Supporting Information

Swelling and Gel Fraction Measurements

The frozen cryogel specimens after preparation were first thawed at 24 °C for 30 min and then immersed in a large excess of water for one week by replacing water several times to extract any soluble species. The swelling equilibrium was tested by weighing the gel samples as well as by measuring the lengths of the gel samples in directions parallel and perpendicular to the freezing direction using a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). The equilibrium swollen gel samples were taken out of water and immediately frozen at −25 °C for 1 day before being freeze-dried at −40 °C/0.12 mbar for 1 day and −60 °C/0.011 mbar for an additional 1 day. The freeze-drying system consisted of a freeze-dryer (Christ Alpha 2−4 LD plus) connected to a vacuum pump (Vacuubrand RZ 6). The pressure during freeze-drying was adjusted using a valve controller and monitored by an active digital controller. All cryogel samples were freeze-dried under the same conditions. The equilibrium weight swelling ratio q_w was calculated as $q_w = m/m_{dry}$, where m and m_{dry} are the masses of the equilibrium swollen and dried gel samples, respectively. The volume swelling ratio of the samples was calculated as described in the text. The gel fraction W_g, that is, the conversion of fibroin to the 3D fibroin network (mass of water-insoluble fibroin / initial mass of the fibroin in the feed) was calculated from the masses of dry fibroin network and from the fibroin in the feed.

ATR-FTIR Measurements

Fourier-transform infrared (FTIR) spectra of the freeze-dried specimens were obtained using a single bounce diamond attenuated total refractance (ATR) module on a FTIR spectrometer (Nicolet Nexus 6700) equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. The resolution of each spectrum was 4 cm^{-1}, and 64 interferograms were coadded in the range of 500 – 4000 cm^{-1}. The conformation of fibroin chains was estimated by analyzing the spectra using PeakFit software (Version 4.12, SeaSolve Software Inc.). Linear baseline correction was applied to the Amide I region (1580 – 1720 cm^{-1}) before the band was deconvolved by Gauss Amplitude function. For the curve fitting procedure, the initial band positions at 1620, 1640, 1660, and 1698 cm^{-1} representing β-sheet, random coil, α-helix, and β-turn conformations, respectively, were fixed, allowing their widths and heights to vary [33-35].

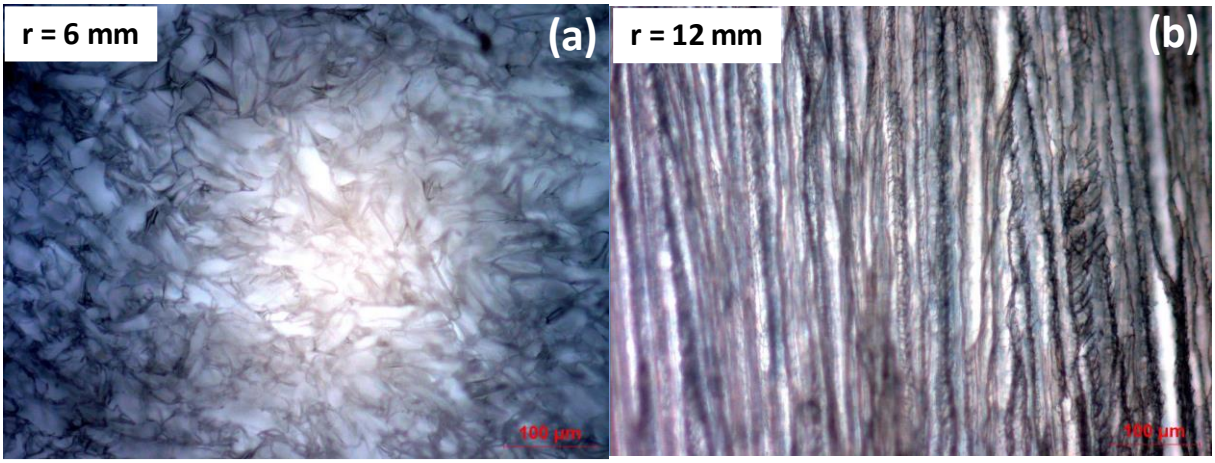

Figure S1. Optical images of fibroin cryogels taken parallel to the freezing direction. The cryogels were synthesized in the reactor shown schematically in Figure 1a of the manuscript using PTFE pipe with an internal diameter *r* of 6 (a) and 12 mm (b). C_{SF} = 4.2 wt. %. At *r* = 12 mm, aligned pore channels in freezing direction form while decreasing *r* to 6 mm results in the formation of randomly distributed pores. Scaling bar = 100 μm.

