**Fig. S1.** Typical ATR-FTIR spectra of freeze-dried silk fibroin cryogel samples formed at various immersion rates $R$ indicated. The original data are shown by the filled blue circles while solid curves are the results of curve fitting for the original spectra (thick red curves) and hidden peaks (thin black curves).
**Fig. S2.** Contents of β-sheets, β-turns, α-helix and random coil conformations of silk fibroin network strands in freeze-dried cryogels plotted against the immersion rate $R$.

**Fig. S3.** SEM images of anisotropic cryogel scaffolds formed at various $R$ indicated. Scaling bars are 500 μm.