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Time-Resolved Structural Studies in Fiber Processing

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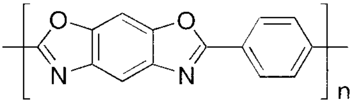
Summary: Time-resolved and off-line synchrotron wide-angle and small-angle x-ray scattering (WAXS and SAXS) was used to study the structure formation in poly-*p*-phenylenebenzobisoxazole (PBO) fibers during various stages of spinning, coagulation, and heating processes. WAXS data could be explained in terms of liquid-crystalline structures of varying degrees of order. A structure model is proposed that is in accordance with the observed SAXS four-point pattern.

Keywords: high performance polymers; fibers; spinning; WAXS; SAXS

Introduction

Poly-*p*-phenylenebenzobisoxazole (PBO, **1**) forms the strongest commercial synthetic polymer fiber known so far. It provides excellent mechanical properties paired with extreme thermal stability, making PBO the optimum material for applications like lightweight bulletproof vests and fire-resistant suits.



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PBO is spun from a lyotropic melt in polyphosphoric acid (PPA). PPA is then removed by coagulation in a water bath, resulting in the as-spun (AS) fiber. Subsequent heat treatment of AS fibers produces the final high-modulus (HM) fiber. The present study aims to provide a better understanding on the structural evolution of the PBO fiber formation.

Experimental

A spinning apparatus consisting of a capillary rheometer-like barrel with an upper temperature capability of 300 °C, a vertical precision movement to shift different fiber regions into the beam, a motor driven plunger, a take-up wheel with adjustable speed to provide defined spin draw ratios, and a coagulation water bath has been set up at the Advanced Polymers Beamline (X27C) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL).[1] The PBO-PPA solution (dope) was provided by Toyobo Co. Time-resolved and off-line wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) 2D patterns were recorded using a MAR CCD detector (*in situ*) and Fuji imaging plates (off-line).

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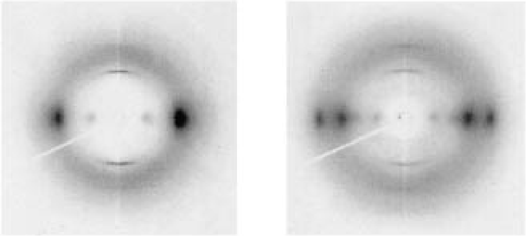


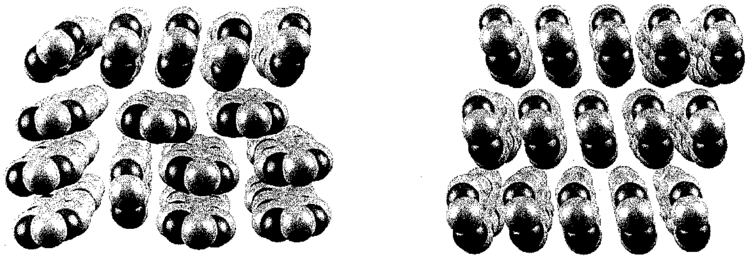
(a) before coagulation (b) after coagulation

Figure 1. *In situ* WAXS patterns of the PBO fiber before and after passing through the coagulation water bath (fiber axis vertical).

WAXS: Lyotropic Packings of Varying Degrees of Order

Figures 1(a) and 1(b) show *in situ* WAXS patterns of the PBO fiber before and after passing through the coagulation water bath, respectively. These two patterns consist mainly of meridional streaks (related to the monomer period) and of equatorial arcs generated by the lateral packing order. In both cases, the equatorial arcs indicate a high degree of preferred orientation, i.e., all PBO molecules are essentially oriented in the fiber direction. The absence of off-axis reflections together with the meridional streaking indicates the presence of a translational disorder in the fiber direction in either case. On the equator, both WAXS patterns show a weak peak at smaller angles (corresponding to larger spacings) and the strongest peak at larger angles (smaller spacings), indicating a peculiar kind of packing order formed by structural units with anisotropic cross-sections, thereby generating the two lateral spacings observed on the equator (both a long-range ordered hexagonal or a short-range ordered nematic system would have isotropic cross-sections with one dominant equatorial length scale). The anisotropic structural units are usually referred to as "plank-shaped", and the resulting mesostructure can be described as "biaxial nematic" or "sanidic" liquid-crystalline.[1] While the two WAXS patterns share their qualitative "sanidic" appearance, they differ in the actual quantitative length scales observed on the equator, indicating that the plank-shaped structural units are not the same in these two cases. In the fully coagulated case after complete removal of PPA, the plank-shaped structural unit is the single PBO molecule (its plank-shaped nature is plausible from structure **1**), whereas in the uncoagulated case the plank-shaped structural unit is larger than a single PBO molecule and is assumed to be a well-defined solvate complex between PBO and PPA.[1,2]

The time-resolved WAXS study of the coagulation and subsequent pure PBO structure formation process reveals several stages; two crucial structures are schematically sketched in Figure 2. Figure 2(a) shows a sanidic liquid-crystalline arrangement of PBO molecules, having short-range order only. The flat molecule cross-sections arrange in short stacks, the period of which corresponds to the strongest equatorial maximum. The larger spacing of the lateral packing of whole stacks generates the equatorial maximum at smaller angles. Its lower intensity is plausible due to poorer inter-stack packing order compared to the intra-stack packing with a graphite-like period



(a) Sanidic liquid-crystalline packing, short-range order only in the cross-section.

