

Spectroscopic evidence for high fraction of ferroelectric phase induced in electrospun polyvinylidene fluoride fibers

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I. FORCESPINNING

It is well known that the applied electrostatic field during electrospinning serves dual purposes: (1) mechanical stretching, and (2) electrical poling on the polymer jet. In this work, forcespinning which stretches the polymer jet through centrifugal forces without electric poling was utilized.¹ Several methodologies have been reported as the pure forcespinning techniques such as spin-coating and mechanical spinning.^{2,3} Here, we used a drill machine (BG-5158, Beking, Co.) to produce fibers. After fixing the syringe and drill head together, the “standard” PVDF polymer solution was loaded into the syringe and wrapped with aluminum foil. Afterwards, the drill with a speed higher than 5,000 rpm was used to make fibers of different morphologies depending on the speed of the motor.

Figure S1 shows the fiber morphology at different rotation speed: (a) 8,000 rpm; (b) 11,000 rpm; (c) and (d) are the enlarged pictures of (b). It is found that at a lower speed at 8000 rpm, forcespinning produces fibers with a large deviation in diameter. As the speed of the rotor increases, the diameter of forcespun fibers is reduced.

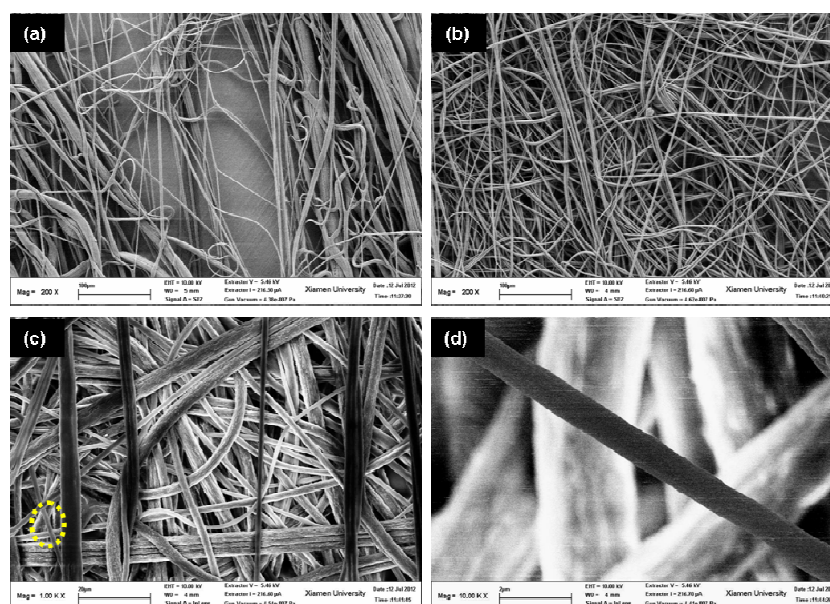
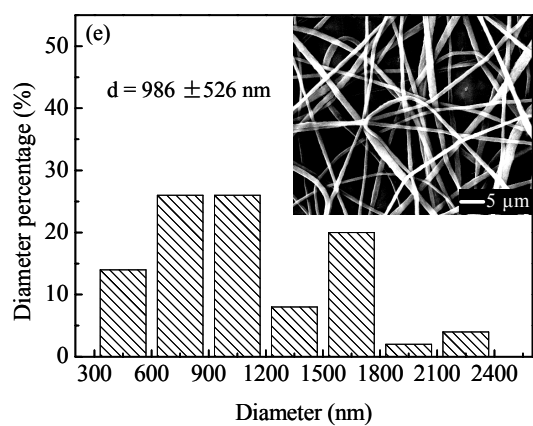
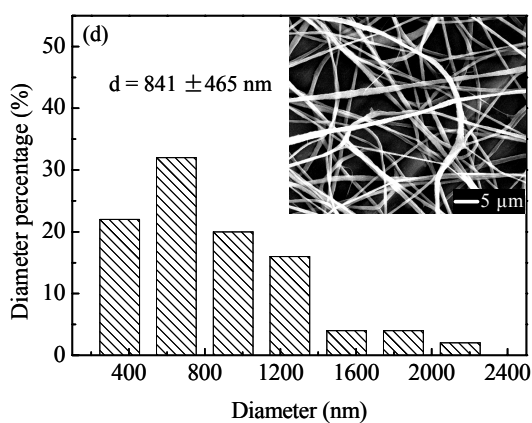
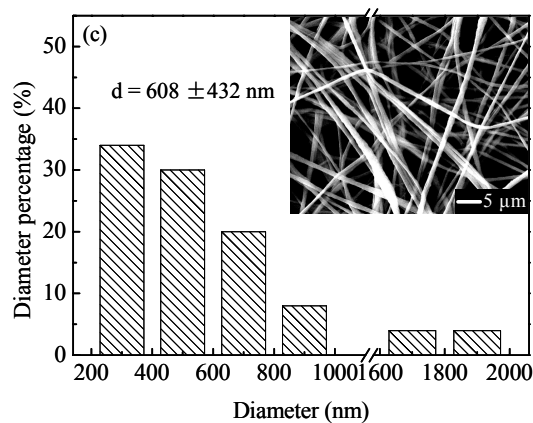
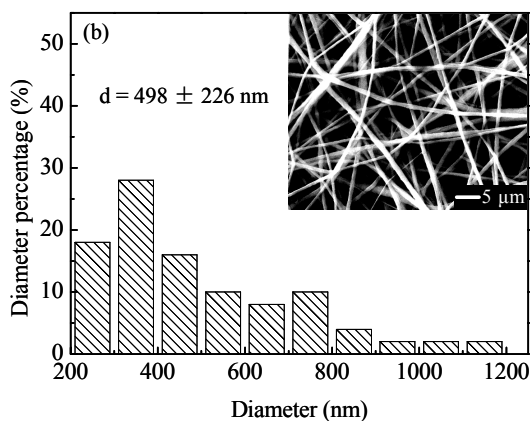
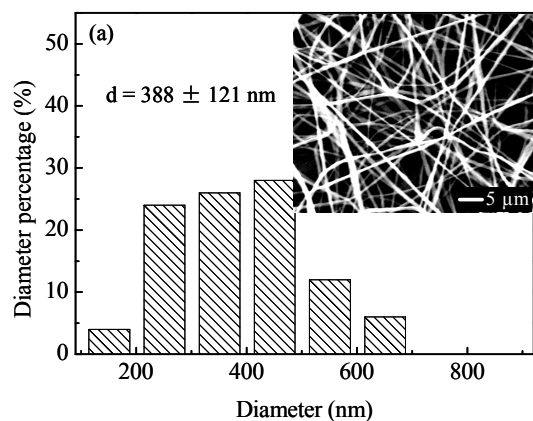


