

Electronic Supplemental Information

Hydrodynamically Directed Multiscale Assembly of Shaped Polymer Fibers

Adam R. Shields, Abel L. Thangawng, Christopher M. Spillmann, Jawad Naciri, Peter B. Howell Jr., and Frances S. Ligler*

Naval Research Laboratory, 4555 Overlook Ave, SW Washington, DC, USA 20375

frances.ligler@nrl.navy.mil

Materials

The synthesis of the two liquid crystal materials, MAOC4 and MACC5, used for the preparation of the liquid crystal (LC) mixture has been previously described.¹ The acrylate solution was prepared as follows: 30 mg of MAOC4 and 40 mg of MACC5 (synthesized in-house) were dissolved in 2 mL of a solution containing 4-hydroxybutyl acrylate (85 wt%), acrylic acid (11 wt%), ethylene glycol dimethacrylate (1 wt%) and photoinitiator (2,2-dimethoxy-2-phenylacetophenone) (3 wt%) (all obtained from Sigma Aldrich). The acrylate solution was sonicated for 2 min in order to solubilize the liquid crystal molecules. All components were in liquid form when combined with the photoinitiator dissolved in dichloromethane at a concentration of 1 g/mL. Prior to mixing the solutions, the hydroquinone inhibitor was removed from the acrylate components using an inhibitor removal column (column SDHR-4 from Scientific Polymer Products, Inc., Ontario, NY). The viscosities of the sheath (glycerol (Sigma Aldrich) diluted with 55% MeOH by volume) and sample solutions, approximately 10 cP, were measured using a digital viscometer (DV-E, Brookfield Engineering Laboratories Inc, Middleboro, MA).

Device Fabrication and Operation

The sheath flow device used in this work was fabricated in two halves utilizing a combination of a computer numerical controlled (CNC) milling system (Mini Mill, Hass Automation Inc, Oxford, CA) and standard soft lithography techniques. Figure S1 shows an overview of a simplified sheath flow device assembly. The base piece, with seven chevrons that are recessed below the channel surface, was machined in transparent polymethylmethacrylate (PMMA) (Plexiglas®; Arkema Inc, Philadelphia, PA). The top piece, with the corresponding seven protruded chevrons, was made of polydimethylsiloxane (PDMS; Dow Corning's Sylgard 184, Ellsworth Adhesives, Germantown, WI) to enable UV transmission (350 nm) necessary for the polymerization. The mold for the PDMS piece was machined in the PMMA using the same process as the base PMMA piece. The base PMMA and the PDMS top of the device were aligned and clamped together using screws. A PMMA interface layer with a window cut out for UV exposure was used to hold the PDMS piece in place. The UV window only exposes the channel beyond the chevron region where the prepolymer stream has been manipulated into the desired shape. The inlets for sample and sheath fluids were integrated on the base aluminum clamp using 1/4-28 flat bottom Peek nut with a corresponding ferrule (Upchurch Scientific, Oak Harbor, WA) and an exposure/viewing window was integrated on the top aluminum clamp. A more detailed description of the device is given in Thangawng et al., 2011 (reference 22 of the main text).

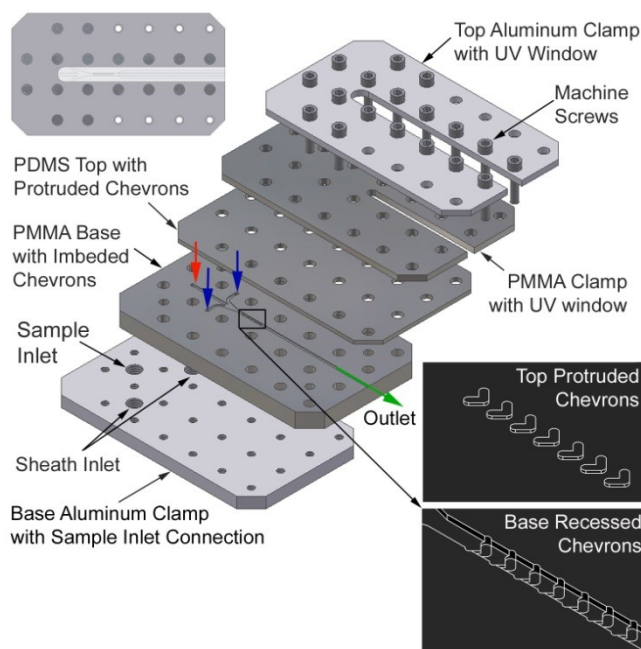


Figure S1. An overview of the sheath flow device. Lower right insets show the protruded and recessed chevrons integrated to the top PDMS and base PMMA pieces, respectively. The upper left inset shows how the PMMA window and the aluminum viewing windows are assembled. (Figure not to scale.)

Both the sheath and sample solutions were injected using syringe pumps. A home-made pulse dampener was also installed between the sheath pump and the device to reduce flow instability. Once the proper sheathing process was confirmed under a stereomicroscope, the device was placed on a holder, with the outlet submerged inside a beaker filled with water, such that the microchannel was in vertical position and the cross-linked fibers and the sheath fluid exited the microchannel into the water bath.

