PVDF Nanofibers Obtained by Electrospinning and Blowspinning: Electrospinning Enhances the Piezoelectric β-Phase – Myth or Reality?

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ABSTRACT

Considerable effort has been devoted to improving the properties of PVDF (polyvinylidene fluoride), arguably the most technologically important piezoelectric polymer. Electrospinning has been found to be a particularly effective method of producing PVDF nanofibers with superior piezoelectric properties due to the resulting exceptionally high fraction of the piezoelectrically active crystalline β-phase. It is typically assumed that the high external electric fields applied during electrospinning enhance the formation of this β-phase, with the confused literature offering various unsatisfactory mechanistic explanations. However, by comparing PVDF nanofibers produced by two different processes (electrospinning and blowspinning), we show that the electric field is entirely unnecessary; indeed, the crystallization dynamics are principally driven by the applied mechanical stress, as evidenced by structurally identical 200 nm diameter PVDF fibers produced with and without external electric fields.

INTRODUCTION

Polyvinylidene fluoride (PVDF) is a piezoelectric polymer whose chemical inertness, biocompatibility, and mechanical flexibility gave garnered considerable interest for a wide range of biomedical and sensor applications[1-3]. It is a semi-crystalline polymer and the thermodynamically stable α phase and the metastable β phase are the two most commonly observed crystal structures[4,5], with the β phase being mostly responsible for the piezoelectric character of the polymer. The chain conformations corresponding to these two crystalline phases are shown in Figure 1.

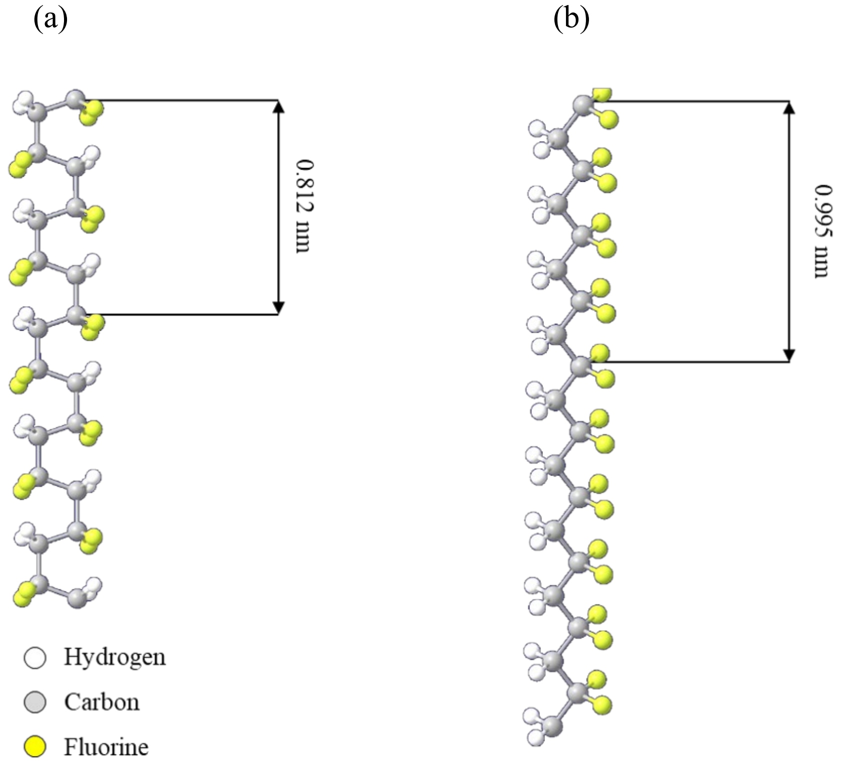

Figure 1. Geometric conformation of: a) α phase and (b) β phase.

PVDF is considered one of the best performing piezoelectric polymers, although its behavior is highly dependent on processing[6-12]. Generally, mechanical stretching of an as-cast PVDF film, which contains predominantly the thermodynamically stable α phase, is the most common technique used to obtain the metastable piezoelectric β phase[9, 13, 14]. Under a mechanical load, the polymer chains align in the direction of tensile stress, orienting the dipole moments perpendicular to the polymeric chain[9]. Alternatively, rapid cooling directly from the polymer melt under high pressure and external electric field can also be used to crystallize the liquid directly into the β phase[11].