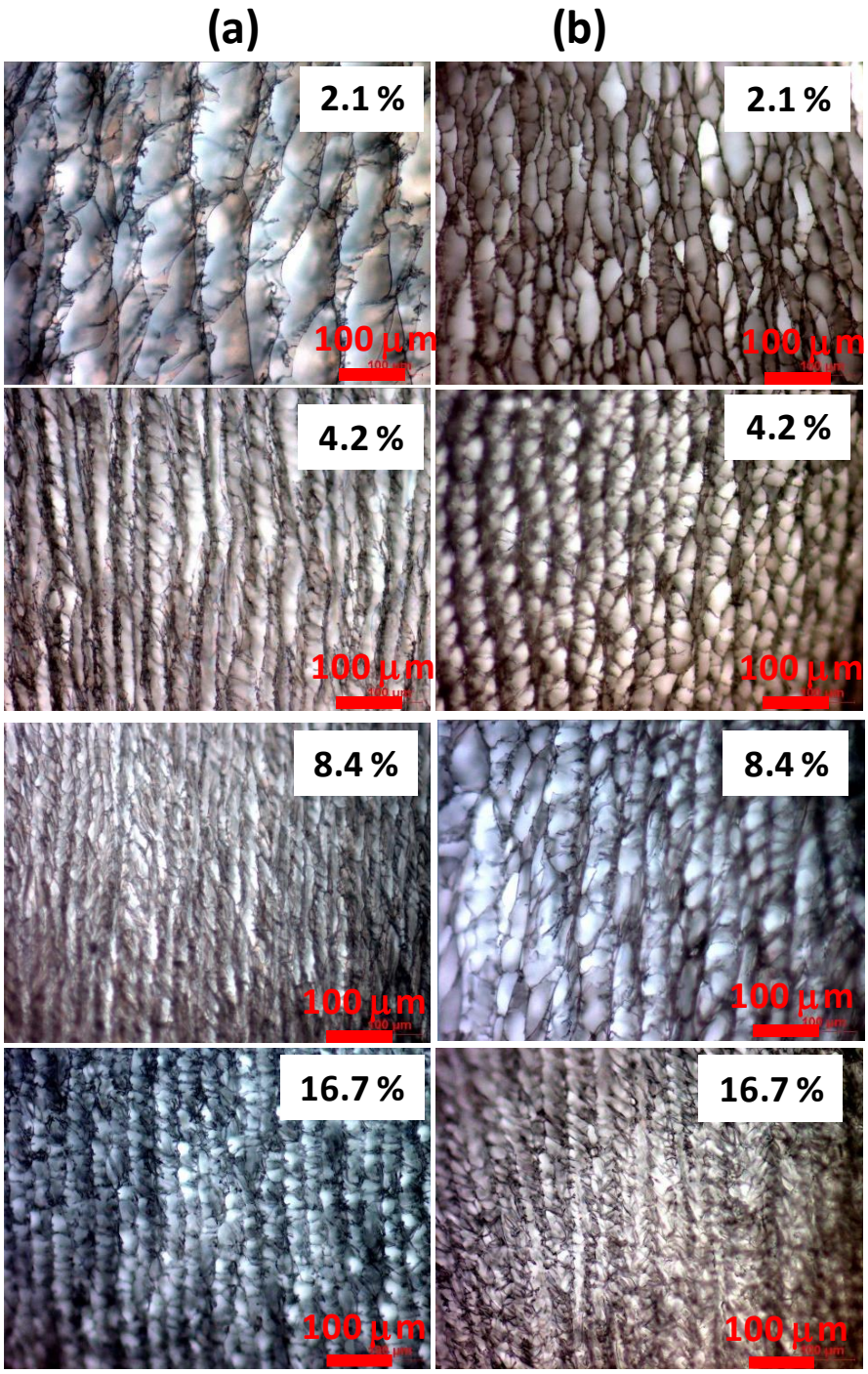

Figure S2. Optical images of anisotropic cryogel samples taken parallel (a) and perpendicular to the freezing direction (b). Fibroin concentrations C_{SF} (in wt %) are indicated. Scaling bars = 100 µm.