The dual 3 mm diameter lightguides of the UV lamp [Bluewave® 200 UV Light Curing Spot Lamp, Dymax, Torrington, CT] were bundled and positioned approximately 1 inch away from the surface of the PDMS window. The lamp power was set at 4.5 W/cm^2 , which at a distance of approximately 1 inch provides an intensity of $\sim 270 \text{ mW/cm}^2$ from each of the two lightguides on the channel surface, with an overall exposure length of 40 mm (length of the window on the PMMA clamp). Exposure times were calculated based on the average velocity of the sample stream along the length of the channel where they were exposed to UV. The average flow velocity was estimated using the sample stream flow rate Q and the cross-sectional area of the fibers A , such that the average velocity is $v = Q/A$.

The cured fibers were then wound onto a rotating, motorized spindle such that the fibers were suspended between the two arms of the spindle. The sheath surrounding the fibers drained into the water bath as the fibers were pulled up. The samples were then stored in air for characterization.

Accumulated Strain

Approximate averages of the accumulated strain experienced by the LC in the core fluid are given in the text (average strain of 70 in the core inlet channel, prior to focusing, and average strain of 5 in the focusing region). For both regions, the strain is given by the product of shear rate and residence time, $= \dot{\gamma}t$. Color maps of strain in each region are given in Figure S2 which correspond to the velocities and shear rates of Figure 1 of the main text. In the core inlet channel (Fig. S2a), the velocity map shown in the main text is constant over the length of the region and

so the residence time is simply the magnitude of the velocity at a given position divided by the length of that segment of the channel (14 mm). In the focusing region, however, the velocity magnitude changes along the streamlines. In this case, the residence time is computed locally for each pixel-pixel distance in the simulation and the accumulated strain at each position is the sum of the product of shear rate and residence time up to that point. Thus, in Figure S2b and 2c the amount of strain accumulated increases as one moves from left to right across the simulation image.

In each image in Figure S2 a subsection of the channel is shown (in Figure S2a 10% of the channel dimensions are omitted from each wall, in Figure 2b 10% of the channel height is omitted from both top and bottom of the image, and in Figure 2c 30% of the height is omitted from top and bottom). This is necessary because the no-slip condition at the channel walls implies zero velocity at the surface, which gives infinitely large residence times. Thus, the average strains given in the text are underestimates of the true averages since they do not include the portion of the core very close to the walls which experiences very large accumulated strains.

Figure S2c simply zooms in on the center line of the channel from Figure S2b. In Figure S2c the extensional strain picked up by the core as it accelerates during focusing can be observed.

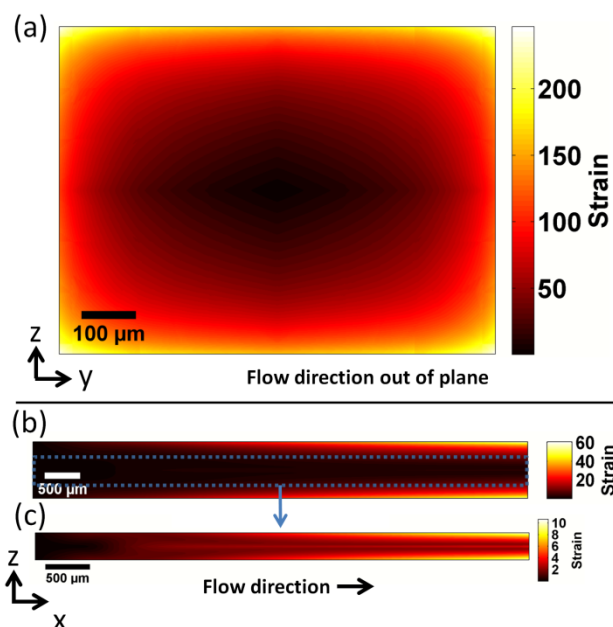


Figure S2. Accumulated strains experienced by the LC in (a) the core inlet and (b) during focusing.

SEM Imaging

To prepare the fibers for scanning electron microscopy, batches of fibers suspended on the spindles were placed onto glass coverslips. An excimer laser (LPX-Pro 220F, Coherent, Göttingen, Germany) was then used to cut the fibers along the edge of the coverslip. Fibers were then coated with ~50 nm of gold/palladium using a sputtering machine (Cressington Auto 108 Sputter Coater, Ted Pella Inc, Redding, CA) and imaged using a LEO Supra 55 (Carl Zeiss SMT Inc, Peabody, MA).

Mechanical Analysis

Dynamic mechanical analysis (Q800 series DMA, TA Instruments, New Castle, DE) measurements were performed on fibers synthesized at a flow-rate ratio of 300:12 μL/min, which were collected onto a cardboard spindle. The cardboard spindle was designed such that it could be placed directly into the tension clamp of the

DMA, and after loading it into the clamp the arms of the spindle were sliced away, freeing the fibers. The tension clamp consists of a fixed upper clamp and floating lower clamp positioned on an air bearing. A high-resolution linear optical encoder in the DMA allowed for precise monitoring of sample displacement as a function of applied force. Cross-sectional area of the collection of fibers was based on the fiber size measurements displayed in Figure 4 of the main text.

