# Molecular Orientation in Electrospun Poly(vinylidene fluoride) Fibers

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ABSTRACT: Electrospun poly(vinylidene fluoride) (PVDF) nanofibers were collected on aluminum foil across a 10 mm gap. Scanning electron microscopy (SEM) images showed that fibers in the gap were macroscopically aligned and those off the gap were macroscopically randomly aligned. Polarized Fourier transform infrared (FTIR) spectra and single fiber selected area electron diffraction (SAED) patterns demonstrated that fibers deposited in the gap were highly aligned at the molecular level with the polymer backbones oriented along the fiber axis. SAED patterns of fibers deposited off the gap were also oriented at the molecular level, but the degree of orientation was lower.
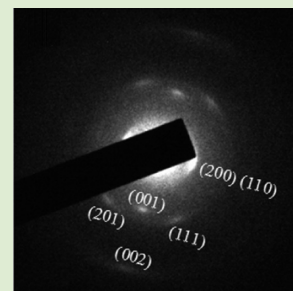
Cooley[1] and Morton[2] produced fibers by dispersing a fluid under an electric field in 1902, which represented the first invention of electrospinning. Electrospinning is now established as an efficient technique to produce small-diameter (10 nm to 10 μm) polymer fibers. The fibers are fabricated from polymer solutions or melts using an applied electric field. Many polymers have been successfully electrospun, and their applications include composites, filtration systems, medical prosthesis, tissue templates, electromagnetic shielding, and liquid crystal devices.[3] Macroscopically aligned electrospun fibers have additional potential applications as compared to random fibrous mats.[3] Researchers have obtained macroscopically aligned electrospun fibers using rotating mandrels,[4] rotating disks,[5] and counter electrodes.[6] Jalili et al. analyzed the effects of gap width and applied voltage on the degree of macroscopic alignment in polyacrylonitrile fibers.[7] Bazbouz and Stylios demonstrated that the electrostatic repulsive forces between fibers have a significant effect on the degree of macroscopic alignment.[8] However, detailed studies of the extent of orientation in electrospun fibers are limited, and the exact explanation of the driving force for molecular orientation is still under investigation.[9−13] Lin used selected area electron diffraction (SAED) to show that the degree of molecular orientation in individual electrospun poly(lactic acid) (PLLA) nanofibers increased as the nanofiber diameter decreased.[14] Kakade et al. demonstrated that an electric field used to macroscopically align poly(ethylene oxide) nanofibers can also align polymer chains at the molecular level.[9] Lee et al. obtained macroscopically aligned and molecularly oriented nylon-6 nanofibers by controlling the linear velocity of a rotating collector.[10] Bellan and Graighead recorded polarized Raman spectra of single electrospun Nylon-6 nanofibers indicating a significant degree of molecular orientation.[11] Cheng et al. revealed the effects of annealing temperature on molecular orientation with electron diffraction patterns of single electrospun sydiotactic polystyrene fibers.[12] Yoshioka et al. analyzed the molecular orientation of electrospun polyethylene using single fiber electron diffraction patterns.[13]

There is considerable interest in electrospun fibers of poly(vinylidene fluoride) (PVDF) because of its piezoelectric

and pyroelectric properties. Several different crystal phases have been found in PVDF.[15] The β phase, which is piezo- and pyroelectric, has the all-trans conformation (Figure 1).[16]
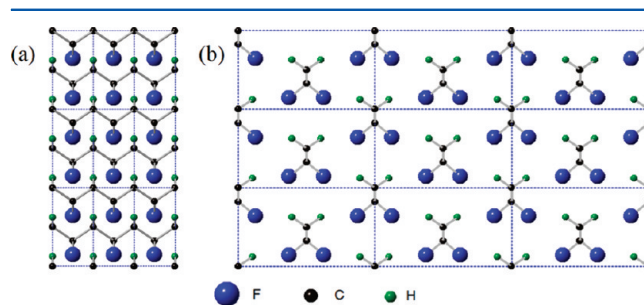

Figure 1. Crystal structure of β phase in PVDF. (a) View direction [100], (b) view direction [001].

Andrew and Clarke concluded that highly crystalline PVDF fibers of primarily β phase were obtained by electrospinning.[17] In this study, PVDF has been chosen since the large β phase content is sensitive to the electric field and can be formed in a simple one-step electrospinning process. In addition, the potential piezo- and pyroelectric properties of PVDF nanofibers have implications for applications as sensors and actuators. Here, the overall size, macroscopic alignment, and molecular orientation of PVDF fibers were characterized by scanning electron microscopy (SEM), polarized Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and selected area electron diffraction (SAED).

