

Supplementary Information: The Evolution of Crystalline Structure during Gel Spinning of Ultra-High Molecular Weight Polyethylene Fibers

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1 Gel Permeation Chromatography

Distribution of molecular weight of the UHMWPE sample is measured with GPC. The results are displayed in Figure S1. Weight average molecular weight and number average molecular weight are measured to be 3,810,000g/mol and 1,004,000g/mol respectively. The polydispersity index of the powder was found to be 3.79.

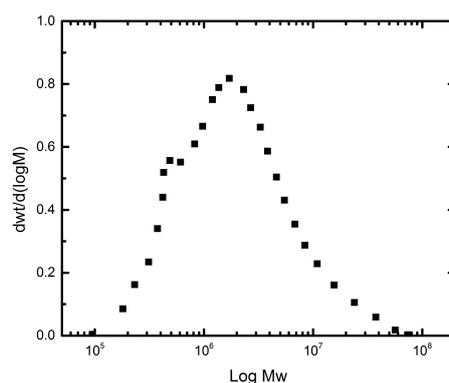


Figure S1: GPC trace of Sigma UHMWPE

2 Isothermal Crystallization Kinetics

Isothermal crystallization experiments were carried out on a DSC Q2000 (TA Instruments), that was calibrated with indium. 8wt% Gels, prepared as described previously, are loaded and cycled at 1° C/min from 50-120° C to determine the crystallization temperature, T_c . It was determined that $T_c = 81^\circ$ C for the saturated gels. To determine the gel crystallization behavior, samples are held at 150° C for 10min to clear thermal history, and are then equilibrated at 120° C to mirror the spinning process, before ramping at 40° C/min to T_c . Samples were held isothermally at T_c for 30min to observe crystallization. The Avrami equation was used to fit the crystallization kinetics. The form used, $1 - V_c = \exp(-kt^n)$, is for isothermal systems with instantaneous nucleation where V_c is the volume fraction of crystalline domains, k is a rate constant with

dependence on nucleation and growth rate, and lastly n is the Avrami index which describes the dimensionality of the nucleation. For questions into the applicability of this model and further reading on polymer crystallization we refer you to a review paper by Piorkowska and coworkers [1]. The data handling and fitting was done using an Origin plugin developed by Lorenzo et. al.[2].

Isothermal crystallization behavior of an 8wt% gel is shown in Figure S2, along with the Avrami fit which is shown to closely follow the experimental data. The Avrami equation provides us with a time scale of the crystallization $\tau^{1/2} = (0.69315/k)^{-n}$ which is a theoretical half-crystallization time. Crystalline saturation can be approximated as two or three times $\tau^{1/2}$. An average of multiple experiments produced a $\tau^{1/2}$ of 53 s, and the isothermal data shown in Fig.S2 represents a case with a $\tau^{1/2}$ of 44s. This time scale is not directly comparable to τ_k as the volume fraction of crystal is unknown during that measurement, but provides a scale for understanding the effect of FIC we have applied. A "worst" case scenario would be one where our τ_k corresponds to a crystalline state near half-crystallization, in which case we can see that we have reduced this time by nearly 40%, from 53s to 34s for low Wi samples. Lastly, the Avrami index parameter n , is a value of 2 for our experiments.

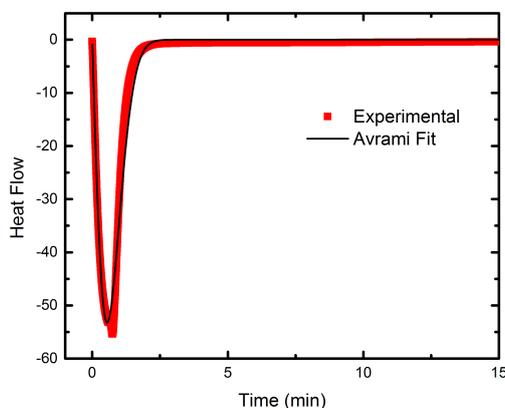


Figure S2: Isothermal crystallization of 8wt% gel with the Avrami fit.

3 Herman's Orientation Factor

To quantify anisotropy in the ASF's, Herman's orientation factor (f) is used, where f is defined as, $f = \frac{3\langle \cos^2 \rangle - 1}{2}$, and the orientation parameter is $\langle \cos^2 \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin(\phi) \cos(\phi)^2}{\int_0^{\pi/2} I(\phi) \sin(\phi)}$. Fig S3 shows the regions from which f is calculated. Due to the symmetric nature of scattering only 90° are necessary to quantify the system orientation. This angle is measured from the horizontal axis and is represented by ϕ . Because of the two distinct bands of scatter at different q spacing's in this system, narrow regions in q have been isolated to determine orientation for specific features. The window for the internal scatter was chosen to be from 0.012 to 0.016 nm^{-1} , and the external feature was measured from 0.048 to 0.052 nm^{-1} .