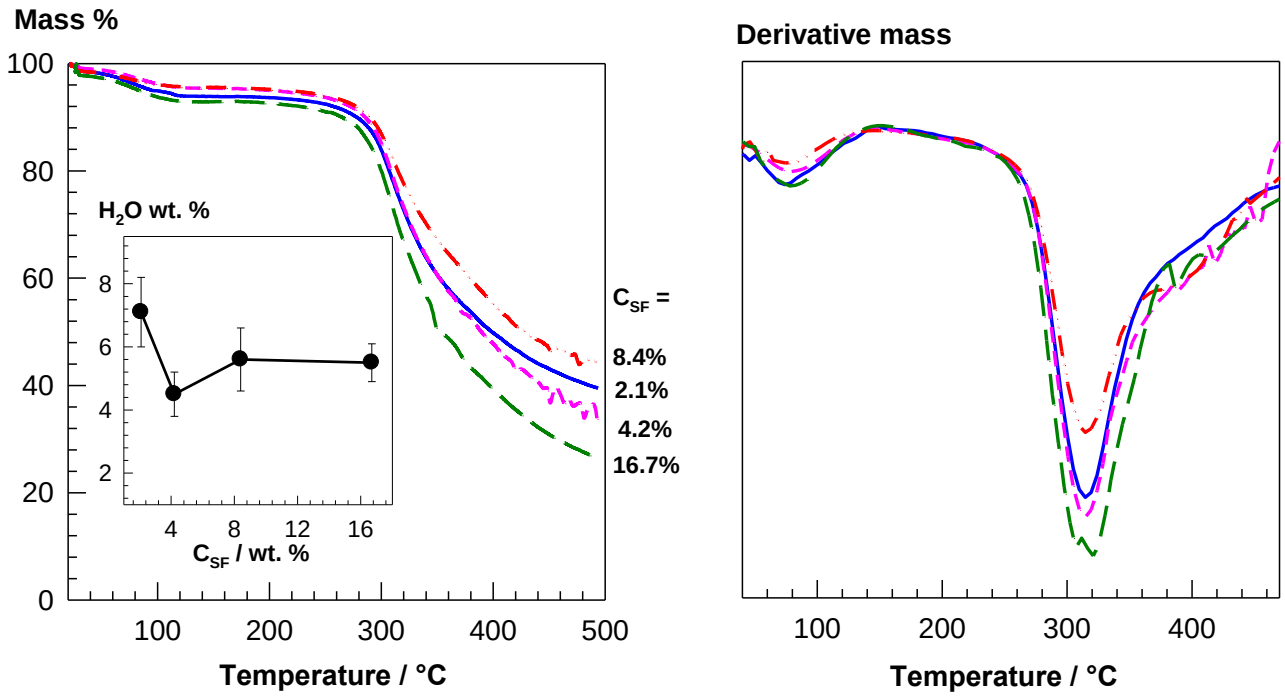

Figure S3. Thermogravimetric analysis (TGA) curves of anisotropic cryogel samples. The inset shows the water content of the cryogels plotted against the fibroin concentration C_{SF}.

