Over the years, electrospinning has been developed as a technique to produce nano- to micron-sized fibers for filtration and biomedical applications [1]. It is well understood that the internal structure of these fibers highly depends on the polymer type, the spinning solution properties and the spinning parameters. In this contribution we present our recent advances in structural insights into electrospun poly(vinylidene fluoride-co-hexafluoropropylene), PVDFhfp, based fiber membranes for non-aligned and aligned (by using a high speed rotating drum) samples using X-ray scattering and diffraction techniques [2]. The densely packed lamellar structures in nanoscale with respect to fiber orientation axis have been analyzed by small angle X-ray scattering (SAXS) while molecular arrangement in orthorhombic structure are visualized by wide angle X-ray diffractions (WAXD). The nanofibrillar surface structures have also be seen by AFM performed on single fibers.

Furthermore, we will discuss our vision for nanoscale structural modification of the fibers by applying extreme drawing achieved using a high speed rotating drum electrospinning collector. The possibilities for significant variation in the ratio of crystalline $\alpha$ and $\beta$ phases will also be discussed. These studies and our further investigation shall establish new strategies for designing and processing novel functional electrospun membranes.