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Melting Temperature of Individual Electrospun Poly(vinylidene fluoride) Fibers Studied by AFM-based Local Thermal Analysis

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Electronic Supplementary Information

Abstract Thermal properties such as melting temperature can well reflect the microstructure of the polymer material, and have practical implications in the application of nanofibers. In this work, we investigated the melting temperature of individual electrospun poly(vinylidene fluoride) (PVDF) nanofibers with diameters ranging from smaller than 200 nm to greater than 2 μm by the local thermal analysis technique. The PVDF fibers obtained under four different conditions were found to crystallize into α and β phases, and the fiber mats showed typical values in the crystallinity and T_m with no significant difference among the four. However, analyses at single fiber level revealed broad distribution in diameter and T_m for the fibers produced under identical electrospinning condition. The T_m of individual nanofibers was found to remain constant at large diameters and increase quickly when reducing the fiber diameter toward the nanoscale, and T_m values of 220–230 $^{\circ}\text{C}$ were observed for the thinnest nanofibers, much higher than the typical values reported for bulk PVDF. The T_m and molecular orientation at different positions along a beaded fiber were analyzed, showing a similar distribution pattern with a minimum at the bead center and higher values when moving toward both directions. The results indicate that molecular orientation is the driving mechanism for the observed correlation between the T_m and the diameter of the nanofibers.

Keywords Electrospun fibers; PVDF; Local thermal analysis; Melting temperature

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INTRODUCTION

Electrospinning is a versatile and facile technique for manufacturing polymeric nanofibers with diameters ranging from several tens of nanometers to micrometers,^[1] and electrospun fibers have found application in a broad range of fields, such as catalysis, filtration,^[2–4] drug delivery,^[5,6] and tissue engineering.^[7–9] It is well known that the electrospinning process condition can affect the structure, which in turn results in different mechanical properties of the fibers. In particular it has been reported extensively that electrospun nanofibers would exhibit a significant increase in the modulus as the diameter decreases to below an onset value, the so-called size-dependence behavior. For example, Wong *et al.* observed an abrupt shift in tensile strength and stiffness for electrospun poly(3-caprolactone) (PCL) fibers as their diameters decreased to around 700 nm.^[10] Rutledge *et al.* studied the Young's modulus and yield strength of individual poly(trimethyl hexamethylene terephthalamide) nanofibers and found that both increased with decreasing fiber

diameter at about 500 nm and less.^[11] In fact, this size-dependent behavior has been demonstrated for electrospun nanofibers in many ways,^[12] including the strength, toughness, stress, and some thermodynamic properties.^[13–19] Among these, thermal properties such as melting temperature can well reflect the microstructure of the polymer material, and have practical significance in application of the nanofibers.

In the past decade, several groups have investigated the thermal properties of electrospun nanofibers. The studies typically involved thermal analyses on fiber mats by differential scanning calorimetry (DSC). For example, Wang *et al.* investigated electrospun poly(ethylene oxide) (PEO) fiber mats with average fiber diameters ranging from less than 100 nm to about 1.3 micron, and showed that both melting temperature and crystallinity of the fibers were lower than that of cast film, and decreased with the average fiber diameter decreasing.^[20] The melting temperature depression observed was attributed to rapid fiber formation in the electrospinning process, which was believed to hinder the development of well-ordered crystals.^[21] Li *et al.* prepared aligned poly(ϵ -caprolactone) (PCL) nanofibers using a two-parallel-conductive-plate collector and observed that as the gap between the plates increased, the average fiber diameter remained constant at

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about 300 nm while the melting point increased slightly, which was ascribed to a higher degree of crystalline perfection under greater stress.^[22] Kolbuk *et al.* fabricated PCL nanofibers with average diameters of ~0.2–1.3 micron, and found that the melting temperature of the fibers did not vary significantly with the electrospinning conditions and remained essentially the same as that of the raw pellet, while the crystallinity was lower.^[23] Arinzeh *et al.* reported that poly(vinylidene fluoride) (PVDF) fibers with average diameters in the range of 150 nm to 300 nm exhibited a similar melting temperature, which was lower than that for raw pellets.^[24] These results from different systems are inconsistent and confusing. Part of the reason is that DSC results on fiber mats are averages over ensembles of individual fibers, often with a broad diameter distribution and hence different thermal properties. Indeed, it has been demonstrated that DSC melting curves for specimens cut from a same fiber mat can exhibit a large scattering.^[23] Therefore, thermal analysis at single fiber level becomes necessary in order to better understand the size-dependent thermal behavior of electrospun nanofibers.