Solution electrospinning is a processing technique that has garnered tremendous interest over the last decade, particularly for PVDF fibers and membranes. This technique manufactures polymer fibers with diameters ranging from a few nanometers to several micrometers from polymeric solutions[15]. This technique involves extrusion and stretching of a polymeric solution by an electrostatic force (Figure 2a), created by the application of an electrical field (on the order of several kV/cm) between a metallic nozzle (emitter) and a grounded collector[16]. The electrospinning process therefore combines two effects to produce polymeric fibers: (1) mechanical stretching and (2) electrical polarization[17-19].

Electrospinning has been reported to greatly enhance the formation of the piezoelectric β phase in PVDF[17, 20-23], although the underlying mechanisms are poorly understood. It has been suggested that the presence of the electric field is essential for the formation of the β phase in electrospinning by aligning the dipole moment of molecules[18, 24]. Some studies have reported that highly polar solvents or addition of electrically conducting salts significantly increase the β phase volume fraction[10, 16, 19, 22, 24]. Much discussion exists in the literature, with most authors attributing the enhanced β phase volume fraction on the strong applied electric field, although there is no overarching consensus. Is the increased β phase volume fraction simply explained by the mechanical stretching of the fiber due to electrostatic attraction, or does the applied electric field directly align the dipole moments in the molecular chains and encourage β phase crystallization? The electric field is integral to the electrospinning process and remains convoluted with the mechanical stretching, making it experimentally challenging to solve this mystery.

In order to isolate the effect of the electric field in electrospinning, the present study employs solution blowspinning: this method is similar to solution electrospinning, but eliminates the electric field [26,27]. Instead, gas (or air) is blown along the outside of the nozzle (emitter), thereby "blowing" the fiber and pulling it out of the nozzle (figure 2b). This method, first described by Medeiros et al. (JAPS, 2009) and since enjoying increasing interest in the literature[27-29], extrudes the polymer solution through a coaxial needle whereby the polymer solution is pumped through the inner nozzle while a constant high pressure gas flow is sustained through the outer nozzle.

Additional details on the apparatus used in the present study, including drawings and nozzle schematics, can be found in Medeiros et al.[27] The fiber is therefore extruded and mechanically stretched, without requiring an electric field; by comparing PVDF fibers produced by electrospinning to fibers produced by blowspinning, it therefore becomes possible to deconvolute the effect of the electric field from the mechanical stretching during fiber manufacture.

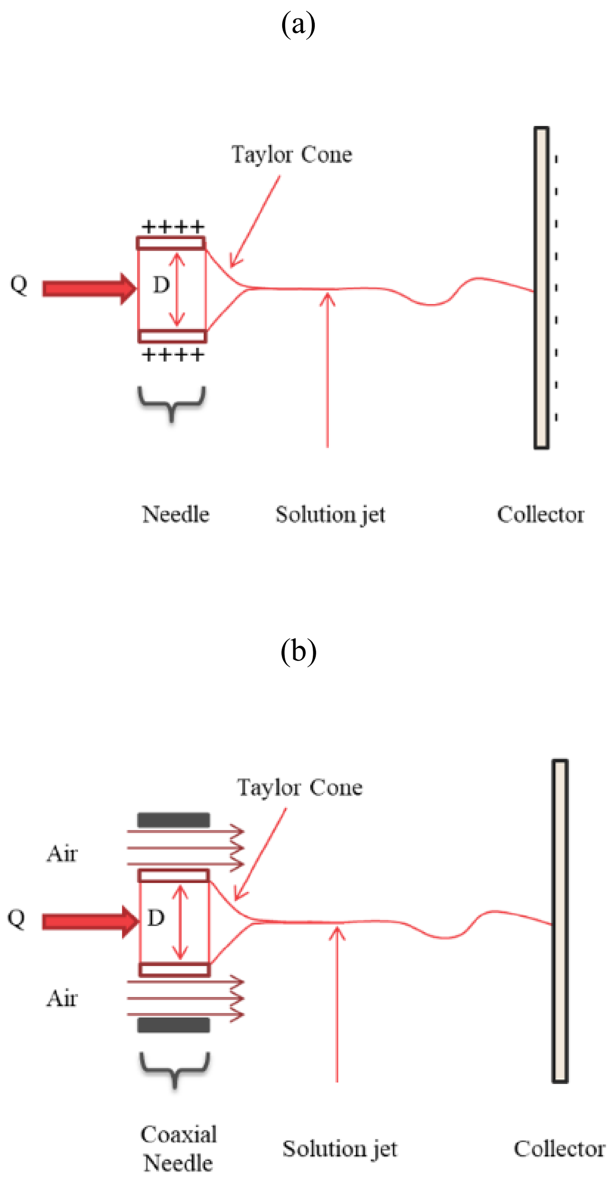

Figure 2. Schematic showing a polymer solution being extruded with a flow rate Q through a nozzle of inner diameter D using either (a) Solution electrospinning (SES) process, or (b) Solution blowspinning (SBS) process.