(b) 2D long-range order in the cross-section; translational disorder in 3D.

Figure 2. Structure models illustrating different degrees of packing order in the PBO fiber cross-section (fiber axis and molecule axes perpendicular to the paper plane).

and possible π-interaction. No mixed hk0 reflections are expected on the WAXS equator of this structure. In contrast to this moderately ordered system, the arrangement of the PBO molecules in Figure 2(b) shows a 2D lattice with long-range order and a well-defined 2D unit cell. Thus, in addition to the two peaks also observed for the short-ranged structure in Figure 2(a), here mixed hk0 reflections corresponding to periodicities along lattice diagonals are also observed, most notably the $2\bar{1}0$ (indexed using the unit cell given by Fratini *et al.*[3]) the onset of which in the time-resolved WAXS investigation can be taken as an indicator for the development of long-range order in the fiber cross-section. The structure in Figure 2(b) still shows translational disorder in the fiber direction, i.e., overall it has 2D order only and, thus, no mixed hkl reflections which would indicate the presence of true 3D long-range order.

SAXS: Inclined Lamellar Superstructures

The SAXS pattern of an as-spun PBO fiber before heat treatment is known to be poor in features, showing only an equatorial streak due to needle-shaped microvoids preferentially oriented in the fiber direction and/or multiple scattering on the the fibrillar structure. This situation changes, however, after heat treatment where a faint but nevertheless well-defined four-point scattering pattern is observed,[4,5] Figure 3. The superstructure generating this four-point pattern is present in the final high-modulus fiber and should influence its mechanical properties.

Small-angle maxima are not uncommon in stretched polymer fibers, usually showing up as a two-point pattern on the meridian or a four-point pattern as observed here with varying tilt angles. Most of these stretched fibers consist of semi-crystalline polymers, and the observed SAXS maxima can be explained in terms of lamellar systems of alternating crystalline and amorphous lamellae. In the case of two-point patterns, the lamella normals point in the fiber direction, whereas for four-point patterns they are tilted with respect to the fiber axis. The obvious question is whether a similar model could be employed to explain the present four-point pattern. While there is no difficulty in recognizing a "crystalline part" in PBO, it is not at all obvious how an

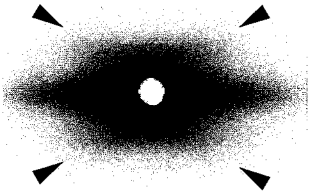


Figure 3. SAXS pattern of a heat-treated high-modulus (HM) PBO fiber showing a four-point pattern as indicated by the arrows (fiber axis vertical).

"amorphous part" should look like. The PBO molecule (**1**) itself is completely rigid and offers no significant degrees of conformational freedom that could give rise to a density contrast. The only readily available conformational change, a rotation about the σ-bonds in the molecule axis, does not generate a density contrast (in the projection onto the molecule axis which is relevant here), and other conformational changes like kinks are energetically quite expensive. This means that a possible "amorphous region" in PBO will not consist of the typical randomly coiled structures forming the amorphous regions in less rigid polymers. Indeed, the high degree of preferred orientation observed in the equatorial arcs of the PBO WAXS patterns, Figure 1, together with the absence of a traditional "amorphous halo" (other than from pure PPA while the solvent is still present) indicates that all PBO molecules are preferentially oriented in the fiber direction, i.e., not coiled. The matter is further complicated by the fact that, with estimates based on the PBO molecular weight, a single rigid molecule passes on average through more than 10 "crystalline/amorphous" periods of about 20 nm thickness each. Thus, how could it generate a density contrast?

An alternative attempt at an explanation of the observed density contrast could start by noting that the heat treatment conditions during the PBO production with temperatures above 600 °C are quite severe and that chemical reactions could take place that would alter the PBO structure and, thus, its density. Such phenomena are not uncommon in the beginning stages of the production of carbon fibers from their precursors. Clearly, the present PBO heat treatment conditions are not comparable to those necessary for a complete carbonization but, since the four-point pattern is very weak and there is spectroscopic evidence that the resulting fiber consists essentially of pure PBO, a complete carbonization is also neither desirable nor suitable to explain the SAXS results. A beginning chemical reaction involving only a small fraction of the material, e.g., a crosslinking between adjacent chains, would be sufficient to be consistent with the experimental observations. Under such conditions, the appearance of a periodic structure is not surprising. Furthermore, a well-defined cross-linking reaction could produce a staggering effect that could explain the observed tilt angle. In this case, the tilt angle should be essentially independent of mechanical influences whereas it should be variable if generated by mechanical shear.