Wang *et al.* investigated individual PEO fibers thinner than 50 nm to ~600 nm in diameter by AFM thermal indentation, and found that the nanofibers exhibited a melting temperature similar to that of the bulk at 350 nm and above in diameter, but decreased with fiber diameter for thinner fibers, especially at 300 nm and below.^[20] The data were fitted to Gibbs-Thomson equation, and the observed melting temperature decrease with the fiber diameter was explained by an increase in the relative amount of polymer chains of higher mobility at the surface.^[20] Liu and Arinstein *et al.* employed shear modulation force microscopy (SMFM) to measure the melting point of a series of single poly(ethylene-co-vinyl acetate) (PEVA) fibers, and revealed depression of the melting point relative to the bulk for fibers thinner than 10 microns.^[25–27] A similar but more gradual decrease in melting temperature was also observed for low density polyethylene in the fiber diameter range of ~2–10 microns.^[26,27] The melting point depression occurred in relatively thick fibers and cannot be attributed to effects of surface or confinement. Instead, Arinstein *et al.* proposed that extreme elongation and rapid solvent evaporation during nanofiber electrospinning can lead to a lower level of chain entanglement in the amorphous part in the fiber, resulting in an additional jump in entropy upon melting and thus a reduced melting point.^[26] In these studies, fibers of various sizes were obtained under different electrospinning conditions, and the melting temperature shifts observed were relatively small, within several to ten degrees. To our best knowledge, there has been no report in the literature on the relationship between melting temperature and diameter for nanofibers prepared under identical electrospinning condition.

PVDF is a commercially important semi-crystalline polymer with interesting electroactive properties.^[28] This polymer can present at least five distinct crystalline forms related to different chain conformations, namely α , β , γ , δ , and ϵ phases. Electrospinning has been shown to promote formation of the β phase,^[29] which has all *trans* (TTTT) chain conformation with unusual piezoelectric and pyroelectric properties^[30,31] for po-

tential application in nanogenerators and piezoelectric actuation among others. Therefore, it is of both fundamental and practical importance to study the thermal properties of electrospinning PVDF fibers.

Local thermal analysis (LTA) is a new nano-thermal analysis technique based on AFM, which enables topography imaging as well as measurement of local thermal properties using a high-resolution heating AFM probe. The AFM tip is placed on the sample at the spot of interest, and an electric current flowing through the tip heats it up, causing thermal expansion of the sample in contact with the tip and upward deflection of the cantilever as a function of the tip temperature, which is correlated to the driving voltage *via* a calibration. The tip penetrates into the sample when the temperature reaches the softening/melting point, resulting in a downward inflection in the cantilever deflection curve.^[32] The sub-100 nm spatial resolution^[33,34] of the technique allows facile analysis of local thermal transitions in individual electrospun nanofibers.^[35]

In this work, melting temperatures of individual PVDF nanofibers produced under same condition but with different diameters were examined by LTA, and the thermal properties for PVDF fibers electrospun under different conditions were then compared. The melting temperature was found to increase with decreasing fiber diameter, and the shift was much more pronounced, with variations up to ~80 °C observed. Our results are presented herein.

EXPERIMENTAL

Materials

PVDF ($M_w=2.75\times10^5$ g/mol, $M_n=1.07\times10^5$ g/mol) pellets were purchased from Sigma-Aldrich Company. *N,N*-dimethylformamide (DMF) and acetone were obtained from Tiantai Chemicals Corporation and Beijing Chemical Reagents Company, respectively. All chemicals were used as received.

Preparation of PVDF Nanofibers

PVDF pellets were dissolved in 10 mL of DMF/acetone (V/V=4/6) mixture under vigorous stirring at 70 °C for 2 h to prepare electrospinning solutions of 2.0 and 2.5 g/mL concentrations. The homogeneous solution was transferred to a 3 mL plastic syringe and a voltage of 15 or 20 kV was applied to the tip using a high-voltage DC power supply (Gamma High Voltage Research ORMOND BEACH, FL32174). A grounded aluminum foil was placed 15 cm away from the needle to collect the nanofibers. In a separate experiment, a rotary wheel collector with 200 r/min was used and the solution flow rate was set at 1 mL/h.

Characterization

Surface morphology of the electrospun fibers was characterized on a Carl Zeiss Gemini 500 microscope operating at a 3 kV acceleration voltage and a 5.9 mm working distance. Fiber diameter was determined by measuring manually with NANO MEASURE software the fibers in single or multiple SEM images obtained from different regions of each fiber mat sample.

Fourier-transform infrared spectroscopy (FTIR) spectra of the fiber mats in the 4000–400 cm^{-1} region were collected on a Bruker ALPHA spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector at 4 cm^{-1} spectral resolution with the signal averaged over 16 scans. Baseline correc-

tion for the spectra was performed with OMNIC software.

Wide angle X-ray diffraction (WAXD) measurements were performed on a homebuilt diffractometer equipped with a semiconductor detector with a resolution of 487×195 (pixel size = $172 \mu\text{m}$) (Pilatus100 K, DECTRIS, Swiss) attached to a multilayer mirror (FOX3D 21-21, Xenocs SA, France). The samples were irradiated with a focused Cu K α ($\lambda = 0.154 \text{ nm}$) X-ray source (Genix^{3D} Xenocs SA, France), and the operating voltage and current were 50 kV and 0.6 mA, respectively. The distance of sample to detector was 31 mm. Each pattern was collected in 60 s and the background was subtracted.

Differential scanning calorimetry (DSC) analysis was carried out on a TA Q-100 calorimeter in a nitrogen atmosphere (50 mL/min). The fiber mats were heated from 25°C to 250°C at a heating rate of $10^\circ\text{C}/\text{min}$, and the data were analyzed with TA Universal Analysis 2000 software (TA Instruments).

