Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information: Polymer entanglement drives formation of fibers from stable liquid bridges of highly viscous dextran solutions

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1 Measuring bulk viscosity as a function of concentration

The bulk viscosity for solutions of 500 kDa dextran in water, ranging in concentration from 35-55 %wt, was measured using the falling ball method. A detailed experimental explanation is presented in section 2.2 of the corresponding paper. The data from these experiments are presented in Fig. (S1) below. Using the MATLAB Curve Fitting Tool, these data were fit with an exponential function and this fit was used to interpolate the viscosity data presented in Fig. 7(b) of the corresponding paper.

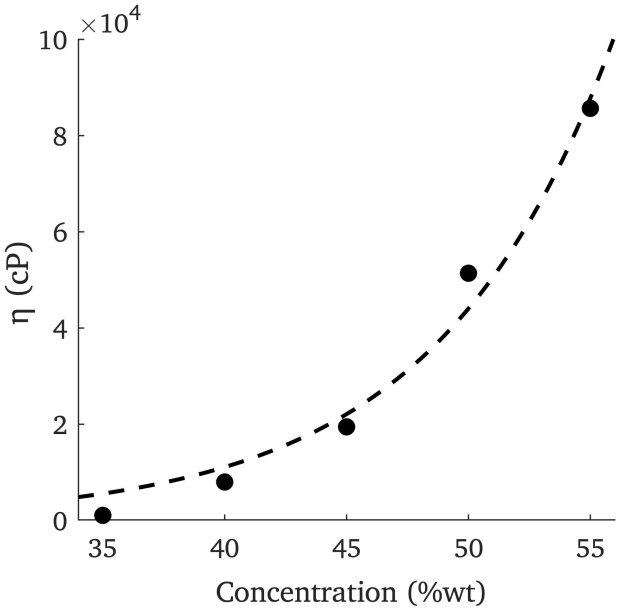

Figure (S1): Viscosity as a function of concentration for solutions of 500 kDa dextran in water, fit with an exponential function (dashed line, $r^2 = 0.98$).

2 Bulk viscosity and extensional viscosity

By analyzing the secondary flows, the final fiber diameter is found to scale linearly with solution viscosity. In determining this scaling, the viscosity was measured using the falling ball method, which is an excellent method for measuring the bulk viscosity (η) of a solution. However, in the work done here, the process of drawing long liquid bridges would involve applying extensional flows to the dextran solutions. In this case, the extensional viscosity (η_e) would be different from the bulk viscosity that was measured and used in the previous discussion.

Viscosity of entangled solutions is dependent on the extension rate ($\dot{\varepsilon}$). As $\dot{\varepsilon}$ approaches zero, η_e approaches 3 times η as per the famous Trouton ratio.[1] Then, in entangled solutions as $\dot{\varepsilon}$ increases, η_e decreases in the process known as shear thinning.[2] This is due to the alignment that occurs as the polymers are strained, decreasing their resistance to flow. The end of this early strain regime is defined by the point at which the individual polymer chains begin to stretch. From this point on, as $\dot{\varepsilon}$ increases, η_e sharply increases beyond η, due to the stretching of individual polymer chains.

To determine η_e, it is necessary to know the time and spatial evolution of $\dot{\varepsilon}$. However, in this study constant speeds were applied, which translate into complex $\dot{\varepsilon}$ space and time profiles. To further complicate matters, as the fiber dries it is no longer strained in the same way as the liquid bridge. This non-uniform strain profile creates additional difficulties in translating the speed of the micro-needle to a $\dot{\varepsilon}$ space and time profile. In order to fully understand the effect of viscosity on fiber diameter it would be necessary to characterize $\dot{\varepsilon}$ and therefore η_e throughout the fibre formation process.

With the understanding that η_e is the best way to characterize viscosity in this study, the ideal analysis would be to plot the fiber diameter as a function of the average extensional viscosity over the pull duration. However, from this discussion it is obvious that η_e should scale with the bulk viscosity, likely as about 3 times larger. Therefore, the linear scaling in Figure 7 of the main text supports the assertion that solution viscosity largely controls fibre diameter.