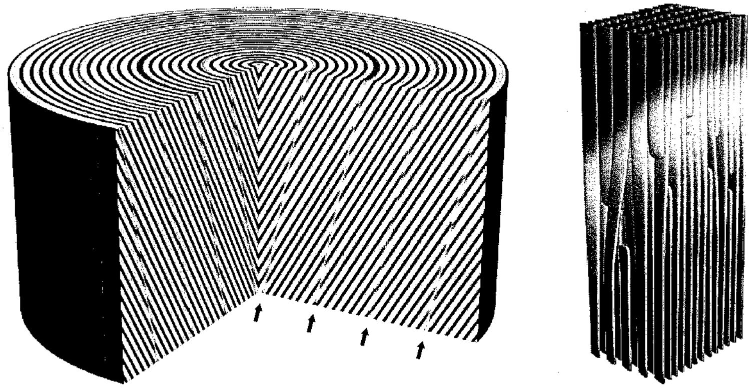
In an attempt to clarify the matter, two experiments have been carried out.[6] Firstly, PBO fibers have been heat-treated at 600 °C for extended periods of time of up to 15 min, both under vacuum and inert gas. The resulting brittle fibers indeed show a strongly enhanced SAXS four-point pattern. Furthermore, the WAXS patterns show a degradation of the ordered PBO arrangement. This result proves that a chemical reaction can indeed take place and that it enhances the density contrast generating the four-point pattern. It does not, however, prove whether this chemical reaction is the original cause for the four-point pattern or if it is merely enhancing the density contrast of a pre-existing superstructure, whether the extremely weak four-point pattern observed in HM fibers are actually caused by this effect.

Secondly, SAXS experiments on as-spun and heat-treated PBO fibers have been carried out at the ChemMAT CARS, Advanced Photon Source, Argonne National Laboratory, using a complete vacuum path for the beam from the source to the detector. Under these idealized conditions, the four-point pattern, although very weak, was also observable in the as-spun fiber. Assuming that the density contrast was not induced by radiation damage during the few seconds of synchrotron beam exposure, it must be concluded that the superstructure generating the four-point pattern is not caused by a chemical reaction but is already present in the pure PBO fiber and that any subsequent heat treatment and/or chemical reaction merely enhances the pre-existing density contrast. This leaves us with the original problem to explain the observed density contrast in a system consisting entirely of well-oriented rigid PBO chains.

In addition to the question of the density contrast, there are also some conclusions to be drawn from the appearance of the four-point pattern, not only its oblique angle but also the shape and orientation of the four maxima. The latter have a tilted elongated appearance with a tilt angle that is different from the main tilt angle of the four-point pattern. The shape and size of scattering peaks is determined by the shape and size of corresponding coherently scattering regions. The coherence of the lattice in these regions can be limited by abrupt cut-off (crystallite size effect, grain boundaries) or by continuous loss of correlation due to lattice disorder. Both scenarios are plausible for the present case of PBO.

Figure 4(a) sketches a schematic model illustrating the inclined superstructure, in this case limited by inclined grain boundaries in order to more clearly demonstrate the effect, i.e., a comparable lattice distortion picture would not show these well-defined borders. The presence of the two different tilt angles excludes the possibility of a herringbone pattern with alternating orientations in neighboring tilted stacks. Such a model could not consistently maintain the grain-boundary inclinations to generate the observed peak shapes. It is, therefore, concluded that the SAXS pattern actually consists of tilted two-point patterns and that the four-point pattern is restored in the cylindrical average.

Returning to the question of the density contrast, we conclude that, if the density contrast is to be generated by pure PBO in the form of well-oriented chains and without the help of significant conformational changes and/or chemical reactions, it can only be caused by chain ends and defects. It is reasonable to assume that chain ends and defects accumulate in regions of slightly lower density, that the segregation into these regions is periodic, enhances itself upon annealing, and offers chemical reactions a starting point for contrasting the structure. A schematic



(a) PBO fiber texture: inclined lamellar superstructures with differently inclinded grain boundaries (indicated by the arrows).

(b) Density contrast generated by accumulated chain ends and defects.

Figure 4. Schematic models illustrating (a) the spatial arrangement of the inclined lamellar superstructures and (b) the nature of the density contrast.

model is sketched in Figure 4(b). It can be expected that the resulting density difference of this model is very weak, in accordance with the experimental observations. The model should have significant influence on the mechanical properties of the fiber.

Conclusion

Time-resolved *in situ* synchrotron WAXS/SAXS (paired with off-line WAXS/SAXS after heat treatment) offers outstanding possibilities to study the structure formation in polymers at various fiber spinning and processing stages, as shown in the present work for the high-performance polymer fiber PBO. Our *in situ* WAXS studies of the early stages of the spinning and coagulation process allowed us to track the structure formation in PBO fibers over various stages of increasing liquid-crystalline order. Based on our SAXS data, we propose a structure model which is in accordance with the experimental data and can explain the observed four-point pattern in terms of its density contrast as well as its shape.

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