Local thermal analysis (LTA) experiments were conducted on a NanoTA module of a NanoIR system (Anasys Instruments). The fibers for testing were electrospun onto a ZnSe prism directly, and the AFM module was used to image the fibers in tapping mode and select the desired fibers and locations for temperature ramps. Individual fibers were heated from 45°C to 300°C using PR-EX-AN2-200-5 ThermoLeverTM probes (Bruker). Before acquiring the melting points of the fibers, the probe was calibrated for temperature accuracy by using three polymer standards, PCL ($T_m = 55^\circ\text{C}$), high density polyethylene (PE) ($T_m = 116^\circ\text{C}$) and poly(ethylene terephthalate) ($T_m = 235^\circ\text{C}$). AFM-IR experiments were performed in an attenuated total reflection (ATR) style on the NanoIR system equipped with a pulsed OPO laser. AFM height and amplitude images were obtained using PR-EX-TnIR-A tips (Anasys Instruments) in tapping mode, and AFM-IR spectra of parallel and perpendicular polarizations (with respect to the fiber

direction) were collected at 4 cm^{-1} spectral resolution in contact mode at the same location on the fiber by turning the polarizer to 0° or 90° , respectively. The dichroic ratios were obtained following a procedure reported recently.^[36]

RESULTS AND DISCUSSION

Fig. 1 presents SEM micrographs of the PVDF nanofibers electrospun under different conditions. These fibers are randomly oriented and show relatively smooth surface morphology. The fibers collected under identical condition exhibit very broad distribution in diameter, varying from about 200 nm to several micrometers. The diameters of many fibers in multiple SEM images were measured and the histograms are depicted in Fig. 2. By comparing the data in Figs. 2(a) and 2(b), we see that the fibers obtained at a higher voltage are thinner on average, with a narrower distribution. This is because at a higher voltage, the polymer jet is subjected to higher elongation by the electrostatic forces, which leads to smaller fibers.^[37] The effect of polymer concentration on fiber size is revealed in Figs. 2(a) and 2(c). When the solution is more concentrated, a greater mass of the polymer is ejected under a same flow rate, and moreover, the stronger viscoelastic forces at a higher polymer concentration hamper the fiber elongation, resulting in thicker fibers.^[24,38] Figs. 1(d) and 2(d) show that the fibers collected on a rotating drum at a low rotation speed exhibit a broad diameter distribution and random alignment, consistent with literature results.^[13]

PVDF is known to have four different crystalline polymorphs, which can be readily distinguished by FTIR spectroscopy.^[39] In order to identify the crystal structure in the fibers, the electrospun PVDF mats were analyzed by FTIR, and the spectra are displayed in Fig. 3(a). All four spectra look similar. The absorption bands at 1180, 975, 796, 762, 613, and 532 cm^{-1} are associated with the α -phase,^[40] while

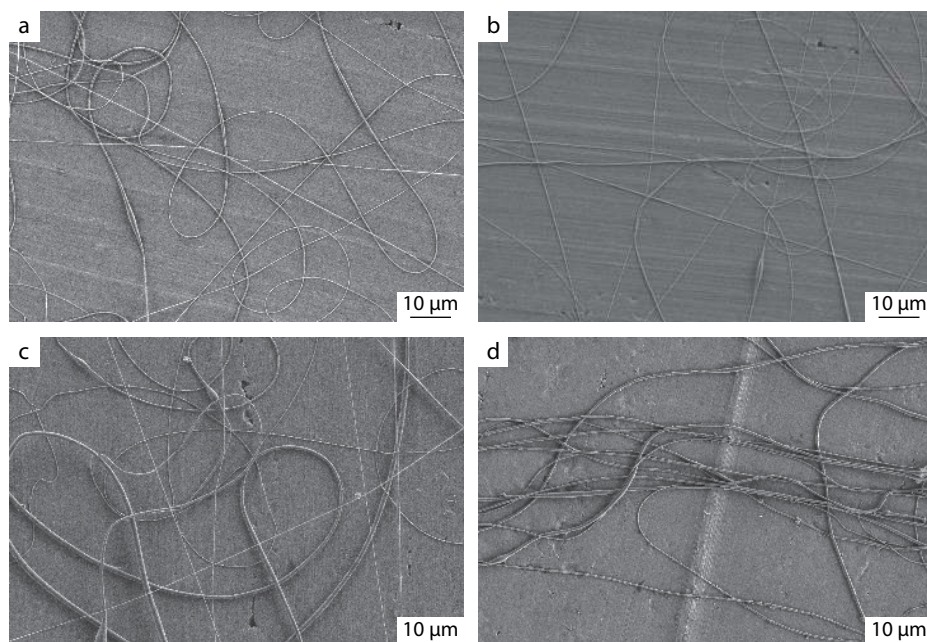


Fig. 1 SEM images of PVDF fibers electrospun under different conditions: (a) 2.0 g/mL solution concentration and 15 kV voltage, (b) 2.0 g/mL, 20 kV, and (c) 2.5 g/mL, 15 kV, all three collected on an aluminum foil, and (d) 2.0 g/mL, 15 kV, collected on a rotary disk.

