Electrospinning of Highly Crystalline Polymers for Strongly Oriented Fibers

Supporting Information

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Table S1. Polarity and volatility of the solvents used for electrospinning PEO nanofibers[1]

Solvent	Dielectric constant ε	Boiling point (°C)	Vapor pressure (kPa)
Chloroform ($CHCl_3$)	4.8	61.2	26.2
Hexafluoroisopropanol (HFIP)	16.7	59	21.2
Methanol (MeOH)	33.0	64.5	16.9
N,N-dimethylformamide (DMF)	38.3	152.8	0.439
Water (H_2O)	80.1	100.0	3.17

The boiling points, vapor pressures, and dielectric constants are measured at 101.3 kPa, 25 °C, and 20 °C, respectively. Despite having a boiling point higher than that of HFIP, $CHCl_3$ has a higher vapor pressure at 25 °C and is thus considered as the most volatile solvent in this work.

[1] CRC Handbook of Chemistry and Physics. 101st ed.; Rumble, J. R., Ed. CRC Press: Boca Raton, FL: 2020

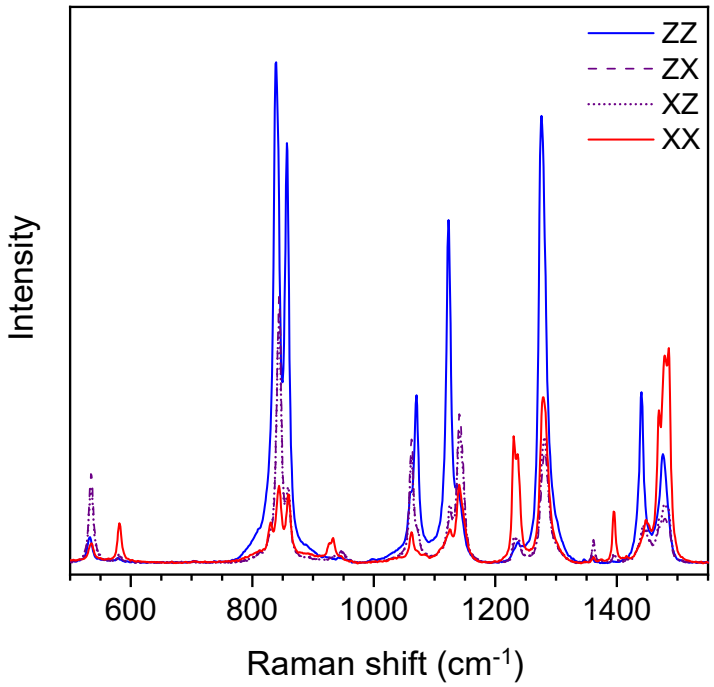

Fig. S1. Set of four polarized Raman spectra (extended spectral range) collected from a PEO fiber with a $\langle P_2 \rangle$ of 0.60 and a diameter of 1200 nm.

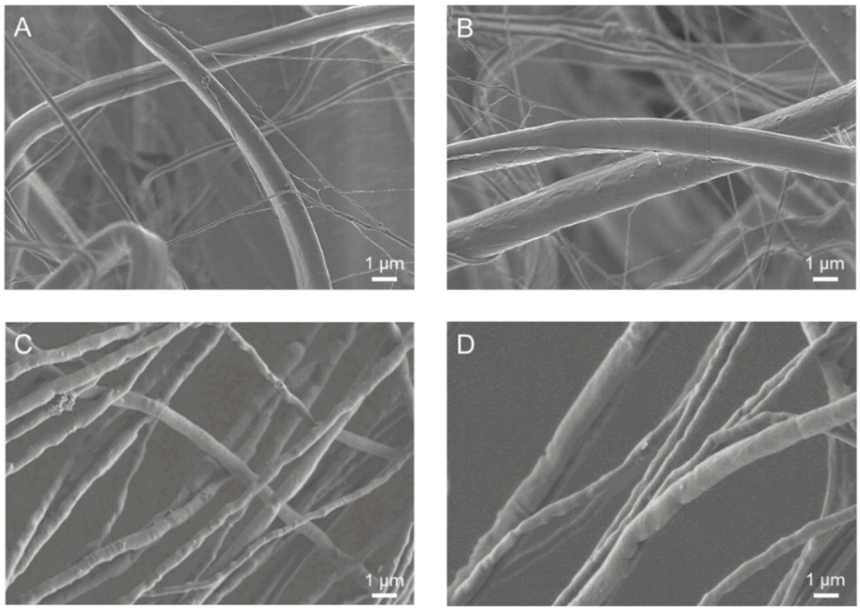

Fig. S2. SEM pictures of PEO nanofibers electrospun using HFIP (A-B) and DMF (C-D). A and C show smaller fibers electrospun from lower concentration solutions while B and D show larger fibers electrospun from higher concentration solutions. The fibers all show a rather smooth surface and a cylindrical shape, including those spun from DMF despite its distinct solvent properties and the lower molecular orientation reached in DMF-spun fibers.