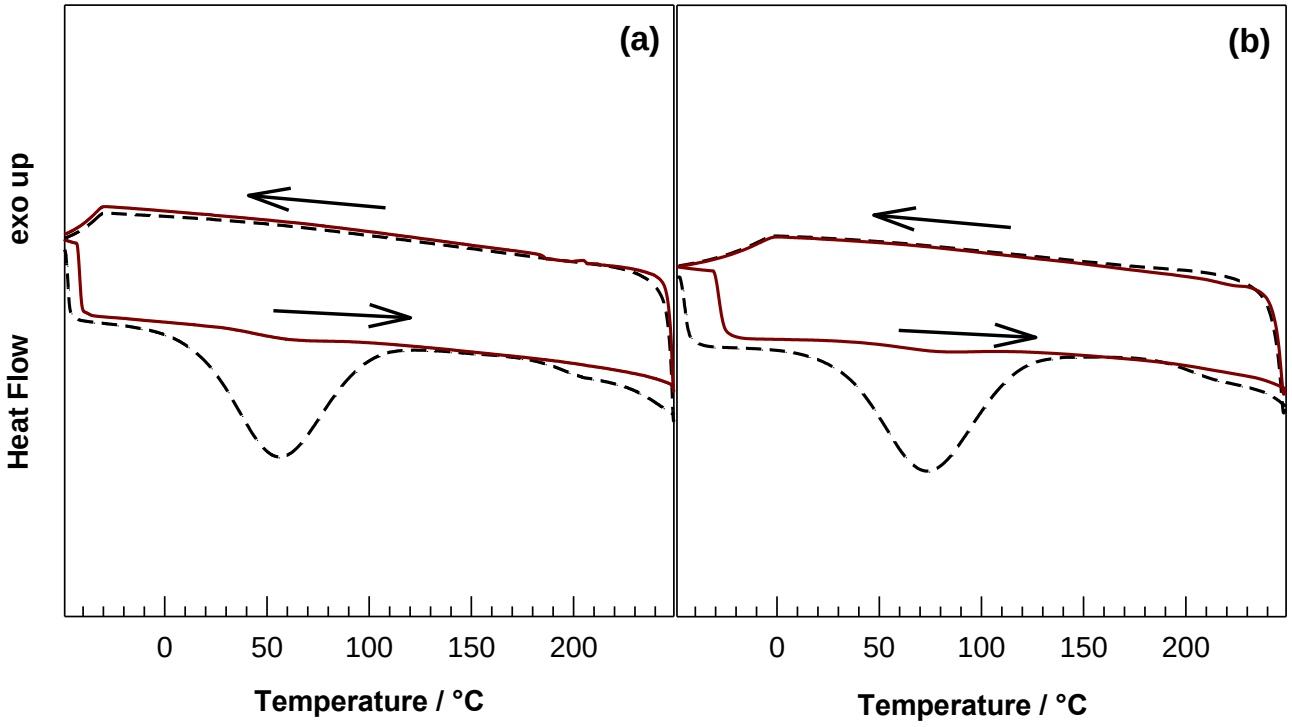

Figure S4. DSC scans of anisotropic cryogel samples formed at C_{SF} = 16.7 wt. % at a heating/cooling rate of 5 (a) and 10 °C/min (b). The 1st and 2nd runs are shown by dashed and solid curves, respectively.