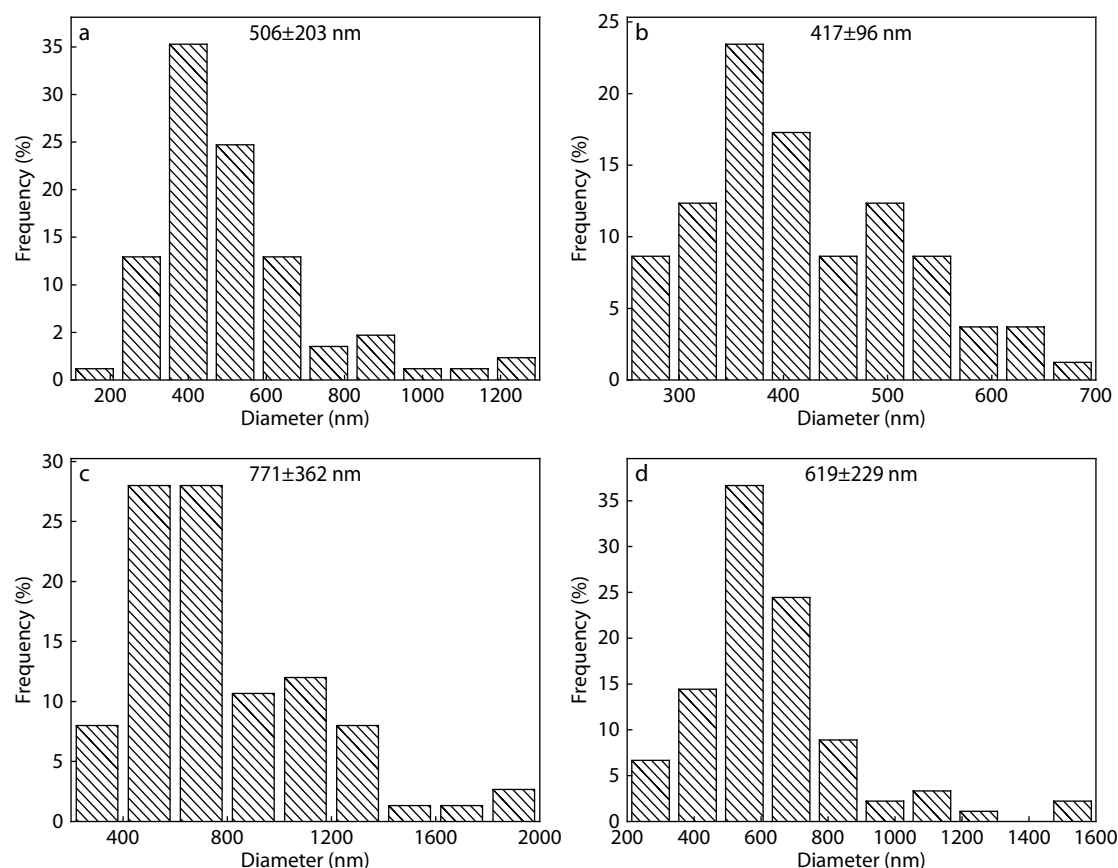


Fig. 2 Diameter distribution of PVDF fibers electrospun under different conditions: (a) 2.0 g/mL solution concentration and 15 kV voltage, (b) 2.0 g/mL, 20 kV, and (c) 2.5 g/mL, 15 kV, all three collected on an aluminum foil, and (d) 2.0 g/mL, 15 kV, collected on a rotary disk.

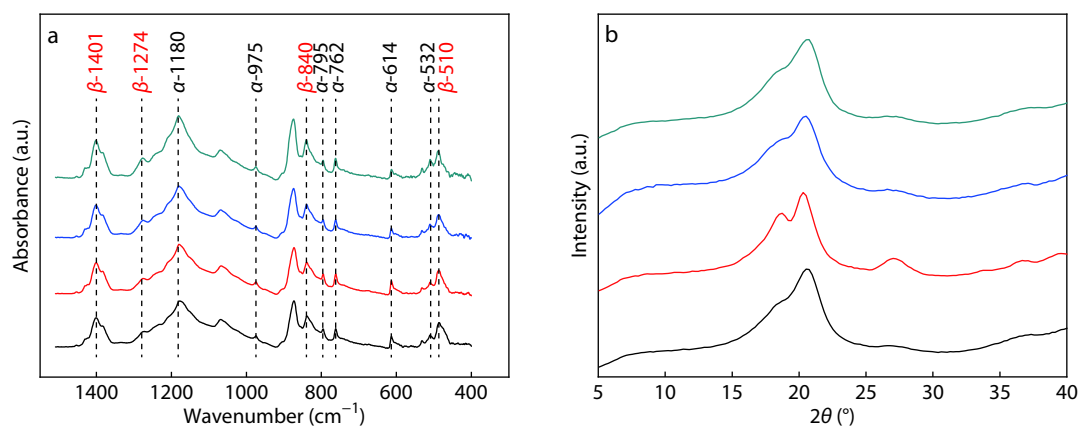


Fig. 3 (a) FTIR spectra and (b) WAXD patterns of PVDF fibers electrospun under different conditions: (black) 2.0 g/mL solution concentration and 15 kV voltage, (red) 2.0 g/mL, 20 kV, and (blue) 2.5 g/mL, 15 kV, all three collected on an aluminum foil, and (cyan) 2.0 g/mL, 15 kV, collected on a rotary disk.

those at 1401, 1274, 840, and 510 cm^{-1} are assigned to the β phase.^[41,42] In addition, two bands centered at 873 and 486 cm^{-1} respectively are clearly identified, which are designated to amorphous PVDF.^[43] The FTIR spectra in Fig. 3(a) clearly demonstrate that the PVDF crystals in all four fiber samples are mainly α - and β -phases, similar to that in the pellets (Fig. S1 in the electronic supplementary information, ESI).

