

Supporting Information
for
**Thermal Transport in Electrospun Vinyl Polymer Nanofibers: Effects of
Molecular Weight and Side Groups**

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Sample preparation

PVDF pellets (Average M_w \sim 180,000, Sigma-Aldrich) were dissolved into an N, N-Dimethylformamide (DMF, Sigma-Aldrich)/acetone (Sigma-Aldrich) mixture (DMF/acetone=60/40 w/w) at 20 wt% concentration by heating and stirring at 60°C. PVA powder (Average M_w =146,000-186,000, Sigma-Aldrich) was dissolved into deionized (DI) water at 5 wt% concentration and stirred at 90°C. PVC powder (Average M_w \sim 233,000, Sigma-Aldrich) was dissolved in a Tetrahydrofuran (THF, Sigma-Aldrich)/DMF mixture (THF/DMF=20/80 w/w) at 5 wt% concentration by stirring at room temperature. Solutions were then poured into separate glass syringes (Cadence Science) with a 20-gauge metal syringe needle (McMaster). A syringe pump (NE-300 Just InfusionTM) was used to maintain a 200 μ l/min flow rate. PE powders (Average M_w =3,000,000-6,000,000 and \sim 35,000, Sigma-Aldrich) and PE pellets (Average M_w \sim 125,000 and \sim 420,000, Scientific Polymer Products) were dissolved in a 1:1 weight ratio mixture of p-xylene and cyclohexanone. To obtain a fully dissolved PE solution, the PE powders or pellets suspended in the solvent were heated on a hotplate at 120°C and stirred for 2 hours. In order to produce electrospun PE nanofibers of different molecular weights, we prepared several PE solutions in different concentrations, namely 0.1 wt% (M_w =3,000,000-6,000,000), 0.2 wt% (M_w \sim 420,000), 0.3 wt% (M_w \sim 125,000) and 0.5 wt% (M_w \sim 35,000), ensuring the viscosity of each was adequate for nanofiber formation. PE solutions were drawn into separate glass syringes with a 20-gauge metal syringe needle.

An infrared quartz radiant heater (Optimus HT-511) was placed \sim 15 cm away from the syringe and syringe pump to act as a heat source to avoid the formation of precipitates in the PE solution. The distance between the end of metal syringe tip and the grounded collector was kept at 15 cm, and the syringe pump flow rate was set to 200 μ l/min. As shown in Fig. 1b, a high voltage power supply (ES100P-50W, Gamma High Voltage Research Inc.) operating at 30 kV was employed to produce all electrospun nanofibers investigated.

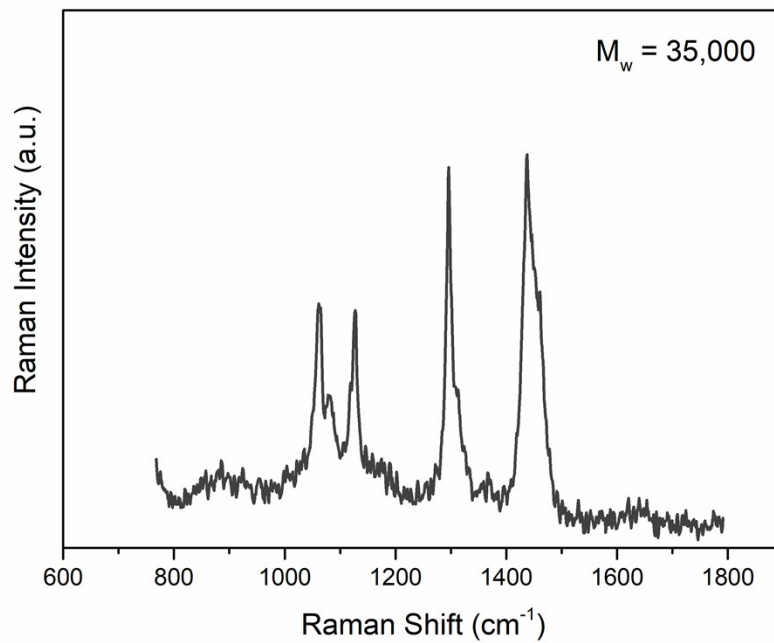


Figure S1. Raman spectrum of an electrospun PE nanofiber with molecular weight of 35,000.