SEM images show that fibers in the gap (Figure 2a) are aligned parallel to one another, while fibers off the gap (Figure 2b) are randomly oriented. The distribution of the angle between the fiber axis and the normal to the edges of the gap on the collector is used to evaluate the degree of macroscopic alignment.
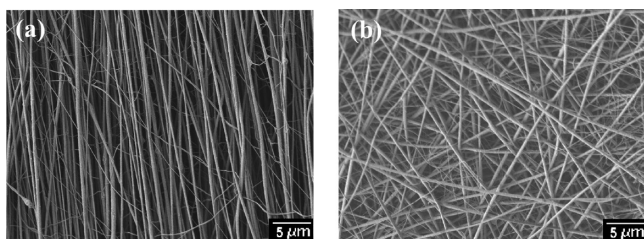
Figure 2. SEM images for fibers spun with 10 kV on the needle and −4 kV on the collector (a) in the gap and (b) off the gap.

For fibers in the gap, around 93% of the fibers are aligned to within 20° and 80% are aligned to within 10°. For fibers off the gap, around 11% of the fibers are aligned to within 20°, which is the value for randomized macroscopic alignment.

Figure 3 shows the polarized FTIR spectra of fibers in the gap and off the gap from the same collector. The band at 1186 cm^{-1}
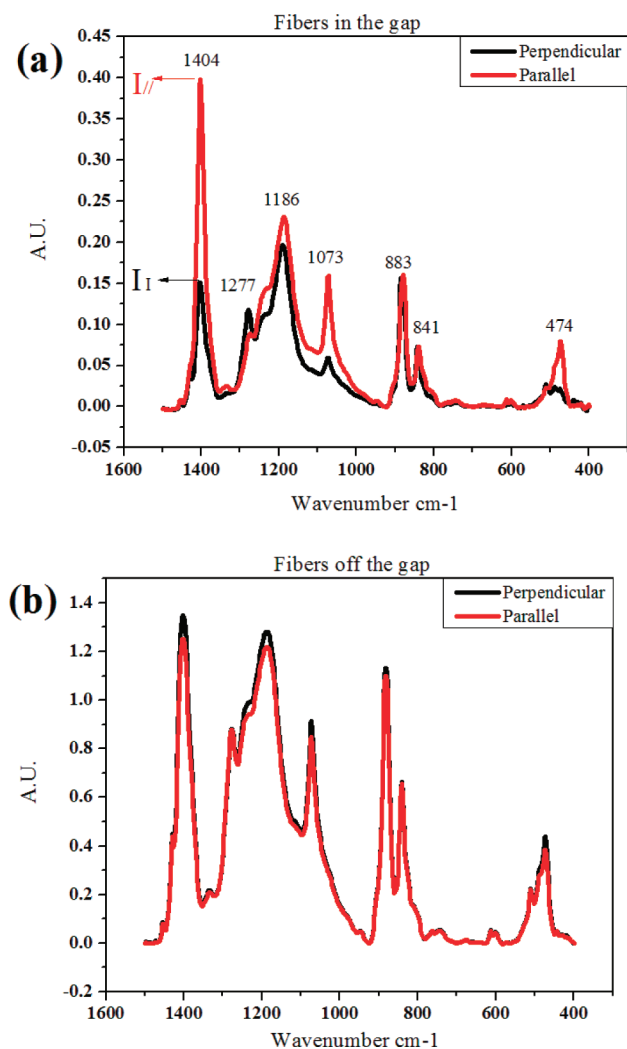

Figure 3. Polarized FTIR spectra for fibers (a) in the gap and (b) off the gap. For fibers aligned in the gap, the red line was obtained with the infrared beam polarized parallel to the fiber axis ($I_{\parallel}$) and the black line was obtained with the beam polarized perpendicular to the fiber axis ($I_{\perp}$). For fibers off the gap, two mutually perpendicular directions were chosen for the polarized IR beam.