Next, the phases of PVDF fibers were explored by WAXD.

Fig. 3(b) shows the WAXD patterns of PVDF fibers collected under different conditions. For all four PVDF fiber mats, the WAXD pattern exhibits a strong diffraction peak at $2\theta=20.3^\circ$, which is characteristic of (200) and (110) reflections of the β -phase,^[44,45] and two distinct peaks at $2\theta=18.6^\circ$ and 26.9° , corresponding to (020) and (021) diffractions of the α -phase.^[44,45] The WAXD result indicates the co-existence of α and β phases in the PVDF fibers, which is consistent with the finding by

FTIR.

The T_m of the PVDF fiber ensembles was then examined by DSC. Fig. 4 presents the DSC heating traces of the fiber mats. The four samples exhibit almost same a melting temperature at about 167 °C, which well corresponds to that of the α and β phases of bulk PVDF reported in the literature, which is about

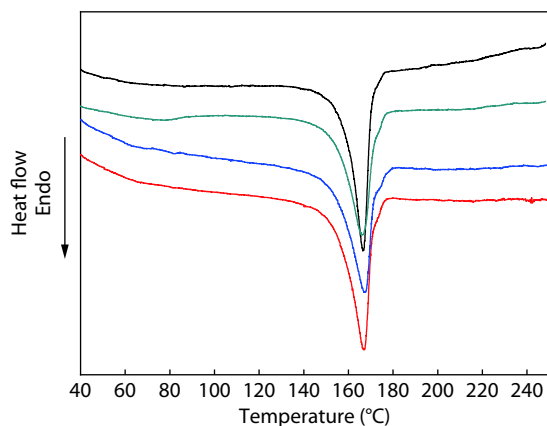


Fig. 4 DSC first heating traces of the fiber mats electrospun under different conditions: (black) 2.0 g/mL solution concentration and 15 kV voltage, (red) 2.0 g/mL, 20 kV, and (blue) 2.5 g/mL, 15 kV, all three collected on an aluminum foil, and (cyan) 2.0 g/mL, 15 kV, collected on a rotary disk.

167–172 °C.^[46,47] In addition, the crystallinity of the nanofibers in the mats can be estimated from the ratio between the melting enthalpy value experimentally determined by DSC and the literature value for the 100% crystalline PVDF, which is 104.6 J/g.^[48,49] The crystallinity of the three samples collected at 15 kV was 48.4%, 48.9%, and 48.7%, respectively, which was essentially the same, showing little influence on the degree of crystallinity by the solution concentration or the drum at low rotation speed. Meanwhile, the fibers collected at a voltage of 20 kV exhibited a slightly higher average crystallinity of 51.2%, which may be attributed to higher elongation the fibers experienced at the higher voltage, facilitating the crystallization of PVDF in the fibers.^[50,51] Thus, our conventional DSC analysis detected no significant influence of the electrospinning conditions on the melting temperature of the nanofiber ensembles, and showed that the average melting temperature of the electrospun nanofibers was indeed not different from that of bulk PVDF. However, we also notice that the melting peaks are rather broad, starting from ~120 °C and with tails extending to ~220 °C, reflecting the structure inhomogeneity of the fibers in each sample, i.e. a broad distribution in lamellar thickness of the crystallites formed in electrospinning process.

In order to explore the size-dependent thermal behavior of the nanofibers, thermal analysis at single fiber level was carried out. Fig. 5 depicts the AFM images of two individual nanofibers collected under identical conditions but of different

