Tooru_Kitagawa@toyobo.jp

Abstract Fibers made of rigid-rod polymers have been developed to utilize the mechanical properties of the molecules to the utmost; the rigidity gives straightness and toughness in the chemical bonds along the molecular axis aligned along the fiber axis. We have previously proposed an estimation method[1-4] to predict the preferential orientation of the (lm0) crystal planes of PBO (poly-p-phenylenebenzobisoxazole) crystals normal to the fiber axis from the diffraction X-ray intensities in diffraction patterns obtained by a micro-focus X-ray diffraction method. Because the PBO molecule have a thin-planar structure with rigidity, it can rotate freely around the molecular axis in the solution state. It is found that the alignment of the (lm0) planes of the crystals was determined in fibers prepared by coagulation during the fiber spinning process (Figure 1). In this presentation a calculation method to predict the intensities of the (lm0) reflections of PBO fibers as a function of the distance from the center of the fiber to the center of the focus point of a micro X-ray beam on the fiber is proposed (Figure 2). The method can estimate the degree of preferential orientation of the <lm0> along the radial direction of the fiber (Figure 3). The process of preferential orientations of the PBO crystals forming in the fiber structure induced by coagulation was revealed.

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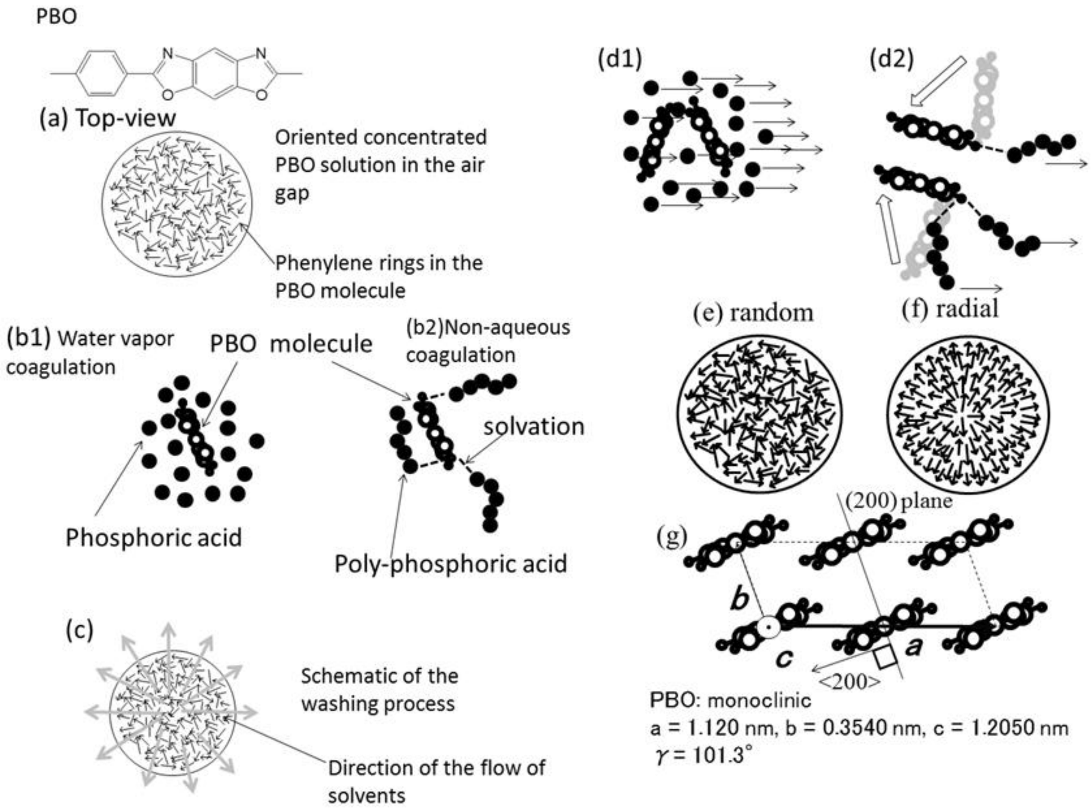


Figure 1. Schematic drawings that explain coagulation process and preferential orientations (a) cross-section of the thread made from PBO concentrated solution (b1) coagulation by water vapor (b2) coagulation by non-aqueous coagulant (c) direction of the flow of solvents (d1) washing water vapor coagulated fiber (d2) washing non-aqueous coagulated fiber (e) random preferential orientation (f) radial preferential orientation (g) PBO crystal structure model after Fratini et al.