(CF$_2$ symmetric stretching and CH$_2$ twisting) is the only one assigned to the α phase; all of the other bands are assigned to

the β phase.[16,18] The most intense band attributed to CH$_2$ wagging and CC antisymmetric stretching at 1404 cm^{-1} has its change in dynamic dipole moment along the polymer backbone. The band at 1277 cm^{-1} is attributed to CF$_2$ symmetric stretching, CC symmetric stretching, and CCC bending and has the dynamic dipole moment change oriented perpendicular to the polymer backbone. For fibers in the gap, the band at 1404 cm^{-1} had a higher absorbance when the infrared beam was polarized along the fiber axis, while the band at 1277 cm^{-1} had a higher absorbance when the infrared beam was polarized perpendicular to the fiber axis. This indicates that the polymer backbone was preferentially oriented along the fiber axis for fibers in the gap. However, the absorbance for fibers off the gap under two mutually perpendicular polarizations did not show a significant difference. Furthermore, the potential orientation of fibers off the gap could not be determined by polarized FTIR because of the randomized macroscopic alignment of the nanofibers.

SAED patterns using low dose TEM were obtained for single PVDF fibers collected from inside the gap, outside the gap, and from aluminum foil without the gap. Typical SAED patterns from all three cases are shown in Figure 4. A comparison between the calculated d-spacings and experimental values is listed in Table 1. In the SAED pattern shown in Figure 4a, the arcs corresponding to a d-spacing of 0.258 nm can be attributed to the (001) reflection with a d-spacing of 0.256 nm representing the molecular chain repeat period.[15] This result confirms the conclusion based on FTIR spectra that the polymer backbone is oriented along the fiber axis.

Polarized FTIR only proves the molecular orientation of fibers in the gap due to the random macroscopic orientation of fibers off the gap. The SAED further demonstrates that local molecular orientation exists in electrospun PVDF fibers in the gap, off the gap, and on the aluminum foil without the gap. The smaller degree of the arc attributed to the (001) reflection represents the higher degree of molecular orientation. Yoshioka et al. found that the degree of molecular orientation calculated from SAED patterns was strongly related to the fiber diameter.[13] We found that, when comparing SAED patterns of fibers with similar diameters, the orientation of fibers deposited in the gap was significantly highly than those deposited off the gap. Figure 4a,c (with fiber diameter around 250 nm) shows that the degree of molecular orientation for fibers in the gap (average degree of the arc = 15°) is higher than that for fibers off the gap (average degree of the arc = 23°). Figure 4e,g (with fiber diameter around 150 nm) shows that the degree of molecular orientation for fibers in the gap was higher (average degree of the arc = 15°) than that for fibers on aluminum foil without the air gap (average degree of the arc = 23°). In addition, when the fiber diameter varied between 150 to 250 nm, the effect of fiber diameter on the degree of the orientation was negligible. These findings unambiguously demonstrate that, while fibers deposited in the gap have the highest degree of molecular orientation, even the fibers deposited off the gap do show some degree of modest molecular orientation. This confirms that some molecular orientation is occurring during the electrospinning process itself, even without an air gap.

By using a collector with a rectangular air gap in the center, either macroscopically aligned (in the gap) or randomized PVDF fibers were obtained (off the gap). The polarization behavior of the FTIR bands at 1277 cm^{-1} (change of the dipole moment perpendicular to the polymer backbone) and 1404 cm^{-1} (change of the dipole moment parallel to the polymer backbone)
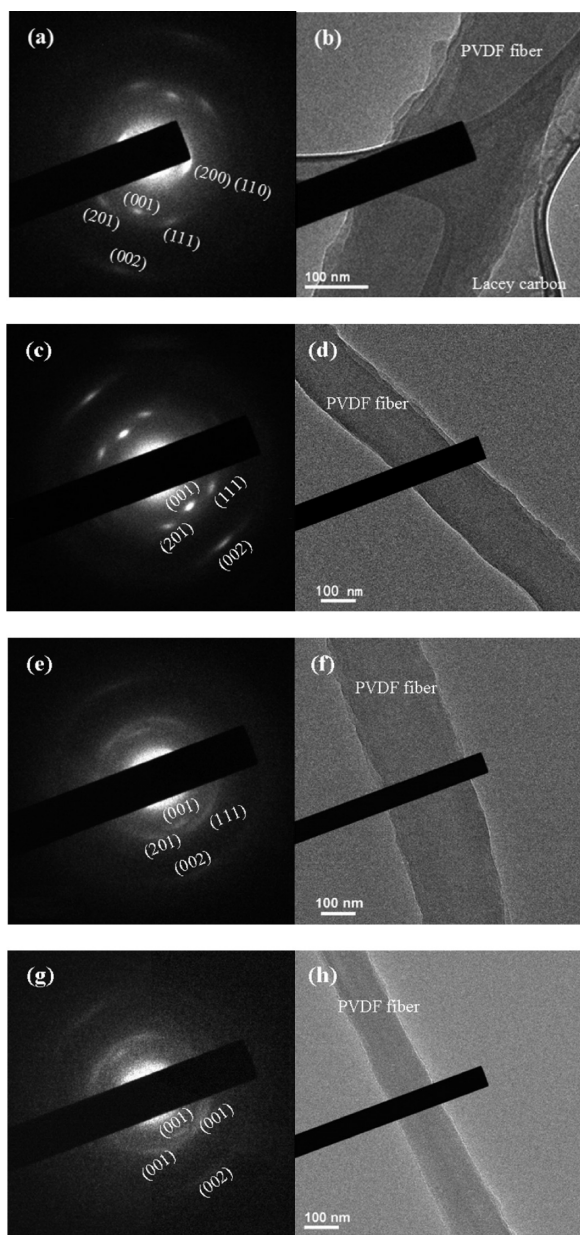
Figure 4. (a) SAED pattern and (b) BF image of a PVDF fiber *in the gap* with diameter ~250 nm, (c) SAED pattern and (d) BF image of a PVDF fiber *in the gap* with diameter ~180 nm, (e) SAED pattern and (f) BF image of a PVDF fiber *off the gap* with diameter ~250 nm, and (g) SAED pattern and (h) BF image of a PVDF fiber on the aluminum foil *without the air gap* with diameter ~150 nm. The applied voltage was 10 kV on the tip of the needle and −4 kV on the collector.