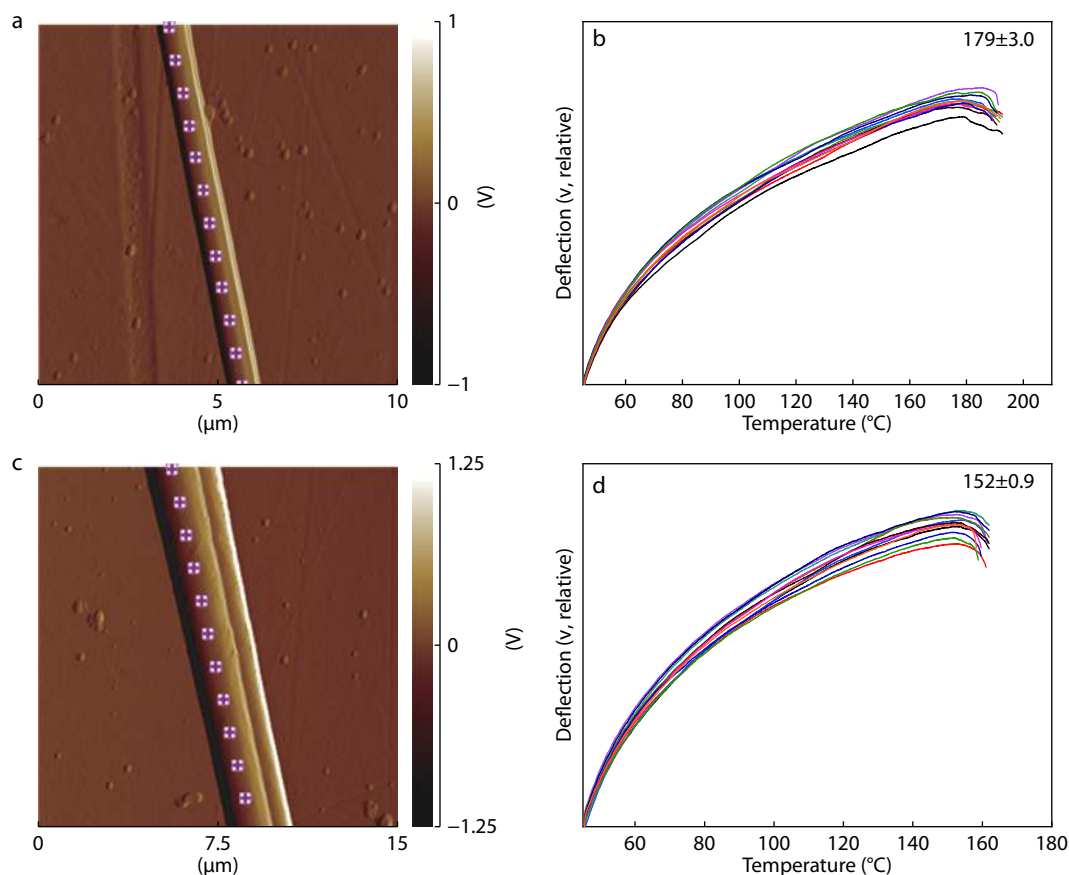


Fig. 5 (a, c) AFM images for two individual fibers electrospun at the same conditions (2.5 g/mL solution concentration and 15 kV voltage) but with different diameters and (b, d) corresponding LTA traces recorded at the marked locations in (a, c).

diameters and corresponding LTA traces acquired at multiple locations along the axes of these fibers. The fiber in Fig. 5(a) exhibits a uniform thickness of 420 nm, and the twelve LTA curves displayed in Fig. 5(b) acquired at locations marked in Fig. 5(a) along the axis of this fiber are essentially the same, with cantilever deflection rising with temperature due to thermal expansion of the fiber and at about 180 °C a clear downward inflection, which is defined as the melting point.^[32,33] The melting point of this fiber is reported as the average of these individual measurements at different locations, which is 179 ± 3 °C. In comparison, Fig. 5(c) shows a much thicker fiber, of about 1300 nm in size, the melting point of which is 152 ± 0.9 °C (Fig. 5d). The data demonstrate the excellent reproducibility of the LTA measurement of melting point in individual nanofibers and suggest that under the same electrospinning conditions, although the size of the fiber can vary in a broad range, the fibers of a same size have the same melting point. Furthermore, the results reveal that the thicker fibers have lower melting points than the thinner ones. It should be pointed out that in order to ensure the accuracy of the LTA measurements, validation of the temperature calibration with the three standard samples was conducted before and after analyzing each individual nanofiber. No temperature drift was observed (Fig. S2, in ESI), showing excellent stability of the instrument and reliability of the melt-

ing point data obtained.

We then analyzed by the LTA method one by one many fibers of diameters ranging from around 200 nm to several micrometers in the mat collected under identical conditions, and the melting temperature thus determined is plotted as a function of the fiber diameter in Fig. 6. For the four electrospinning conditions investigated, a similar trend is clearly observed between the T_m and the diameter of nanofibers. That is, T_m goes down quickly with the fiber diameter increasing at small diameter region, and then gradually levels off when the fiber becomes much thicker, exhibiting an exponential decay with the diameter increasing. This trend is opposite to the previous reports in the literature, where the T_m was found to decrease with the fiber diameter decreasing,^[20,25,27] and the ranges of T_m variation we observed are much greater, about 50–80 °C as compared to 10 °C or less reported previously. In addition, it is surprising to notice that T_m values as high as 220–230 °C were recorded (for the thinnest fibers with diameters of <200 nm). These T_m values, although still well below the equilibrium melting temperature of PVDF α -form, 259 °C as calculated by Nandi and Mandelkern,^[52] are much higher than the typical values reported for PVDF fibers, films and bulk, which are 167–172 °C.^[44,53] Furthermore, the fibers of same diameter but produced under different spinning conditions were found to exhibit different T_m s. For example,