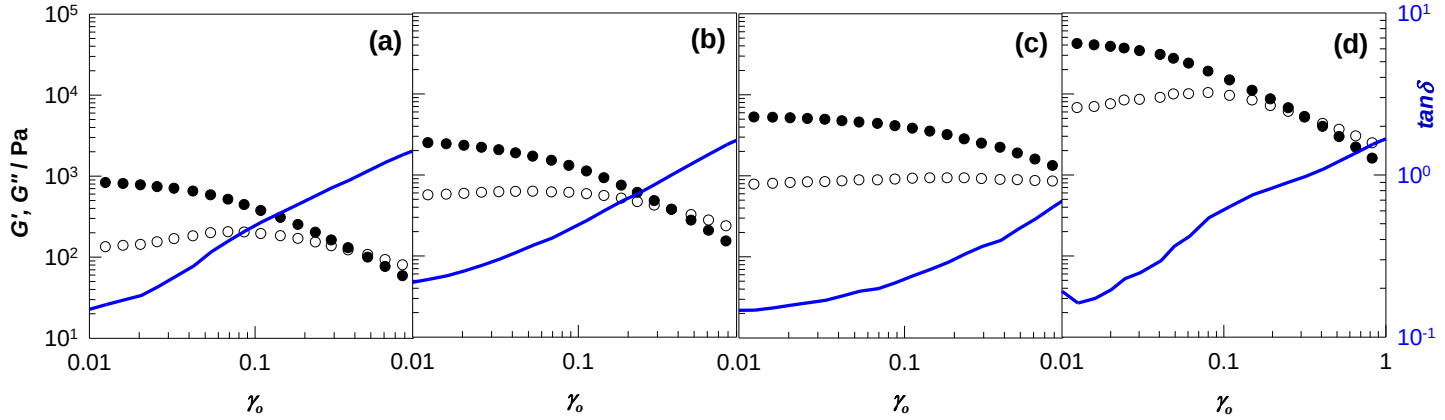

Figure S5. Storage modulus *G'* (filled circles), loss modulus *G''* (open symbols), and loss factor *tan δ* (curves) of cryogels plotted against the strain amplitude γ. $\omega = 6.28$ rad s^{-1}. $C_{SF} = 2.1$ (a), 4.2 (b), 8.4 (c), and 16.7 wt. % (d).

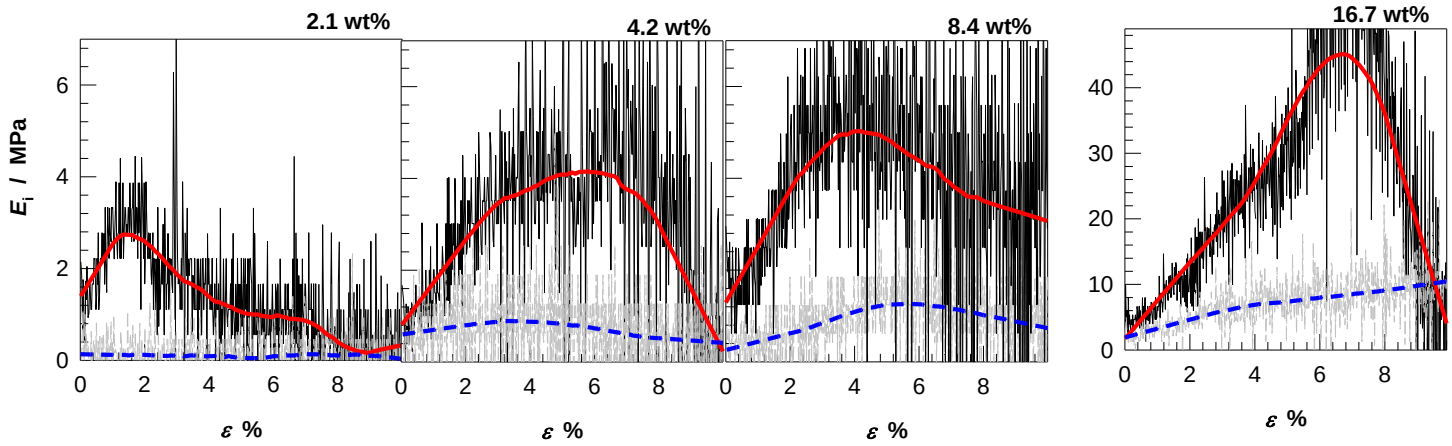

Figure S6. Instantaneous modulus E_i of the cryogels plotted against the strain ε. Solid red and dashed blue curves are the results obtained from parallel and perpendicular to the freezing direction, respectively. They were obtained after smoothing the raw data shown by black and gray scattering data using negative exponential procedure with a sampling proportion of 0.4.

