Supporting Information

Hydrodynamic Shaping, Polymerization, and Subsequent Modification of Thiol Click Fibers

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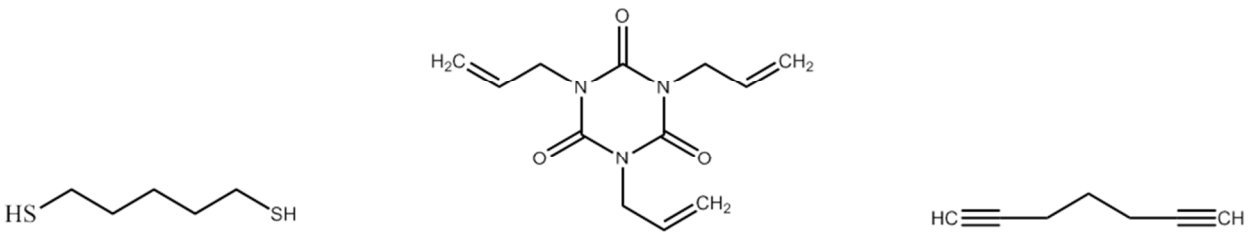

Chart S1. Additional components used in fabricating thiol click fibers.

In order to demonstrate the ability to fabricate fibers of various compositions and viscosities, several thiol click prepolymer solutions were prepared and ultimately fabricated into thiol click fibers. The complete list of thiol and alkene/alkyne compounds used in the work presented was pentaerythritol tetrakis (3-mercaptopropionate) (PETMP); 1,6-hexanedithiol (HxDT); 1,4-butanediol divinyl ether (BDDVE); (1,3,5-triallyl-1,3,5-triazine-2,4,6 (1*H*,3*H*,5*H*)-trione (TATATO); 1,6-heptadiyne (HpDY); and 1,7-octadiyne (ODY).

Table S1. Additional component combinations with the corresponding suggested sheath for proper fiber shape.

Core Solution	Sheath
PETMP + HpDY	PEG 400
PETMP + TATATO	PEG 600
HxDT + TATATO	PEG 200

By adjusting the sheath:core flow rate ratio it is possible to fabricate fibers with any of the reported combinations using PEG 400 as the sheath solution. However, to avoid deformation by viscous buckling and to ensure proper fiber shape, it is important to use the appropriate sheathing solution. Included here is a table of additional solution combinations used to make thiol click fibers along with the recommended sheathing solutions for proper fiber shaping at RT (~22 °C).

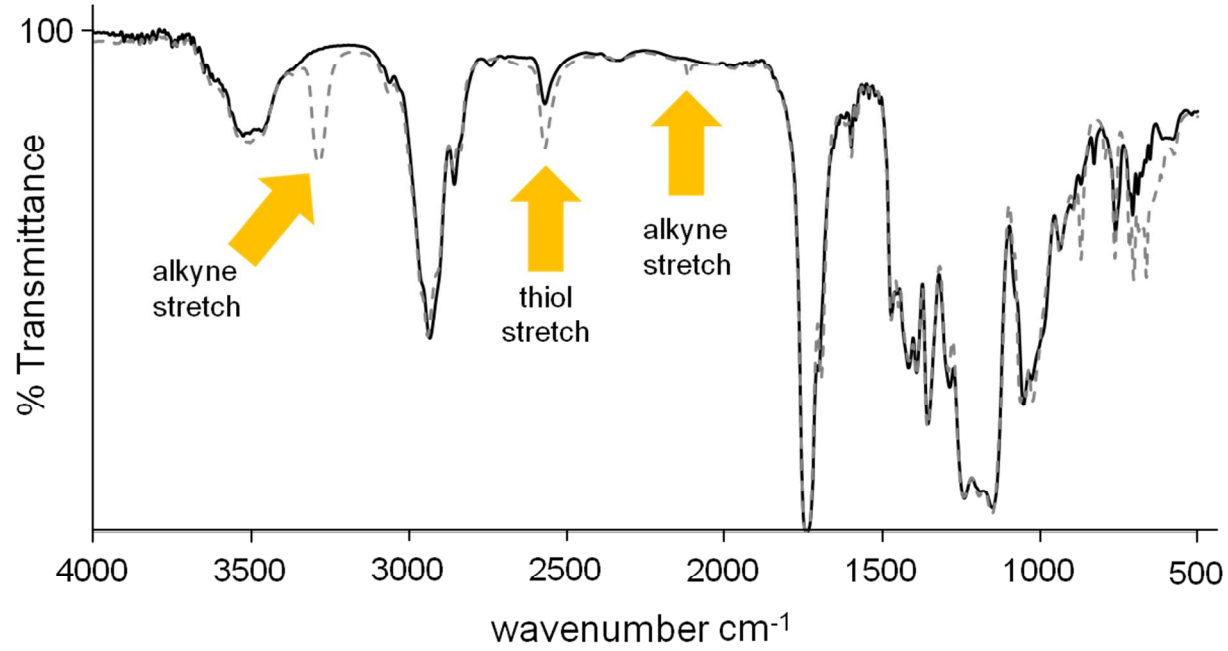

Figure S1. FT-IR of thiol–yne solution before (dashed, gray line) and and after (solid, black line) polymerization.