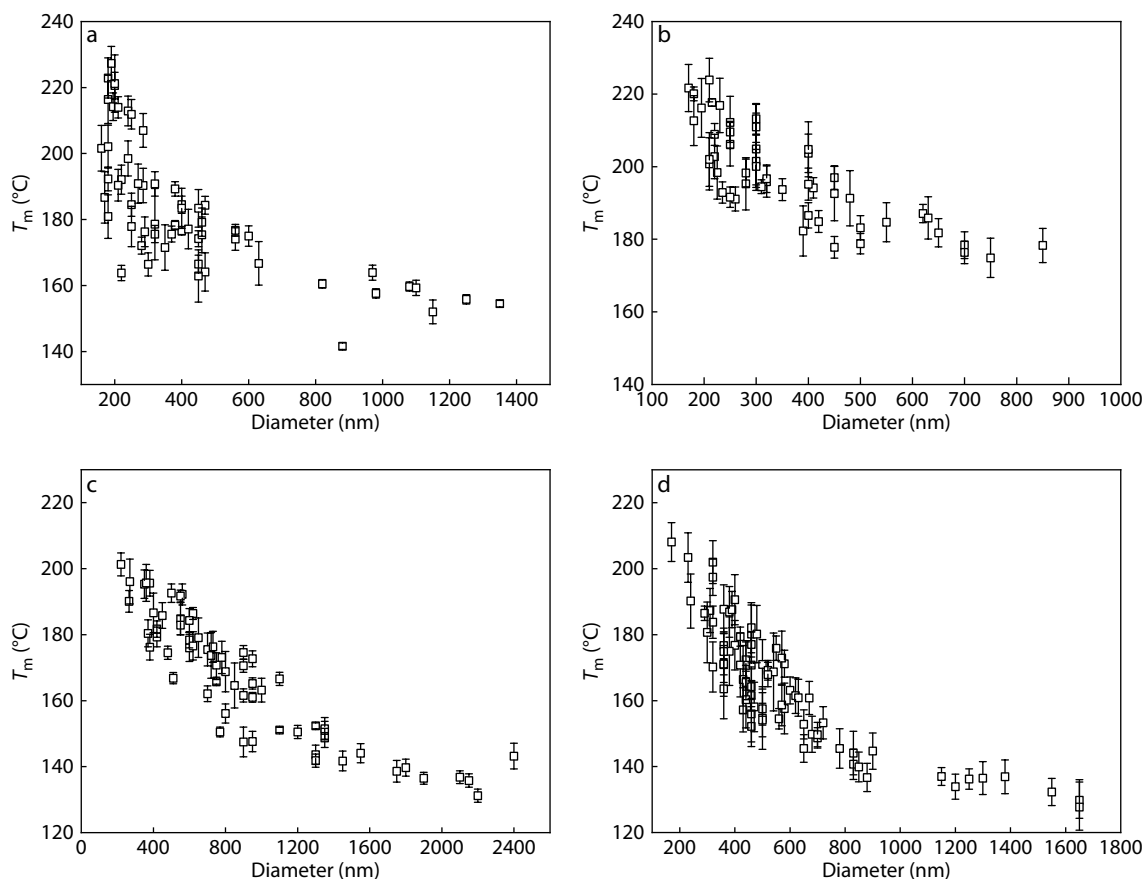


Fig. 6 Dependence of T_m of individual fiber on diameter for PVDF fibers electrospun under different conditions: (a) 2.0 g/mL solution concentration and 15 kV voltage, (b) 2.0 g/mL, 20 kV, and (c) 2.5 g/mL, 15 kV, all three collected on an aluminum foil, and (d) 2.0 g/mL, 15 kV, collected on a rotary disk.

the T_m for fibers of 800 nm diameter in Figs. 6(a), 6(b), 6(c), and 6(d) are about 159, 180, 165 and 146 °C, respectively. This phenomenon indicates that diameter is not the essential parameter to determine the T_m ; rather the T_m is more likely to be related to the molecular orientation, among other factors.^[54] In our previous work, we showed that for PVDF fibers spun under identical conditions, the molecular orientation in the nanofibers exhibits an exponential increase with the fiber diameter decreasing.^[36] In the electrospinning process, the polymer jet is stretched by the electrostatic forces, resulting in thinning of the jet and orientation of the polymer chains along the elongation direction. The stretched chains can partially relax before being frozen due to rapid solvent evaporation and the final molecular orientation is the result of the competing dynamics of stretching and partial retraction. However, due to the inhomogeneity of the electric field and instabilities of the jet, the elongation force the jet experiences varies with time and space.^[1] Higher elongation forces result in thinner fibers and higher degrees of molecular orientation. In addition, the thinner fibers solidify more rapidly than the thicker ones due to their greater surface areas and hence faster solvent evaporation, allowing less time for the stretched chains to relax, further promoting molecular orientation.^[11] Therefore, the molecular orientation in nanofibers spun under identical conditions increases with the fiber diameter decreasing, as we observed previously in PVDF nano-

fibers prepared under the same conditions as in the present study. Subsequently, the better alignment of the polymer chains facilitates the crystallization,^[55,56] resulting in bigger and more perfect crystals,^[57] which exhibit higher T_m in thinner fibers. This driving mechanism also well explains the observation that in general the fibers collected at 20 kV voltage (Fig. 6b) exhibit higher T_m 's than the ones of same diameter produced at 15 kV (Figs. 6a, 6c, and 6d). At a higher electrospinning voltage, the polymer jet experiences greater electric field forces and the degree of molecular orientation is higher.