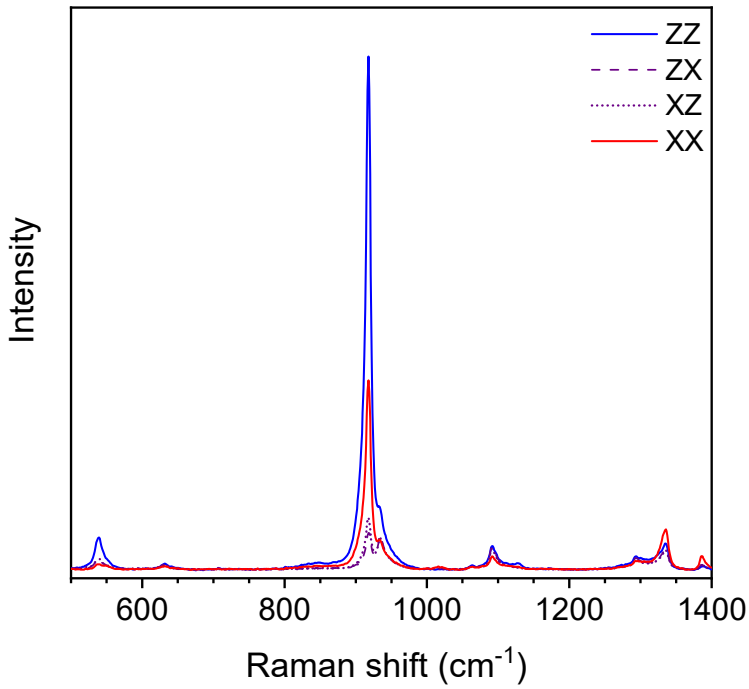

Fig. S3. Set of four polarized Raman spectra collected from a POM fiber with a $\langle P_2 \rangle$ of 0.60 and a diameter of 1150 nm.

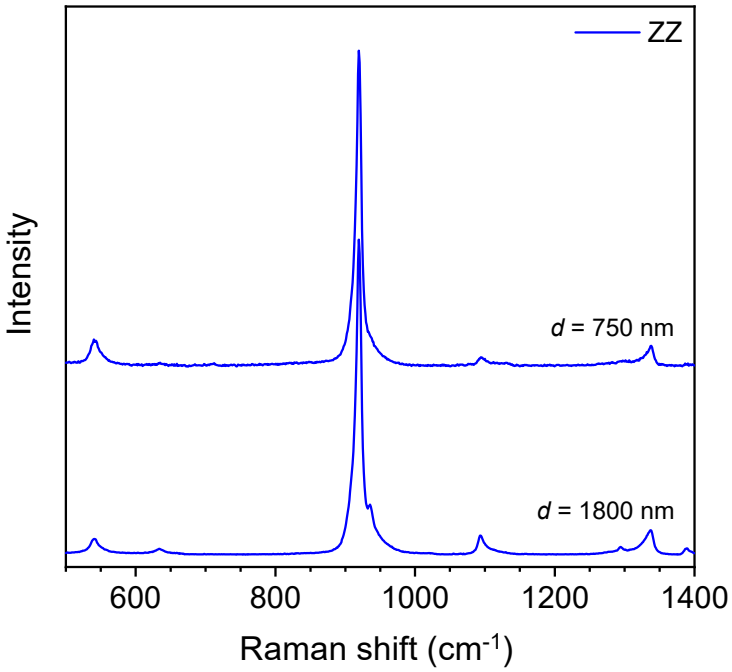

Fig. S4. Polarized Raman spectra of POM fibers with a $\langle P_2 \rangle$ of 0.66 and a diameter of 750 nm (top) and a $\langle P_2 \rangle$ of 0.22 and a diameter of 1800 nm (bottom). Differences in band intensities are due to different level of molecular orientation.

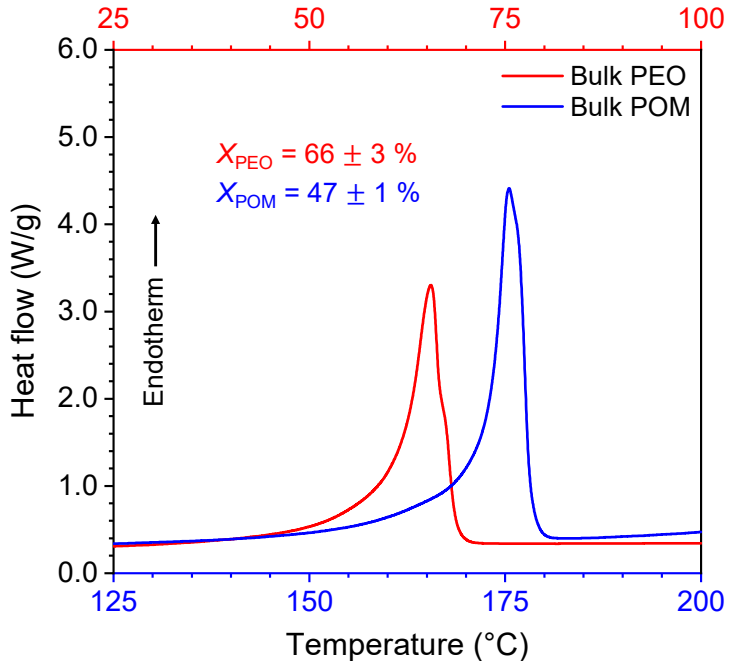

Fig. S5. DSC thermograms corresponding to bulk PEO and POM samples obtained by erasing the thermal of NF mats followed by a 30 K min^{-1} cooling scan. The relative degrees of crystallinity follow the trend found for PEO and POM NFs in Fig. 5.