EXPERIMENTAL SECTION

Polyvinylidene difluoride (PVDF) powder with the trade name Kynar 741 was obtained from Arkema. A solvent solution was prepared from 7 parts (by weight) of N,N-Dimethylformamide (DMF) and 3 parts (by weight) of acetone. This solvent solution was used to dissolve the PVDF powder to obtain a final solution that contained 18%wt. of PVDF. The same solution was used for all experiments.

Solution Electrospinning

During the electrospinning process, an electric field of 1.25×10^5 V/m was applied to the needle and a solution flow rate of 5 μL/min was used.

Solution Blow Spinning

The polymeric solution was injected through the inner nozzle with a flow rate of 33 μL/min. Compressed air was delivered at a constant pressure of 140 kPa through the outer nozzle.

All tests were performed at room temperature, and the distance between the emitter and the collector was held constant at 20 cm.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) was used to visualize the membrane morphology (fiber diameter and shape). The fibers obtained from both electrospinning and blowspinning are similar, free from defects, and with an average diameter (as measured using statistical image analysis) of about 196 nm for electrospun fibers and 206 nm for blowspun fibers. Figure 3 shows representative SEM images of electrospun and blowspun PVDF fibers. The fibers obtained by the two processes are generally similar, except that the blowspun fibers appear more aligned. This is consistent with the observation that the fiber production rate using blowspinning is faster than using electrospinning: the slower flight of electrospun fibers toward the target increases turbulent instabilities and therefore results in a more random alignment upon deposition.