Fig S4 shows the scattering intensity for the feature shown in Fig S3 at 0.048 to 0.052 nm^{-1} . For the scatter shown in Fig S4, and the data presented in this paper, a 2nd order polynomial was found to provide the best fit to the data. This fit function is represented in the figure as a

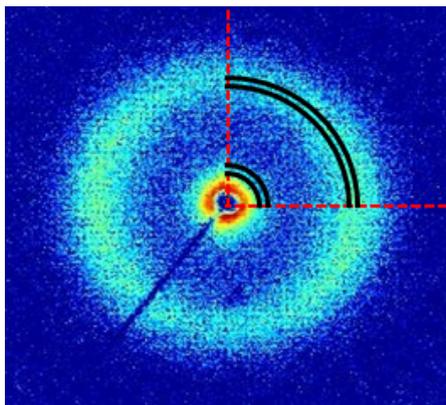


Figure S3: Regions from which Herman's Orientation parameter is calculated. The two distinct q 's are bracketed by black lines. Only the scatter in quadrant one, ie. from 0 to 90° as measured from the horizontal, is used. This is indicated by the dotted red lines.

black line over the data. The fit is integrated, using Eq. 3 from the main text and the second equation presented above, to provide the orientation parameter used in calculating f .

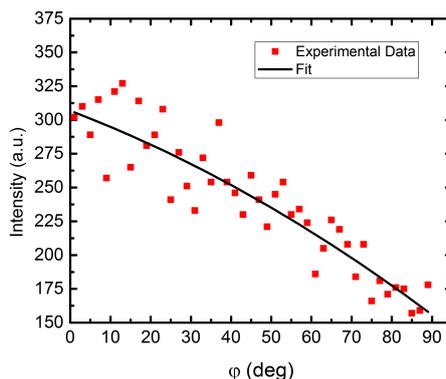


Figure S4: Intensity of scatter as a function of theta between 0 and 90° with the fit used to calculate Herman's Orientation Factor.

4 Percent Crystallinity

Wide-Angle x-ray scattering (WAXS) is used to calculate an average percent crystallinity of the spun fibers. The 2-D scattering data, where the x-ray beam passes perpendicular to the fiber axis, spans from $10 \geq 2\theta \leq 40$. This range allows for analysis of the primary orthorhombic crystal cell peaks, as well as monoclinic diffraction patterns. For this study, no significant monoclinic peaks were observed.

To measure percent crystallinity, the 2D scatter pattern is integrated over all ϕ to construct a plot of intensity versus 2θ . The 2D scatter pattern is first corrected for both the image center and

tilt before summation of the 1D spectra. The calibration function in the Datasqueeze analysis software is used to ensure accurate and reproducible centering and angle correction. Failure to correct these parameters results in smearing of the peaks and erroneous percent crystallinity.

A representative 1D scatter pattern is shown in Figure S5 in red. We use a ratio of peak areas to quantify the amount of crystalline material [3, 4]. The first step in calculating peak areas is to fit and subtract a baseline from the raw data. A quadratic function was fit to intensity data between $14 \text{ deg} \leq 2\theta \leq 16 \text{ deg}$ and $26 \text{ deg} \leq 2\theta \leq 28 \text{ deg}$ where there is no influence of crystalline peaks. Next, the amorphous peak is fit by minimizing the residual of a Gaussian function with a fixed standard deviation, $\sigma_{Amorph} = 2.21 \text{ deg}$. The standard deviation of the amorphous and orthorhombic Gaussian functions were fixed to the best fit value determined from the gel casted sample. The amplitude of the Gaussian distribution for the amorphous domain, A was determined via the bisection method, with initial range of amplitudes from 1×10^3 to 1.01×10^5 . The minimization function is given by:

$$E = \sum_{i=1}^N \left(F(2\theta) - Y_s(2\theta) \right)^2 \quad (1)$$

where N is the number of experimental data points, Y_s are the intensity of the signal evaluated at 2θ , and $F(2\theta)$ is the Gaussian distribution evaluated at 2θ , given by,

$$F(x) = \frac{A}{\sigma\sqrt{2\pi}} e^{-(x-2\theta_c)^2/(2\sigma)^2} \quad (2)$$

where $2\theta_c$ is the location of the amorphous peak center. The bisection method was run until the approximate fractional relative error, ϵ_a was less than,

$$\epsilon_a < 0.01\%$$

which is equivalent to five significant figures of precision in the best fit amplitude. The best fit Gaussian distribution was subtracted from the 1D intensity data, such that only scatter from the orthorhombic peaks remain. The amplitude of the orthorhombic Gaussian distribution corresponding to the (110) and the (200) crystal planes were fit as described above. The percent crystallinity is calculated as previously documented in the literature [3]

$$\%cryst = \frac{A_{110} + A_{200}}{A_{110} + A_{200} + A_{amorph}} \quad (3)$$

An example of the best fit sum of all three Gaussian distributions is shown as a black line in Figure S5.