Figure S1 SEM images of forcespun fibers. (a) 8,000 rpm; (b) 11,000 rpm; (c) and (d) enlarged pictures of (b)

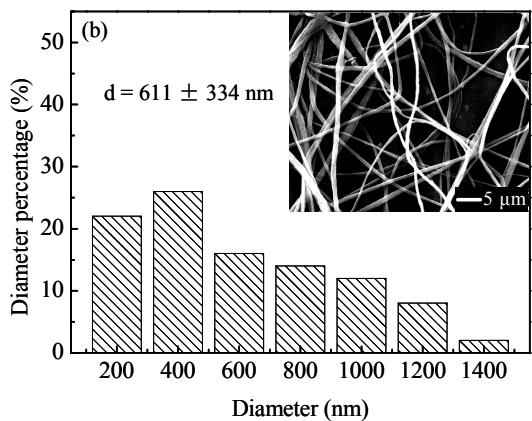
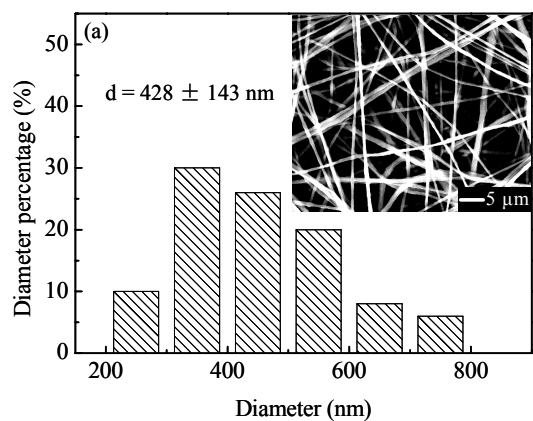
II. ELECTROSPINNING