The stress-strain measurements were conducted under isothermal conditions at 30 °C with a preload force of 0.002 N to ensure that the sample was held in position. The tensile modulus and breaking strain were determined by ramping the force on the fibers from 0.002 N at 0.001 N/min until fiber failure (Figure S3). Tensile modulus was determined from the slope of the stress versus strain in the low strain regime. The viscous loss was measured using similar conditions, except that the force was repeatedly cycled from 0.002 to 0.02 N and back to form a passive work loop. The area under the curve, which reflects the hysteresis of the material in response to an applied stress, was then used to calculate the viscous loss, W , based on:

$$W = \int F dl$$

where the force, F , was integrated over the length of the sample, dl . Converting the expression to the variables collected during a passive work loop results in an expression of the viscous loss scaled by the mass, m , of the material:

$$\frac{W}{m} = \frac{1}{100\rho} \int \sigma d(\%\epsilon)$$

where the integral, equal to the area under the curve of a passive work loop, now consists of the measured parameters stress, σ , and strain, $\%\epsilon$. The variable ρ is the density of the material, equal to $\sim 1.04 \text{ g/cm}^3$, and the factor of 100 accounts for the strain reported as a percentage. The end result is a measure of the viscous loss of the fibers reported in units of J/kg . The nine passive work loops and the viscous loss for each loop are plotted in Figure S4.

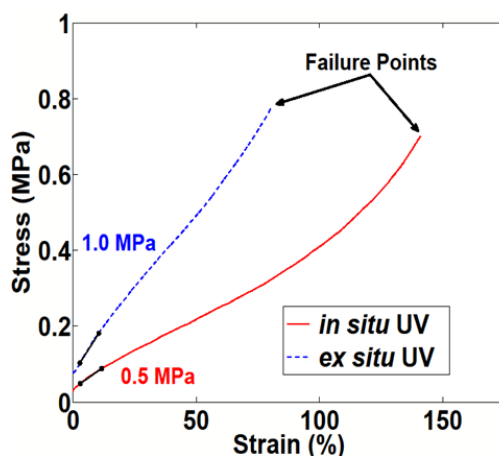


Figure S3. Stress-strain curves and Young's moduli for fibers only polymerized *in situ* (within the microfluidics channel, in red) and fibers exposed to an additional 10 minutes of UV after fabrication. This suggests the fibers may not be fully polymerized by exposure in the channel, and that post-fabrication exposure can be used to complete polymerization.

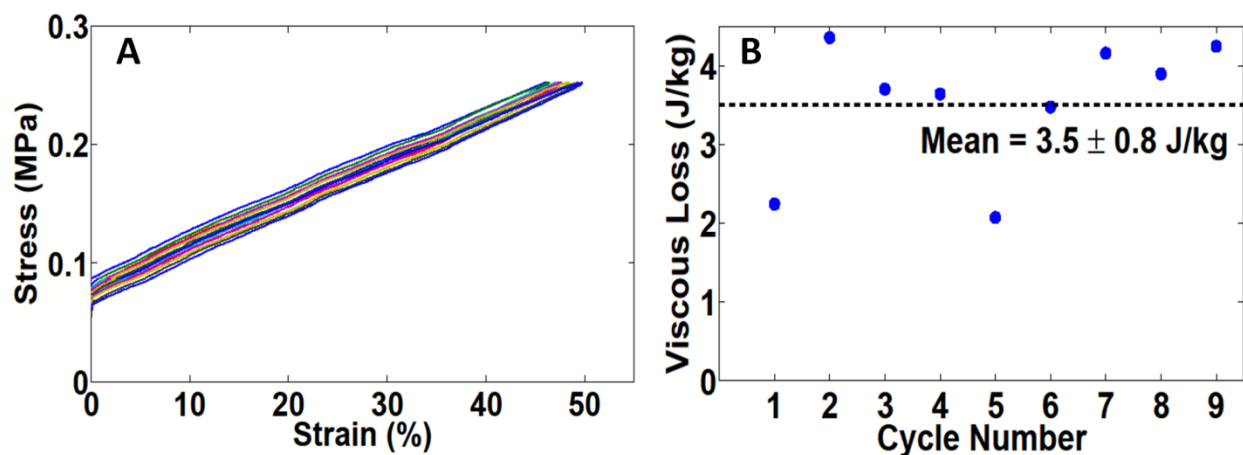


Figure S4. (A) Nine successive passive work loops of the bundled fibers synthesized with a flow ratio of 300:12. Only cycles 1 and 9 were plotted in the main text for clarity, as the loops are essentially on top of one another. (B) The hysteresis in each work loop provides a measurement of the viscous loss of the material, as described in the text.

References:

1. D.L. Thomsen, D. L.; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B. R., *Macromolecules* **2001**, *36*, 5868.