Table 1. d-Spacings Calculated for the β Phase[15] and Observed from SAED Patterns of Electrospun PVDF Fibers in the Gap

reflection index (hkl)	(200)	(110)	(001)	(201)	(111)	(002)
calculated d-spacing (nm)	0.429	0.426	0.256	0.220	0.219	0.128
experimental d-spacing (nm)		0.427	0.258		0.221	0.129

indicated that the PVDF polymer backbones of aligned fibers deposited in the gap were oriented along the fiber axis. The

SAED patterns confirmed the molecular orientation of nanofibers deposited both in the gap (with an average misorientation of (001) reflection = 15°) and off the gap (average misorientation of the (001) reflection = 23°). While the fibers deposited off the gap were not as highly oriented as those in the gap, these results do confirm that molecular orientation occurs during the electrospinning process, even without an air gap.

■ EXPERIMENTAL SECTION

PVDF pellets (M_w = 275 000 g/mol) were obtained from Aldrich, and N,N-dimethylformamide (DMF) was from Fisher Scientific. An 18% (w/w) PVDF/DMF solution was prepared by heating and stirring at 100 °C for two hours until all of the pellets dissolved in the solvent. The solution was then transferred to a 3 mL syringe attached to a 14 gauge needle. The working distance was set to 12 cm, and the flow rate maintained at 0.2 mL/h with a syringe pump. In the conventional system, an aluminum foil covered cardboard sheet was used as the collector. Motivated by Kakade's work,[9] a rectangular hole (35 mm × 10 mm) was cut in the cardboard sheet. Then aluminum foil was used to cover the cardboard thoroughly, leaving only the hole as a 35 mm × 10 mm air gap (Figure 5a). After applying an adequate electric field between the needle and the collector, fibers in the air gap (region I) and off the gap (region II) were obtained on the same collector (Figure 5b).
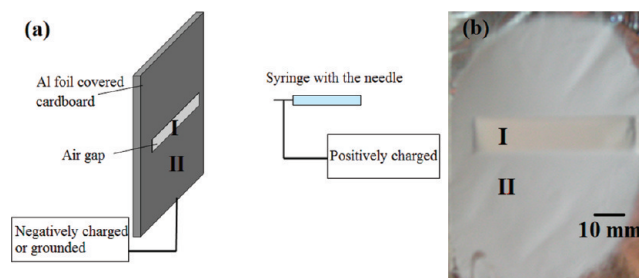

Figure 5. (a) Experimental setup (syringe pump is not shown) and (b) digital photo of the collector with fibers in the gap (I) and off the gap (II).

SEM (JEOL JSM 7400F) images were obtained to investigate the macroscopic fiber alignment. The accelerating voltage used for the SEM experiment was 2.0 kV, and the current was 10 μA. The molecular orientation of polymer chains was characterized by polarized FTIR (Thermo Nicolet NEXUS 670) using a ZnSe polarizer. The resolution of the FTIR measurement was 4 cm^{-1}, and the number of scans collected was 128. Both bright field (BF) images and SAED patterns were acquired by TEM (JEOL JEM-2010F FasTEM) with 200 kV accelerating voltage. Digital images were analyzed with ImageJ (National Institute of Health) software.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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