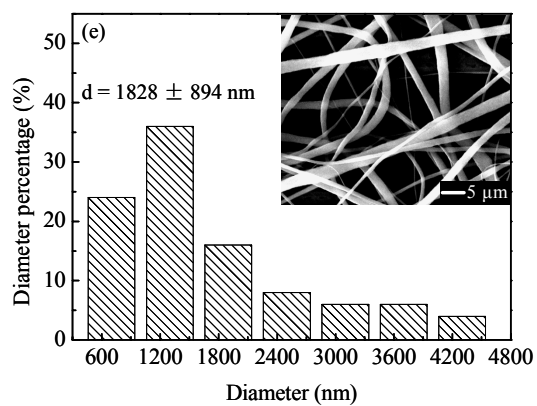
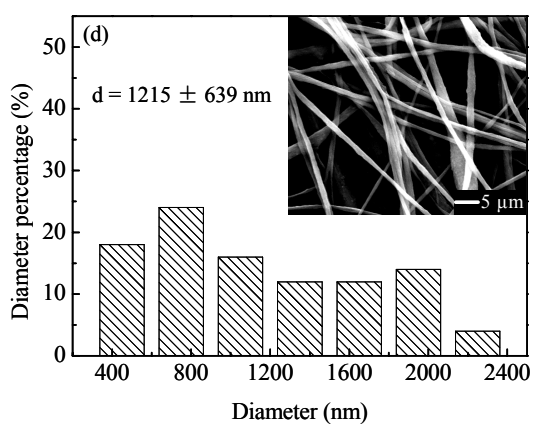
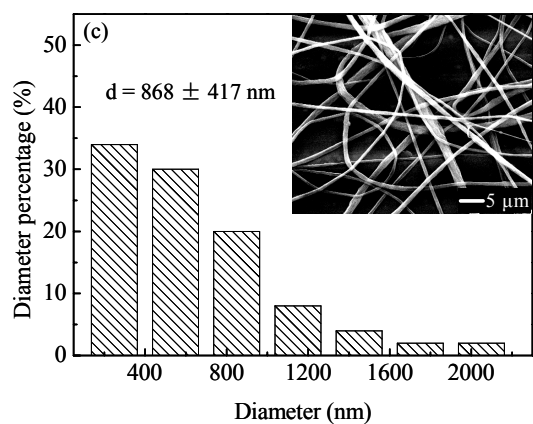
Figure S2 details the effects of PVDF wt% concentration and polymer solution flow rate on the fiber morphology and diameter distribution. A total of 50 measurements were made for each sample.

(A)

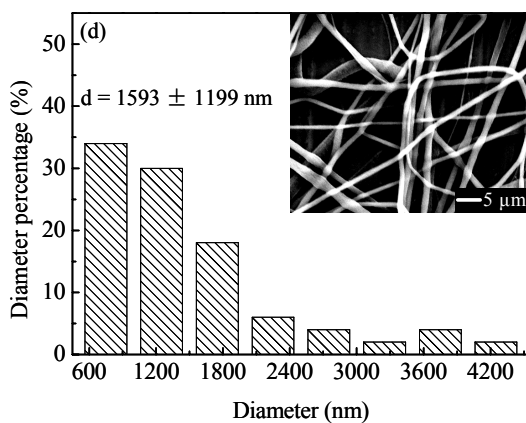
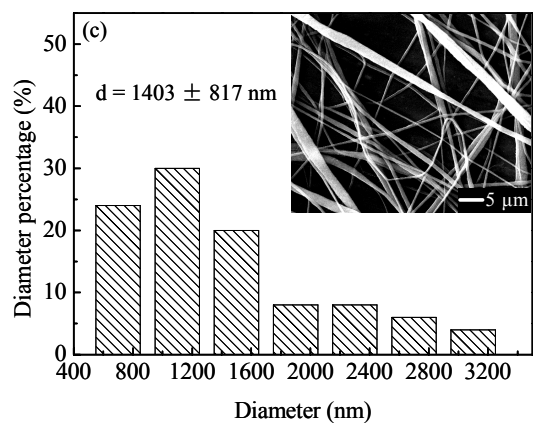
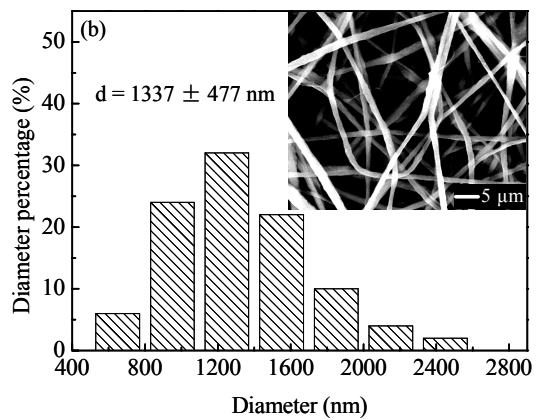
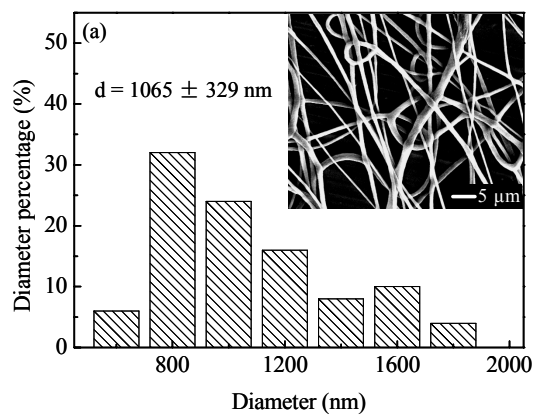