5 Ruland Streak Analysis

The Ruland Streak analysis is used to measure the orientation and length of extended chain crystals. Ruland showed that the behavior of the azimuthal width of a streak feature, when measured as a function of scattering parameter s , where $s = \frac{q}{2\pi i}$, corresponds to the length and orientation of the scattering structure. The diagram in Fig. S6 shows how the azimuthal width is measured. A subsection of the 2D scatter which contains the streak feature is isolated. Due to the fiber orientation during exposure this subsection is from $45\text{-}135^\circ$. Ranges in s , with a width of $.004 \text{ nm}^{-1}$, are summed to produce $I(\theta)$ of the streak, and are considered to be at the s value which is the middle of the chosen range. This window is represented in Fig. S6 as the region

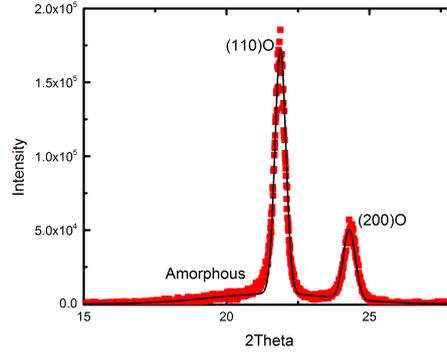


Figure S5: WAXS diffractogram of UHMWPE Fiber. Experimental results represented in red. Fit function is a black line.

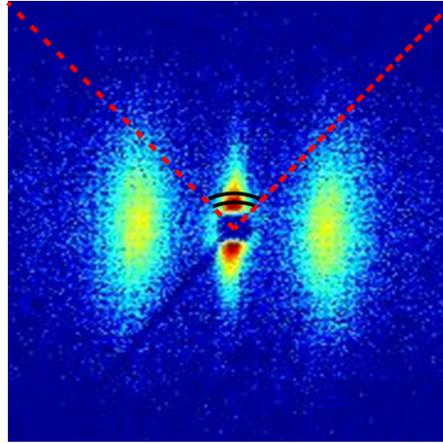


Figure S6: Diagram showing the area from the 2D scatter pattern over which one single measurement is taken. ϕ ranges from 45 to 135°, and a q window of 0.004 Å⁻¹ is summed.

bracketed by the black arcs, and note that this is not to scale and is exaggerated in range for easier indication. Step size in s of $.004 \text{ nm}^{-1}$ is chosen to ensure complete coverage of data.

Figure S7 shows the azimuthal width for sample $Wi=1.5$, $DR_L=6$ at $s=0.016 \text{ nm}^{-1}$. A gaussian fit is shown as a black line on top of the data. The fit parameter, δ , is the half width at half maximum (HWHM) and is used in the calculation of the integral width, σ , through the following transform: $\frac{(2\pi\delta/360)^2}{2ln2} = \sigma^2$. As shown in Eq. 5 of the main text, which shows the gaussian form of the Ruland analysis, the integral width relationship is second order. HWHM can also be found for a Lorentzian fit and used in the same manner, but only a first order expression is needed as shown in Eq. 4 of the main text. By performing the above calculations along the complete length of the streak feature the integral width as a function of scattering parameter s is constructed and a linear fit to the Ruland equations can be found, see Figure S8. In Fig.S8 the width for the $Wi=1.5$ $DR_L=6$ sample is shown as well as a line of best fit. The slope of this

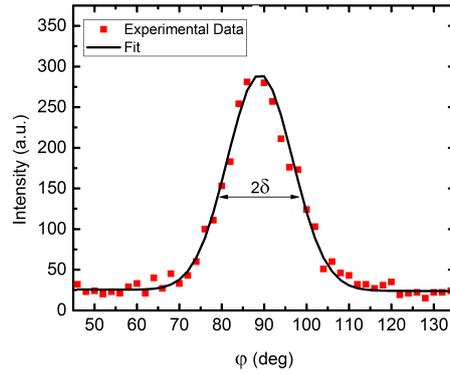


Figure S7: The scatter intensity at a particular value of q as a function of ϕ . A gaussian fit is applied to the data, and the delta parameter is shown which is used to calculate shish length.

line is $8.56 \times 10^{-6} \text{ nm}^{-2}$ which is equal to an average shish length of 342 nm. The slope of this linear fit corresponds to the average shish length and the intercept is an orientation parameter.

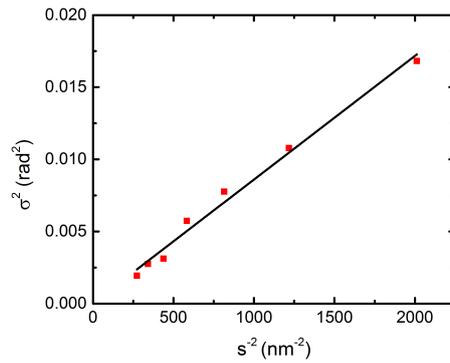


Figure S8: An example of the fit to the Ruland Streak equation for Wi 1.5 at DR 6. This is the gaussian form of the equation.

References

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