To further verify the above argument of molecular orientation effect on the T_m of the fibers, we studied the molecular orientation and T_m of a single fiber containing beads. Fig. 7(a) displays the AFM image of a PVDF fiber with bead structure, and the degree of molecular orientation determined by polarized AFM-IR presented as the dichroic ratio (DR)^[36] at different positions along the fiber axis as marked in the AFM image is shown in Fig. 7(b). We see that at the center of the bead and the nearby locations, the DR values are around 1, indicating little or no preferred molecular orientation, while the straight parts of the fiber exhibit some degrees of orientation, the further away from the beaded part, the higher the molecular orientation. The finding is consistent with that observed by Yoshioka *et al.* by selected area electron diffraction.^[58] Figs. 7(c) and 7(d) are the AFM image of the same beaded fiber and the corresponding T_m 's measured by LTA

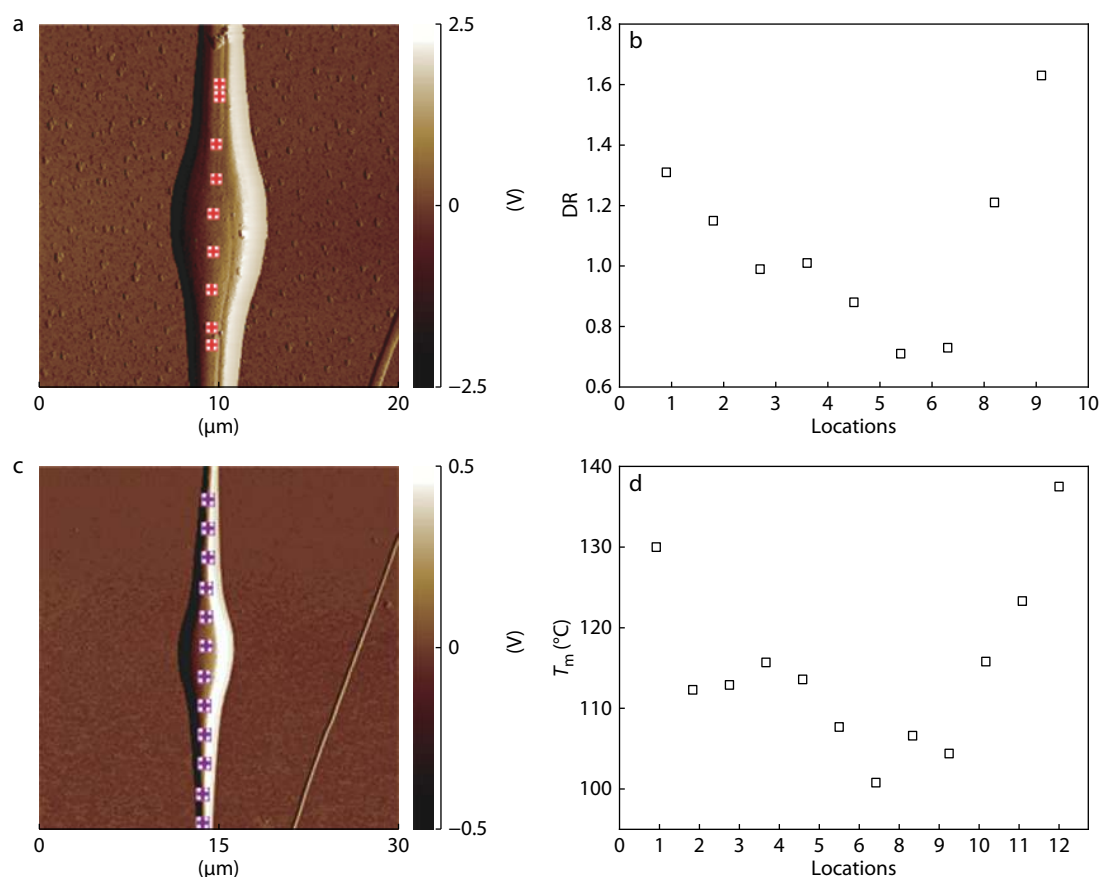


Fig. 7 (a) AFM image of a beaded PVDF fiber and (b) corresponding dichroic ratio collected at the locations marked in (a), and (c) AFM image of the same beaded PVDF fiber and (d) corresponding T_m acquired at the locations marked in (c).

along the fiber. The T_m distribution pattern well matches that of molecular orientation in Fig. 7(b), where the T_m is the lowest at and around the center of the bead, and increases upon moving away from the bead toward both directions. This agreement between the molecular orientation and T_m patterns further indicates that molecular orientation dominates the T_m of the PVDF fibers in this study.

CONCLUSIONS

We have investigated the melting temperature of individual electrospun PVDF nanofibers with diameters ranging from smaller than 200 nm to greater than 2 μ m by the novel LTA technique. While conventional analysis detected no significant difference among the PVDF fiber mats spun under different conditions, analyses at the single fiber level revealed broad distribution in diameter and T_m for the fibers produced under each identical electrospinning condition. The T_m of individual nanofibers remains constant at large diameters and increases quickly when reducing the fiber diameter toward the nano-scale, and T_m values 50–60 °C higher than the typical values reported for PVDF fibers, films and bulk were observed for the thinnest nanofibers. The correlation between the T_m and the diameter observed can be attributed to the molecular orientation in the nanofibers. This work demonstrates that LTA is a powerful technique for the investigation of individual nanofibers, and sheds light on the underlying mechanisms for the size-dependent properties of electrospun nanofibers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2476-9>.

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