(B)





(C)



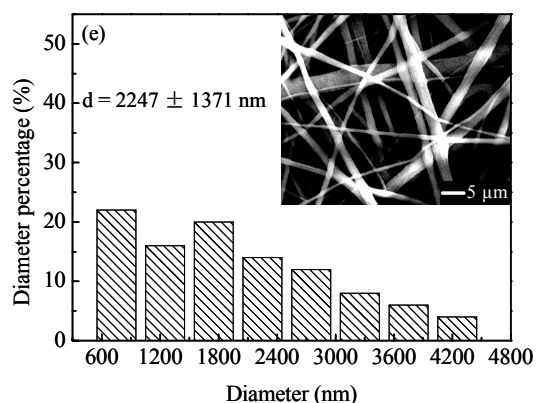


Figure S2 SEM photos of electrospun fibers and size distribution of fiber diameters with (A) 11 wt%, (B) 16 wt%, and (C) 19 wt% of PVDF, respectively, under different polymer solution flow rate of: (a) 80 $\mu\text{L/hr}$, (b) 200 $\mu\text{L/hr}$, (c) 500 $\mu\text{L/hr}$, (d) 1000 $\mu\text{L/hr}$, and (e) 2000 $\mu\text{L/hr}$, respectively.

Figure S3 shows effect of applied voltage on the IR spectra of electrospun fibers made from baseline system (16 wt%, $V_{\text{NMP}}/V_{\text{acetone}}=5/5$) with varying applied voltages from 4 to 11kV. The polymer solution flow rate and the tip-to-collector were 60 $\mu\text{L/hr}$ and 10 cm, respectively. It is found that the fraction of β -phase is very high for all samples ($\geq 95\%$) and the influence of applied electrical field on the formation of β -phase is not significant.

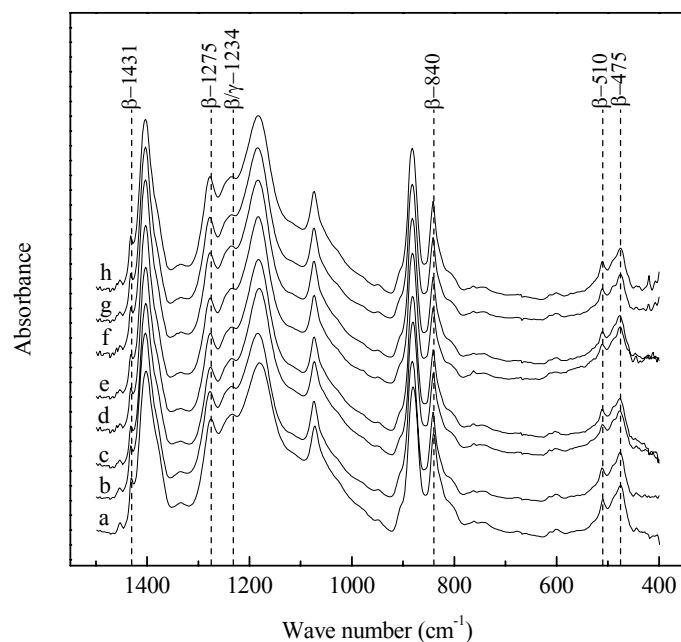


Figure S3 Effect of applied voltage on the IR spectra of electrospun fibers: a, b, c, d, e, f, g and h, corresponding to 4, 5, 6, 7, 8, 9, 10, and 11 kV of applied voltages, respectively.