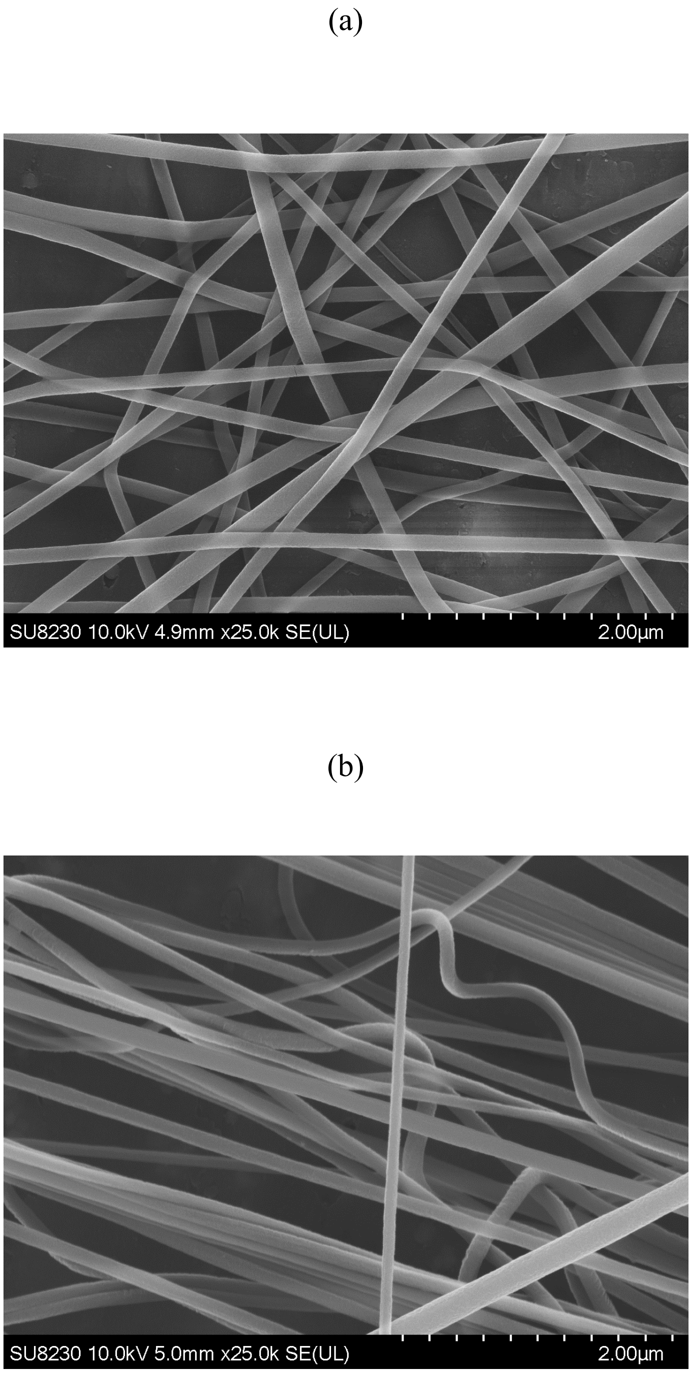

Figure 3. Representative SEM images of PVDF fibers obtained by (a) Solution electrospinning, and (b) Solution blowspinning.

Fourier transform infra-red (FTIR) spectroscopy was used to perform an advanced structural characterization of the manufactured fibers. Figure 4 shows representative FTIR spectra of PVDF powder, electrospun fibers and blowspun fibers.