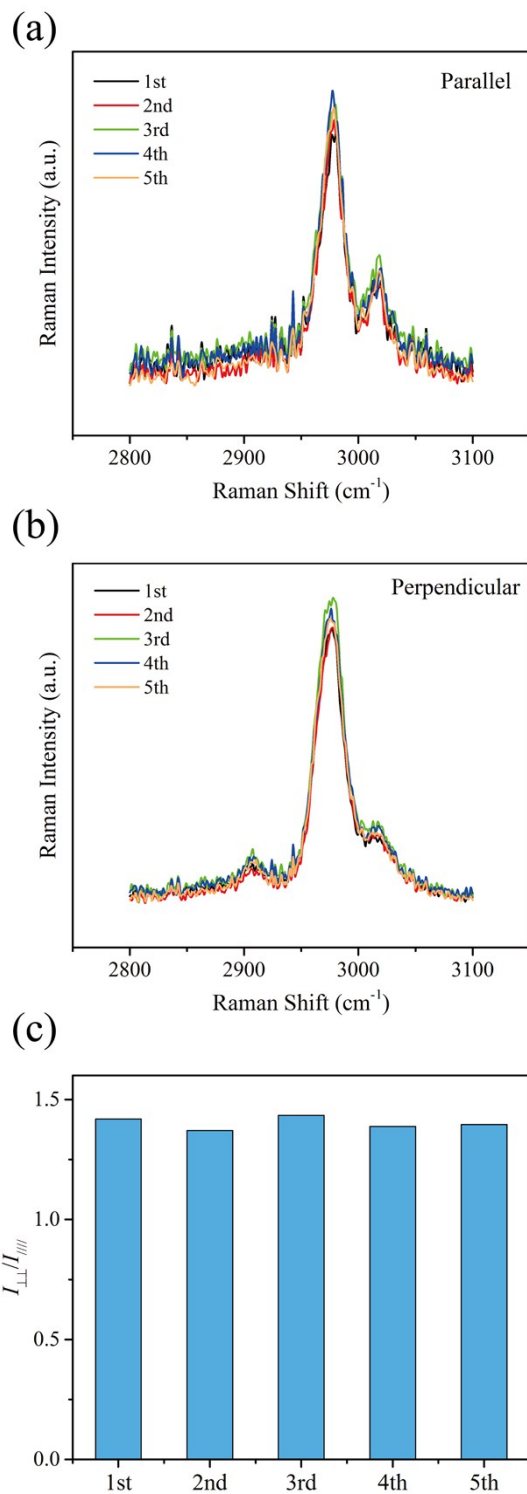


Figure S2. Polarized Raman spectra for a PVDF nanofiber taken at the same position five times. The overlapping parallel (a) Raman spectra and perpendicular (b) Raman spectra and the similar values of I_{\perp}/I_{\parallel} (c) suggest marginal microstructural damage during Raman characterization.