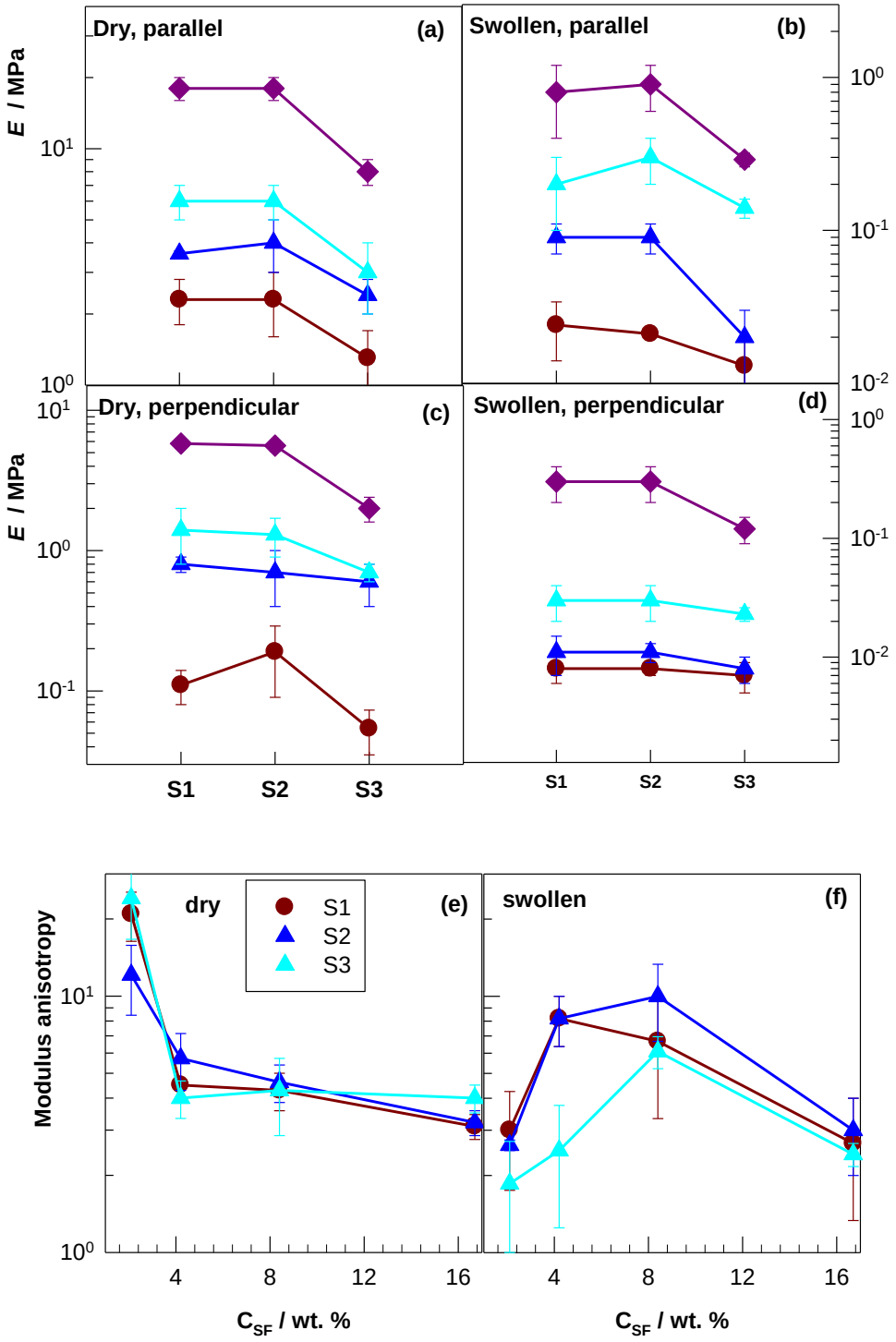

Figure S7. **(a-c):** Young's modulus *E* of dried (a, c) and swollen cryogels b, d) measured in parallel (a, b) and perpendicular to the freezing direction (c, d) plotted against the type of cryogels. For the types S1, S2, and S3 cryogels, the freezing temperatures are -196, -196, and -30 °C while the cryogelation temperatures are -18, -6, and -18 °C, respectively. **(e, f):** Modulus anisotropies of dry (e) and swollen cryogels (f) plotted against fibroin concentration C_{SF}.