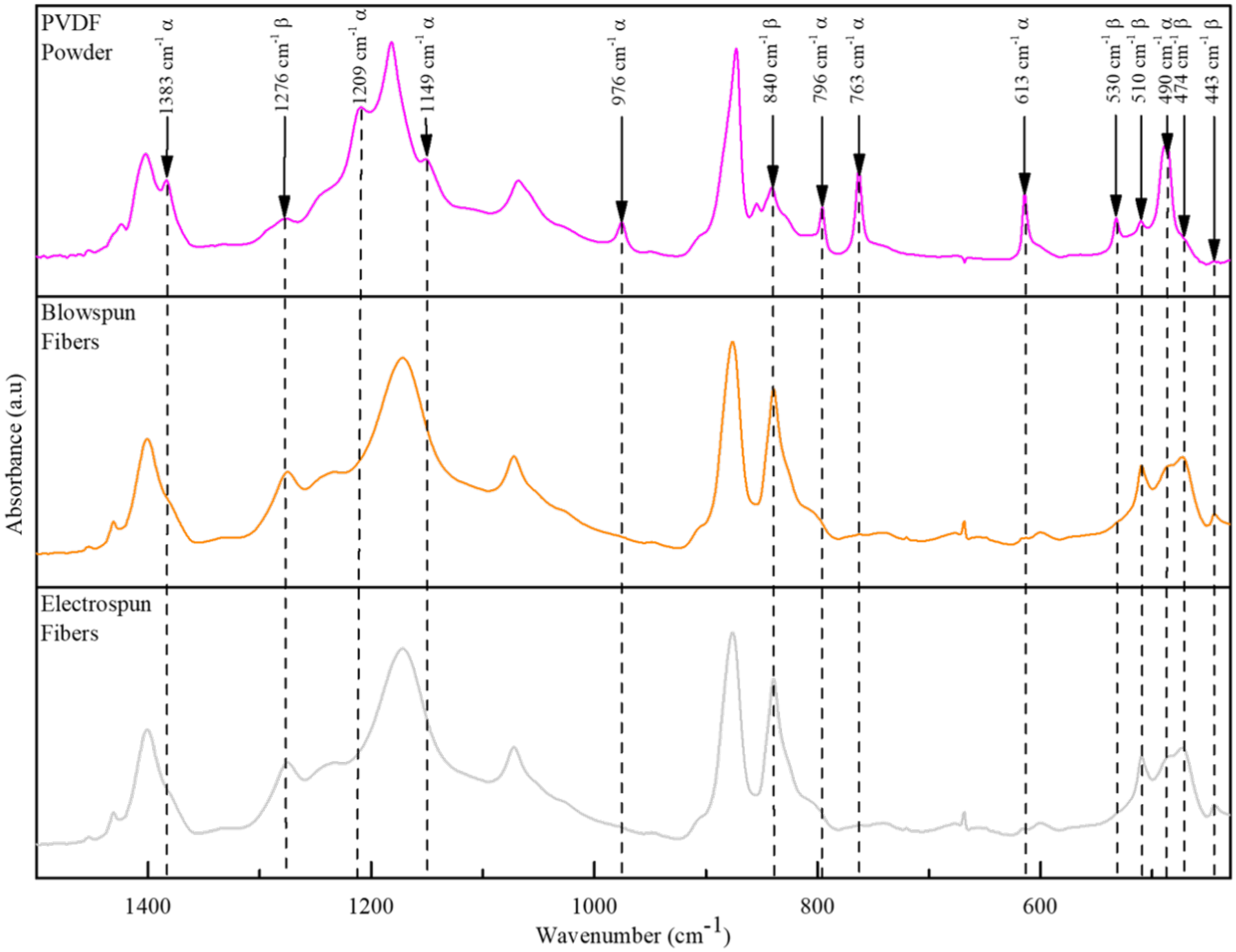

Figure 4. FTIR Spectra of PVDF powder, blowspun fibers and electrospun fibers.

An identification of absorption bands at 490, 613, 763, 794, 1149, 1209, and 1383 cm^{-1} indicates that these bands are associated with the α phase[8, 30] and those located at 443, 474, 510, 840, and 1275 cm^{-1} are associated with the β phase[8, 30, 31]. According to the FTIR spectra, it can be clearly seen that the virgin PVDF powder is mainly composed of the non-polar α phase. The polar β phase is mostly absent in the virgin powder, and appears when the PVDF is processed either by electrospinning or blowspinning. No difference in functional groups, including chemical degradation, is observed after either processing. The spectra obtained from electrospun and blowspun fibers are indistinguishable.

X-ray diffraction (XRD) was used to further characterize the crystalline structure of PVDF fibers. A Panalytical X'pert Pro MPD X-ray diffractometer using Cu Kα radiation λ = 1.54 Å was used at ambient temperature. All diffraction peaks were fitted to Voigt functions, and the relative volume fractions of crystallographic phases were quantified using structure factor calculations. The non-polar PVDF α phase displays monoclinic symmetry[32, 33], while the piezoelectric polar β phase displays orthorhombic symmetry[11, 30].

Figure 5 shows representative X-ray diffractograms of PVDF virgin powder, electrospun fibers and blowspun fibers.