The thiol click photopolymerization process can be observed via FT-IR. Figure S1 depicts the disappearance of the characteristic alkyne (3300 cm^{-1}, 2200 cm^{-1}) and thiol (2550 cm^{-1}) FT-IR stretches of thiol-yne. The disappearance of these bands confirms that the thiol click reaction has taken place.

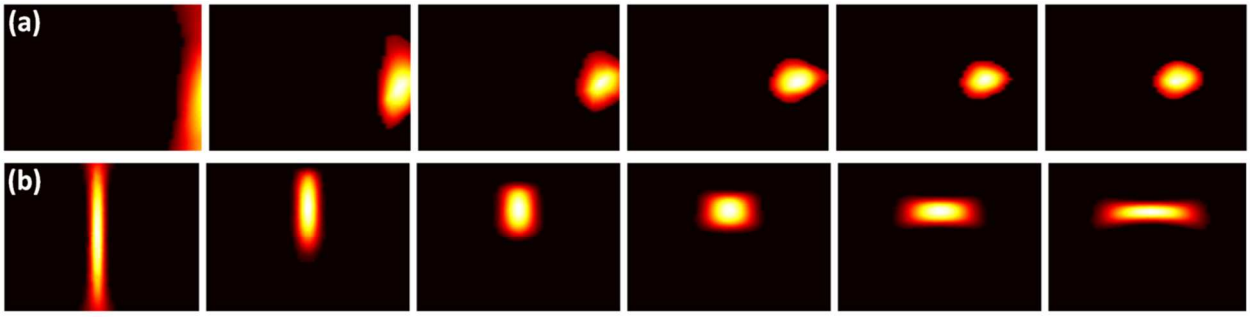

Figure S2. Supplemental videos S1 and S2 depicting the shaping of the prepolymer core solution as it flows through the shaping region.

COMSOL simulations of the hydrodynamic focusing and shaping regions of the system were performed with coupled Navier-Stokes and concentration-diffusion models and fluids were treated as Newtonian. Because the components are monomeric, we would not expect significant non-Newtonian behavior until after polymerization is initiated. An adaptive solver was used to obtain an optimized mesh density. Movies for both the round fiber device (S2A) and the ribbon-shaped fiber device (S2B) as the

fluids pass through the shaping region of each device. These movies represent the same simulations displayed in Figure 1 of the main text and are shown here for clarity.

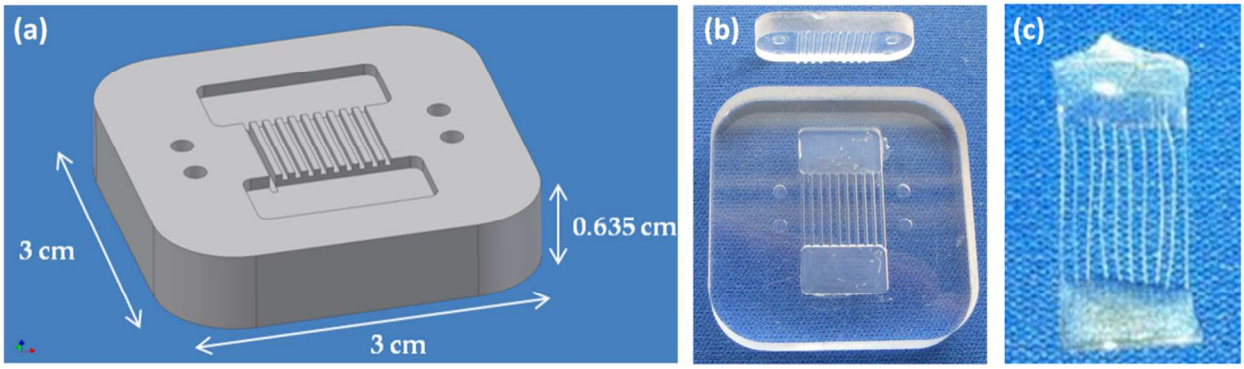

Figure S3. Custom machined fiber alignment device used to uniformly align fibers for DMA. (a) CAD image of the device design. (b) Photograph of the device, including the top cover piece used to mask fibers to prevent additional UV exposure during curing of the tabs. (c) Photograph of cured tabs and aligned fibers prior to loading into the DMA.

In order to achieve reliable dynamic mechanical analysis results using the TA Q800 DMA it was necessary to test multiple fibers simultaneously to increase the sample stiffness above the threshold specified in the instrument's user manual (above 100 N/m). To ensure uniform alignment of the 8-10 fibers typically used, a device was developed with uniformly spaced trenches, one trench per fiber, as shown in Figure S3. After being aligned and secured, the fibers were removed from the alignment device and loaded onto the dynamic mechanical analysis (DMA) instrument. The alignment device made this process easily reproducible and significantly improved the consistency of results.

The device is milled from poly(methyl methacrylate) material. Ten fibers are cut into lengths of 1.8 cm each and individually placed into one of the ten trenches such that the ends of each fiber extend into the large wells at each end of the trenches. Thiol-yne material used to make fibers was deposited into each well and cured via UV exposure. These 'tabs' secured the fibers in place and served as a means to secure the array of fibers into the DMA holder. A top cover piece (Figure S3B) was also milled and placed over the aligned fibers to prevent further UV light exposure during curing of the tabs.