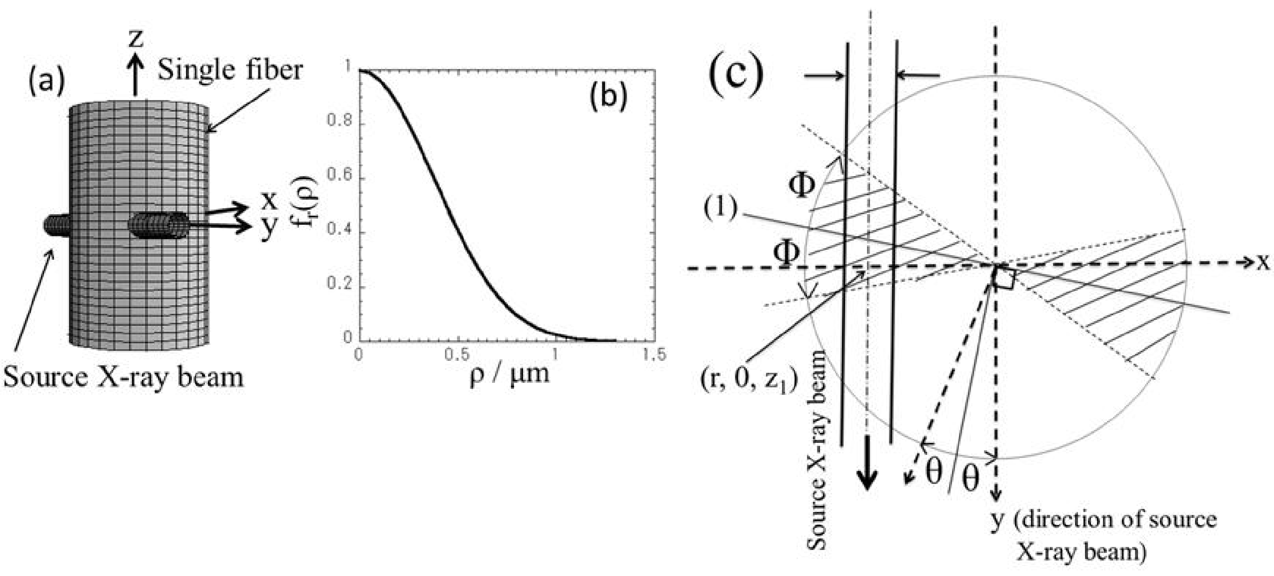
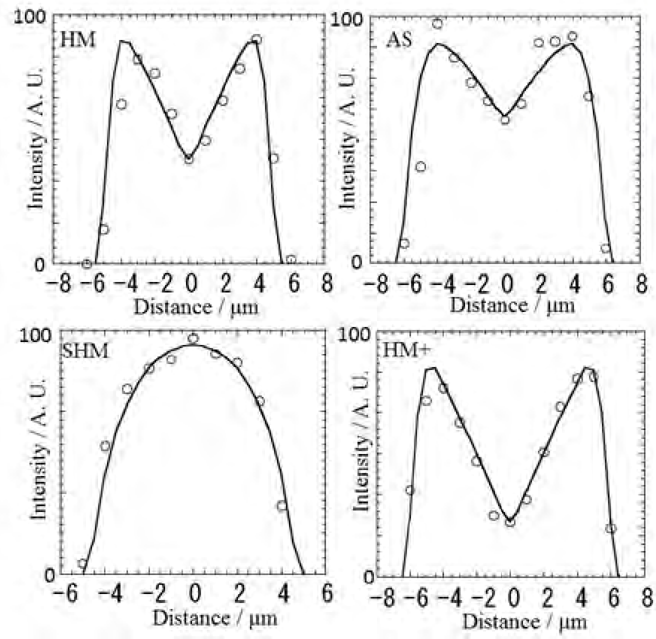


Figure 2. (a) Schematic diagram of a single PBO fiber and a source X-ray beam. A single fiber is set in which the center of the fiber is in agreement with the z-axis. The direction of the X-ray beam is parallel to the y-axis on the xy plane (z=0). (b) Relative intensity profile fr(ρ) of the source X-ray beam as a function of the distance ρ from the center of the beam. (c) Cross-section of the fiber and the explanation of the two-phase model. 2θ indicates the diffraction angle of the (200) crystal plane. Line (1) indicates the normal to the (200) crystal planes that satisfy Brag's Law. The height position of the cross-section is set at z=z1 and r is the distance from the center of the fiber to the center of the beam. The sectors surrounded with the circumference of the single fiber and the two dashed lines having an opening angle of 2Φ, highlighted with slanted lines, show the part in which the crystallites are assumed to give X-ray diffraction intensities.



Sample	Coagulation	Heat-Treatment
HM+	non-aqueous coagulant	yes
SHM	water vapor at 97°C	yes
HM	dilute phosphoric acid	yes
AS	dilute phosphoric acid	no

Figure 3. Comparison of the integral diffraction intensity of the (200) plane between prediction and measurement. ○: measured data points. —: prediction based on the 3D two-phase model.