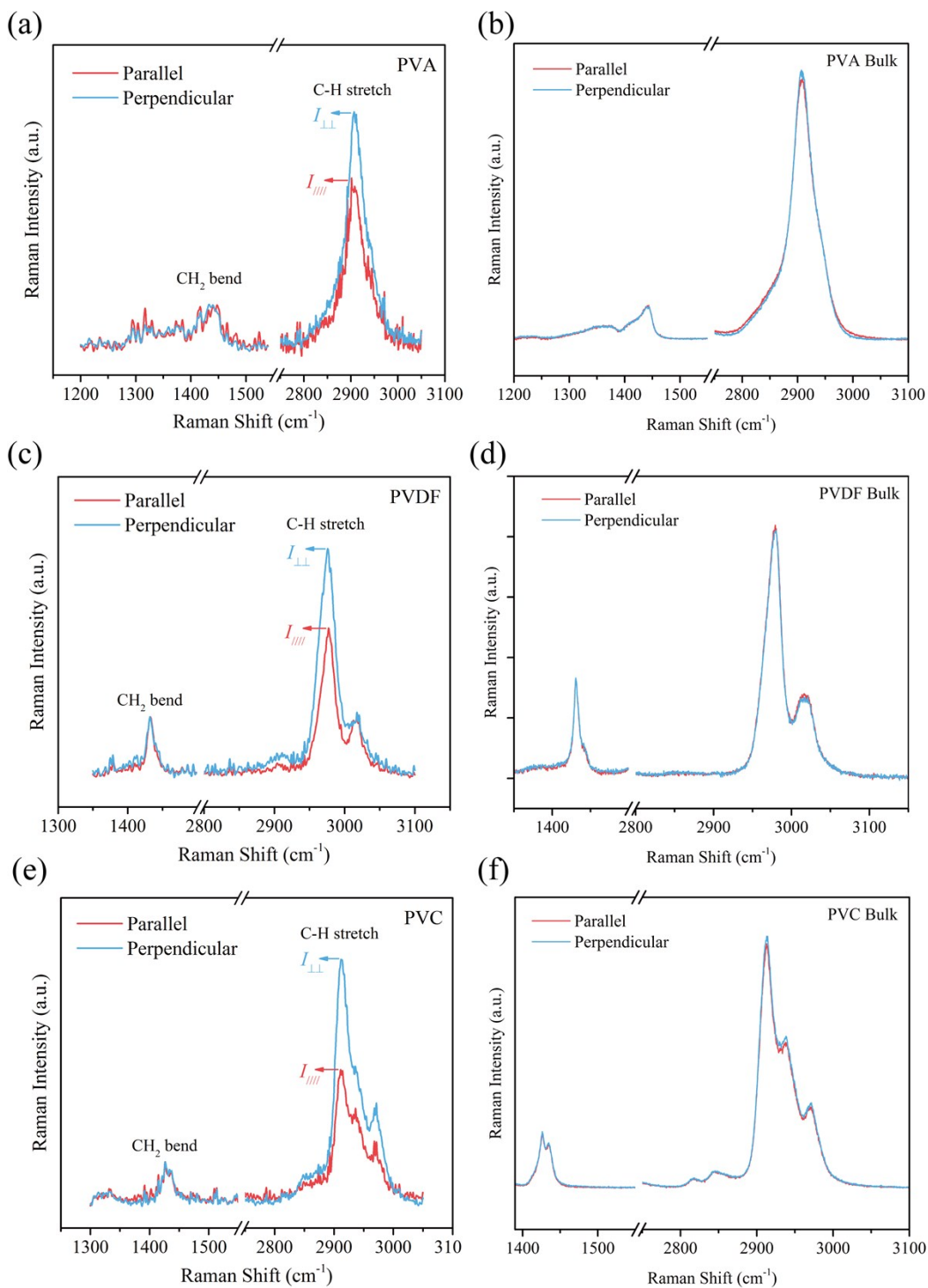


Figure S3. Polarized Raman spectra of individual nanofibers (a, c & e) and the corresponding bulk material (b, d & f). Random molecular orientation within bulk polymer samples results in overlapping parallel and perpendicular Raman spectra ($P_{\text{Bulk}} = I_{\perp\perp}/I_{\parallel\parallel} \approx 1$). $P_{\text{Nanofiber}} = I_{\perp\perp}/I_{\parallel\parallel} > 1$ indicates enhanced molecular orientation.

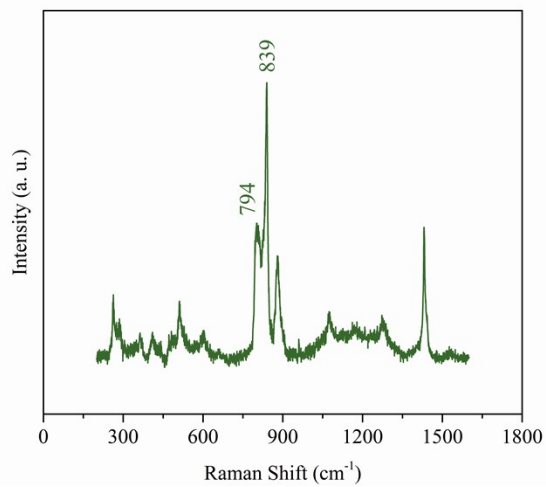


Figure S4. Raman spectrum of a single PVDF nanofiber. The high peak at the 839 cm⁻¹ mode relative to the peak at 794 cm⁻¹ indicates that the nanofiber consists of substantially more β phase than α phase.

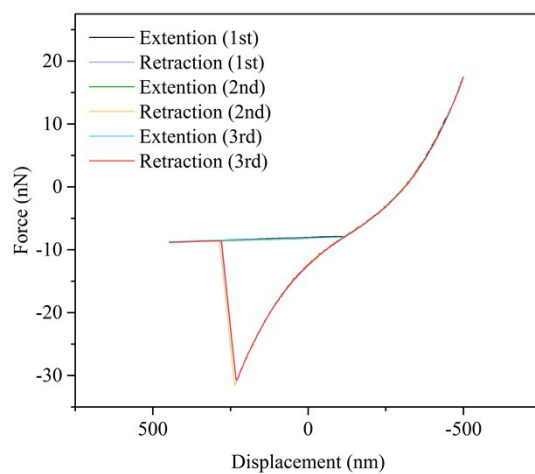


Figure S5. Force-displacement (F-D) curves acquired on a single nanofiber with three separate measurements. The overlapping F-D curves show that van der Waals force can firmly anchor the fibers at the trench edges, and the deformation of the nanofiber is elastic rather than plastic.