Microdomain Structures in Electrospun Micro-Fibers of Polystyrene-\textit{block}-
polyethylene\textit{-block}-polystyrene Triblock Copolymer

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The electrospinning technique was applied to a lamellar-forming polystyrene-\textit{block}-poly(ethylene-co-1-
butene)-\textit{block}-polystyrene (SEBS) triblock copolymer. During the electrospinning, the polymer solution sample is subjected to the high elongation along the spin-line and rapid evaporation of solvent, which freezes the oriented, deformed, or ruptured microdomain structures in the as-spun fibers. We report experimental results of two-dimensional small-angle X-ray scattering (2d-SAXS) measurements for a bundle of the SEBS aligned microfibers, electrospun by using disk collector at various take-up velocities from 31.5 up to 1260 m/min.

The disk collector enables us to align electrospun fibers and hence a series of anisotropic 2d-SAXS patterns were successfully measured, based on which we can quantitatively analyze the oriented, deformed, or ruptured microdomain structures in the as-spun fibers. The 2d-SAXS patterns are peculiar consisting of elliptic ring with a prominent “dark streak”, as presented in Fig. 1. The elliptical peak indicates a deformation of the lamellar microdomains, namely that the repeating period gradually changes with azimuthal angle (as defined clock-wise starting from 0° at the meridional direction pointing upward (parallel to the fiber axis) with respect to the fiber axis). In other words, the repeating period is the largest in the direction parallel to the fiber axis and it decreases with an increase in the azimuthal angle for the direction of the lamellar normal. As for a prominent “dark streak”, at the equatorial direction, the scattering intensity is much reduced as compared to the other directions, the shape of which reminds us a streak but not bright one so that we refer it as the dark streak. For clear demonstration of the dark streak, the distribution of the scattering intensity with the azimuthal angle along with the elliptic peak in the 2d-SAXS pattern is presented in Fig. 2. One can see a sudden intensity drop around 90° and 270° of the azimuthal angle, corresponding to the dark streak. It indicates lacking of lamellar microdomains oriented parallel to fiber axis. The formation of these microdomain structures in electrospun fibers being ascribed to the stress field might be due to the drawing of the SEBS spinning jet during the electrospinning process, and cause the rupture of lamellae which are oriented parallel to the fiber axis. Therefore, the microdomains should form first, followed by their orientation parallel to the fiber axis. In other words, their result supports the microdomain structures in our SEBS electrospun fibers due to the stretching of the spinning jet.

The azimuthal scans for fibers obtained with different rotational speeds of the collector show a similar pattern where the peaks appear at about 65°, 115°, 245° and 295°. One can see in Fig. 2 that the lowest speed has the most intense peak, while the intensity at the equator (the azimuthal angle of 90° and 270°) are almost comparable for all samples. The former fact indicates that the lamellar domain orientation parallel to the spin-line is the best for the lowest speed, while the latter fact suggests that the lamellae which are oriented almost perfectly parallel to the spin line are subjected to rupture at the certain extent, irrespective of the collector speed.

To understand effects of the collector speed on the higher-order structure, we should consider two opposed effects; one is promotion of parallel orientation of lamellar micro domains and another is reduction of time required for the spinning. If the time is reduced, solvent evaporation is not well completed during the spinning, which results in incomplete lamellar formation. This further may spoil stress-transmission mechanism, and in turn resulting in the poorer orientation of the lamellae. The optimum condition may be around 31.5 m/min.

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![1](image1.jpg) 2d-SAXS pattern for a fiber obtained with the collector speed of 31.5 m/min.

![2](image2.jpg) Azimuthal scans for fibers obtained with different rotational speeds of the collector.