Figure S4 shows the Infrared spectra of electrospun PVDF fibers prepared with 16 and 19 wt% PVDF with increasing flow rate from 80 to 2000 $\mu\text{L/hr}$.

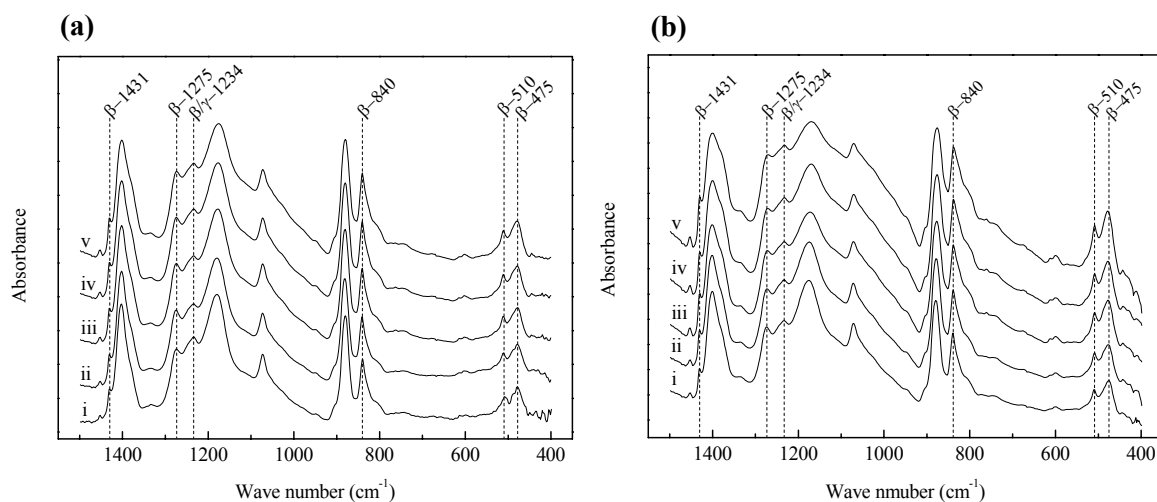


Figure S4 Infrared spectra of electrospun PVDF fibers prepared with (a) 16, and (b) 19 wt% of PVDF concentration, respectively, under polymer solution flow rate at (i) 80 $\mu\text{L/hr}$, (ii) 200 $\mu\text{L/hr}$, (iii) 500 $\mu\text{L/hr}$, (iv) 1000 $\mu\text{L/hr}$, and (v) 2000 $\mu\text{L/hr}$.

III. SOLUTION-CASTING

Figure S5 shows the IR spectra of thin films cast from NMP-rich ($V_{\text{NMP}}/V_{\text{acetone}} = 9/1$) solutions with 16 wt% PVDF crystallized at different temperatures. The cast films are prepared by spreading PVDF solution onto a previously cleaned aluminum foil and then heated unless evaporation of the solvent is completed.

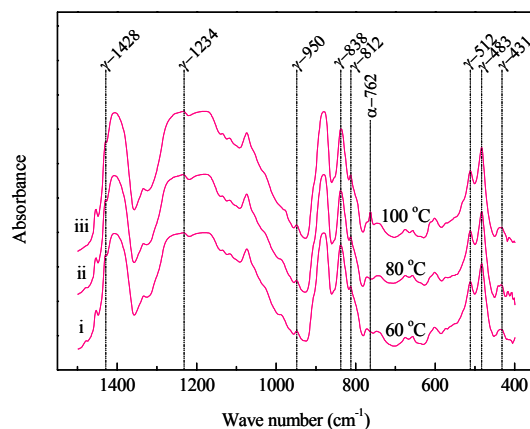


Figure S5 (b) Infrared spectra of films cast from NMP-rich ($V_{\text{NMP}}/V_{\text{acetone}} = 9/1$) 16 wt% solutions and crystallized under different temperatures at: (i) 60 °C, (ii) 80 °C, and (iii) 100 °C.

References

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- 2 R. Weitz, L. Harnau, S. Rauschenbach, M. Burghard and K. Kern, *Nano Lett.* 2008, **8**, 1187-1191.
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