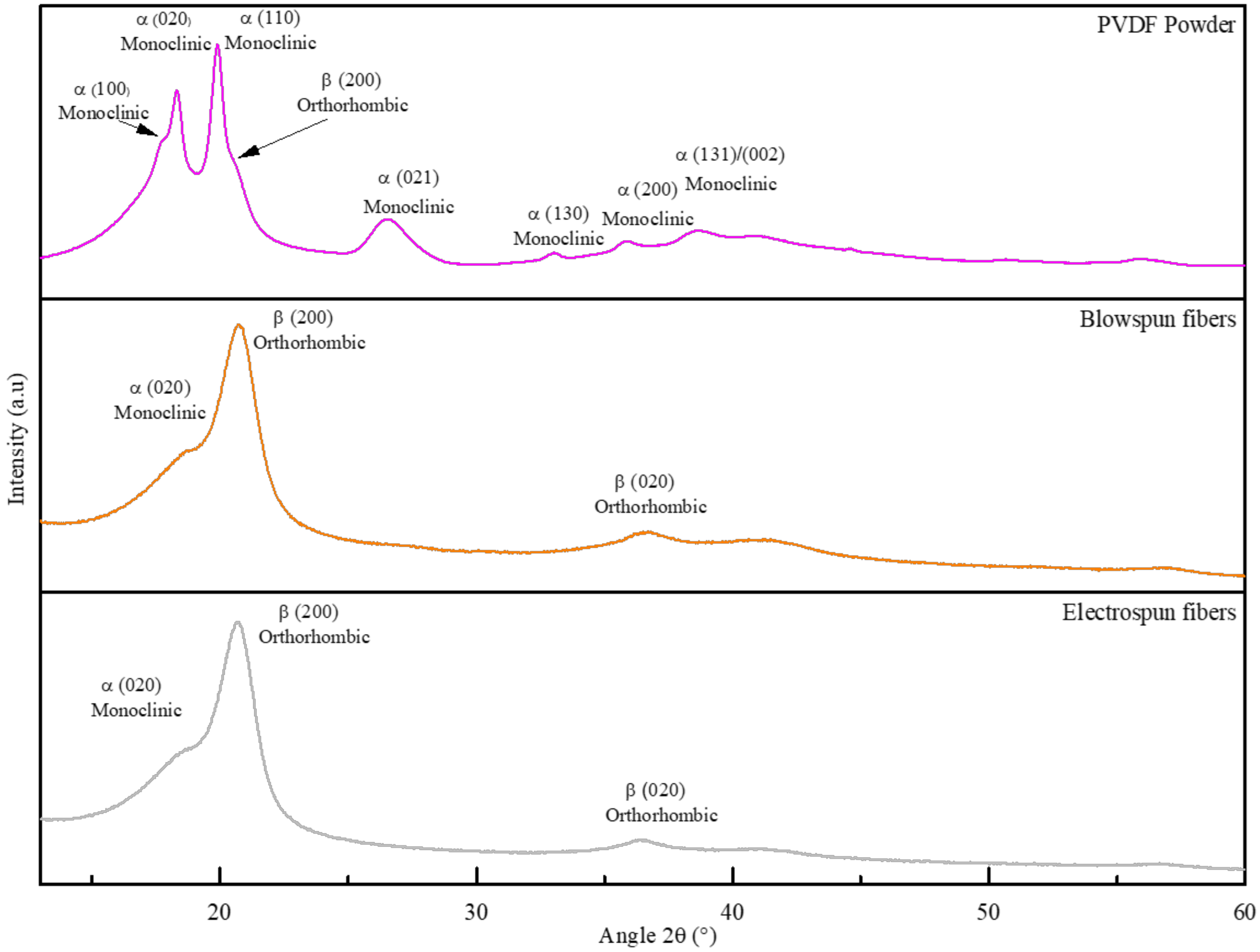

Figure 5. Representative X-ray spectra of: PVDF powder, blowspun fibers and electrospun fibers (PVDF fibers were obtained from polymeric solution of 18% wt.).

The virgin PVDF powder is semi-crystalline (40 % crystallinity) and the non-polar α phase predominates. As was seen in the case of FTIR analysis, the spectra obtained from blowspun and electrospun fibers are indistinguishable. Moreover, the processed PVDF fibers have increased crystallinity (56-58%) compared to the virgin powder (40%), consistent with improved crystallization when molecular chains are aligned during mechanical stretching. In addition, the relative volume fraction of the β phase increased from 11% in the virgin powder to 53-56% for the processed fibers.

In the case of the fibers, we also note the marked absence of a peak at 35.04°, which would correspond to the (001) plane in the β phase; all other expected β phase peaks are present. The "missing" (001) peak can only be explained by the (001) plane being perpendicular to the fiber axis. This confirms that the molecular chains that form the β phase are oriented along the length of the fiber axis[34-36] – as one would expect when a polymer fiber is extruded and mechanically stretched during processing. Such orientation of the molecular chain along the fiber length cannot be explained by the electrostatic field.

A comparative table summarizing the materials characterization performed is provided in the table below.

	PVDF powder	Blowspun	Electrospun
Average diameter (nm) ± std. dev.	N/A	206 ±36	196 ±35
Degree of crystallinity (%)	40	56	58
Volume fraction of polar β phase (%)	11	53	56

Table 1. Volume fraction and degree of crystallinity in PVDF fibers obtained by SES and SBS.

The fibers obtained by electrospinning and blowspinning are comparable in every way, with the molecular chains oriented along the fiber length. This confirms that it is indeed the mechanical stretching during processing that results in the enhanced β phase, independent of the electrostatic field. The development of the piezoelectric β phase necessarily forms electrostatic dipole moments in the fibers; what we find is that this "charging" is intrinsic to the PVDF material and requires no applied external electric field. The mechanical stretching is sufficient to explain the structural changes that occur during processing, resulting in the increased crystallinity and β phase volume fraction.

CONCLUSIONS

Structurally indistinguishable PVDF nanofibers (diameter ~200 nm) were produced using both solution electrospinning and solution blowspinning. This confirms that the electric field that has often been invoked to explain the improved piezoelectric properties of electrospun PVDF is unnecessary, and that the increased β phase volume fraction is fundamentally a result of mechanical stretching – regardless of the origin of that stress. By eliminating the effect of the electric field, we determine that the transformation to the β phase during the electrospinning process is principally caused by the mechanical alignment and extension of the molecular PVDF chains along the nanofibers, thereby encouraging crystallization in the piezoelectric β phase. This suggests that although electrospinning is a useful technique for manufacturing high quality piezoelectric PVDF fibers, other manufacturing methods that optimize the mechanical stretching process may be more effective for practical applications.

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