3 Calculation for scaling of η with τ_{rep}

The falling ball method was only used to measure viscosity (η) of 500 kDa dextran solutions because of the large volumes needed to use this technique. For all other molecular weight (M_w) dextrans, the experimentally determined reptation time (τ_{rep}) was used as a proxy for η. For entangled solutions of neutral polymers in θ-solvents, the viscosity is predicted as:

$$\eta - \eta_s \sim N^3 c^{14/3}, \tag{S1}$$

where η_s is the solvent viscosity, N is the number of Kuhn monomers in the polymer chain, and c is the solute concentration within the solution.[3] Since the viscosity of the polymer solutions (Fig. (S1)) is 3-5 orders of magnitude larger than η_s ($\eta_{water} = 1$ cP),

$$\eta - \eta_s \approx \eta. \tag{S2}$$

Equation (S1) can thus be rearranged to:

$$N^3 \sim \frac{\eta}{c^{14/3}}. \tag{S3}$$

For neutral polymers in θ-solvents, reptation theory predicts that τ_{rep} scales as:[3]

$$\tau_{rep} \sim N^3 c^{7/3}. \tag{S4}$$

Thus, substituting equation (S3) into (S4) yields:

$$\eta \sim \tau_{rep}\, c^{7/3}. \tag{S5}$$

This simple calculation shows how τ_{rep} can theoretically be used as a proxy for η.

4 Images of 250 kDa fibers

In this study, fiber diameters were found to range from 2-20 μm. Fig. (S2) shows a fiber from each of the concentrations studied with 250 kDa dextran, providing a visual representation of the range of fiber diameters.

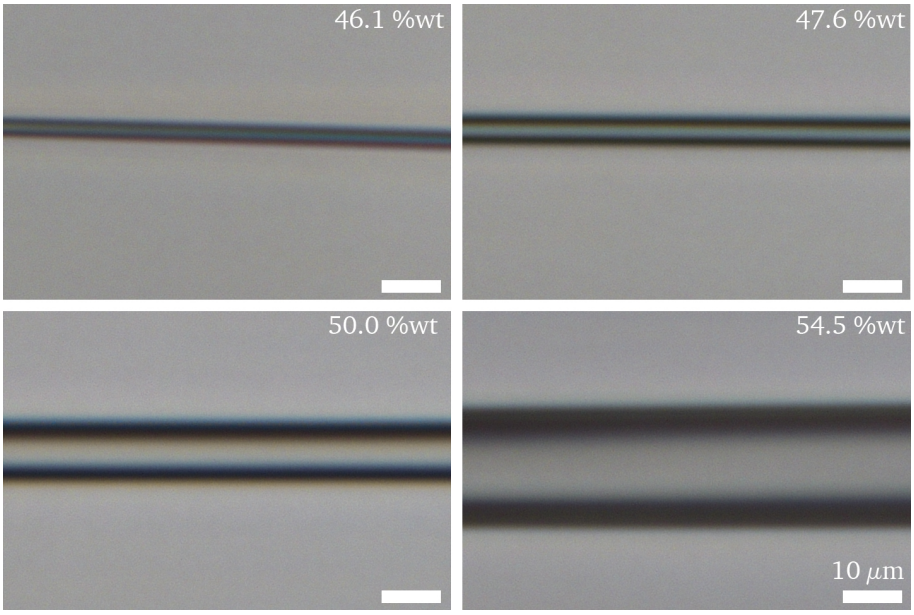

Figure (S2): Brightfield images of fibers formed at various concentrations of 250 kDa dextran in water. The diameter is seen to increase with increasing dextran concentration.

5 Description of supplementary movies

Supplementary movie 1(a) shows a successful fiber elongation cycle, where the fiber remained attached to the caddie via a liquid bridge throughout the entire pull duration (τ_{pull}) of 1.04s.

Supplementary movie 1(b) shows a mode I failure, in which the liquid bridge fully retracted into the caddie before t = τ_{pull} for a pull duration of 5.02 s, stopping the fiber formation process.

Supplementary movie 2(a) shows the secondary flow for a 45 %wt solution of 500 kDa dextran in water. This video begins (t = 0) at the moment the needle comes to rest. The liquid bridge connecting the fiber to the caddie retracts into the caddie, and at this concentration this whole process occurs in less than 1 s.

Supplementary movie 2(b) shows the secondary flow for a 50 %wt solution of 500 kDa dextran in water. This video begins (t = 0) at the moment the needle comes to rest, and the τ_{pull} is the same as supplementary movie 2(a). The liquid bridge connecting the fiber to the caddie retracts into the caddie, and at this concentration this whole process takes more than 2 seconds.

References

[1] F. T. Trouton, *Proceedings of the Royal Society A*, 1906, **77**, 426–440.

[2] P. K. Bhattacharjee, J. P. Oberhauser, G. H. McKinley, L. G. Leal and T. Sridhar, *Macromolecules*, 2002, **35**, 10131–10148.

[3] R. H. Colby, *Rheologica Acta*, 2010, **49**, 425–442.