Supporting Information

Calculation of the network mesh size in swollen hydrogels

The network mesh size ξ of swollen hydrogels is related to the number of repeat units between two successive cross-links, *N*, by:[1]

$$\xi = a N^{0.5} (\upsilon_2)^{-1/3} \quad \text{(S1)}$$

where *a* is the bond length (1.5 A^o) and ν_2 is the volume fraction of cross-linked fibroin in the equilibrium swollen gel. To estimate *N*, we assume phantom network behavior and the existence of tetrafunctional cross-links in the gel network. The swollen modulus G_{sw} of the hydrogels is then related to the effective length *N* of fibroin chains by:[2, 3]

$$G_{sw} = 0.5 (N \overline{V}_r)^{-1} RT (\nu_2)^{1/3} (\nu_2^0)^{2/3} \quad \text{(S2)}$$

where $\overline{V}_r$ is the average molar volume of the repeat unit, ν_2^0 is the volume fraction of cross-linked fibroin just after preparation, *R* and *T* are in their usual meanings. The volume fractions ν_2^0 and ν_2 of fibroin network can be calculated from the experimental parameters as:

$$\nu_2^0 = \frac{m_{dry}}{m_o \rho} \quad \text{(S3)}$$

$$\nu_2 = [1 + (q_w - 1)\rho]^{-1} \quad \text{(S4)}$$

where ρ is the density of fibroin (1.35 g/ml).[4] From the composition of silk fibroin, the average molar volume $\overline{V}_r$ of the repeat unit was calculated as 70 mL/mol. Using these parameters together with the moduli data of hydrogels, one may solve eqs S1 and S2 for the mesh size of gels swollen in water.

(1) De Gennes, P. G. *Scaling Concepts in Polymer Physics*. Ithaca, NY: Cornell University Press, 1979.

(2) Flory, P.J. *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press, 1953.

(3) Treloar, L.R.G., *The Physics of Rubber Elasticity*, University Press, Oxford, 1975.

(4) Park, S. J.; Lee, K. Y.; Ha, W. S.; Park, S. Y. *J. Appl. Polym. Sci.* **1999**, 74, 257.

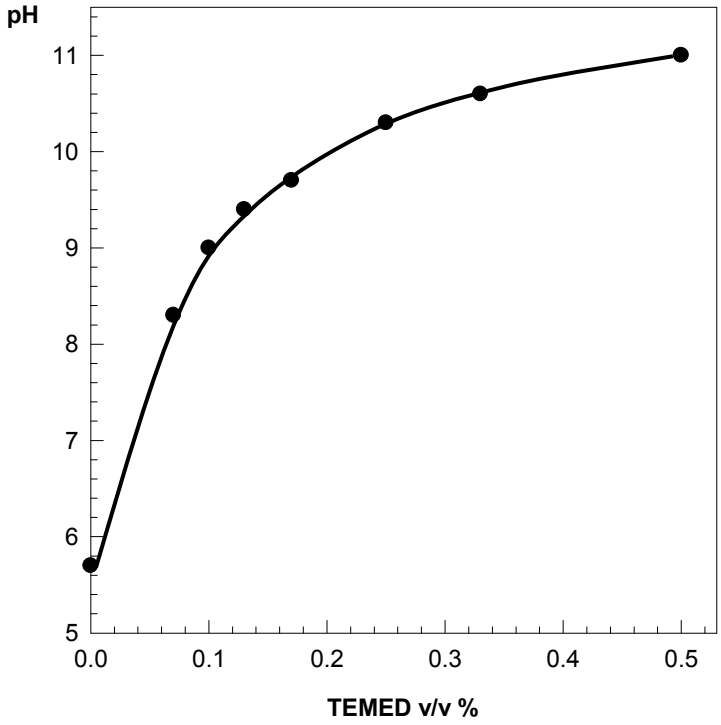

Figure S1. pH of the reaction solution shown as a function of TEMED concentration. Silk fibroin = 4.2 w/v %. EGDE = 150 %.

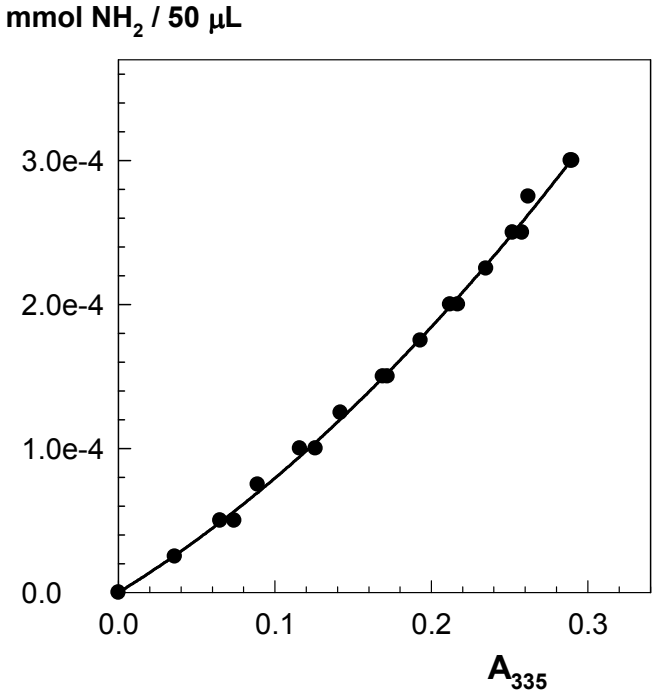

Figure S2. Concentration of the free amino groups on silk fibroin plotted against the absorbance A_{335}.

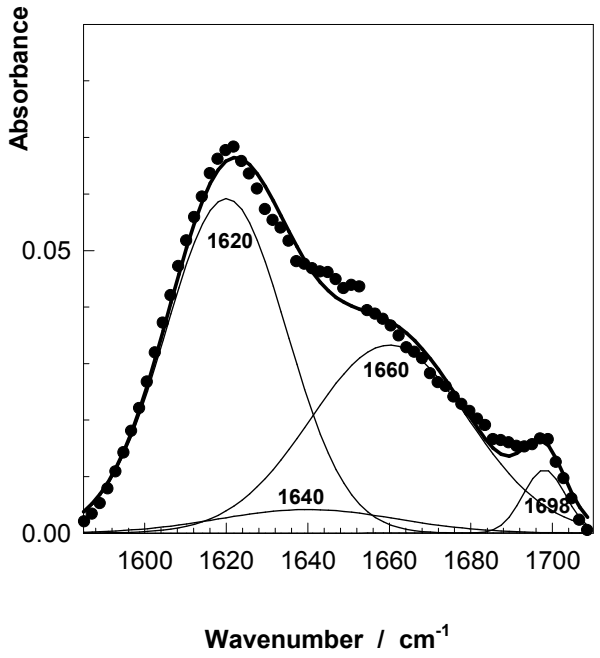

Figure S3. Typical ATR-FTIR spectrum of a freeze-dried silk fibroin hydrogel sample formed at pH = 8.3 after baseline correction. The original data are shown by the filled circles while solid curves are the results of curve fitting for the original spectrum (thick curve) and hidden peaks (thin curves).

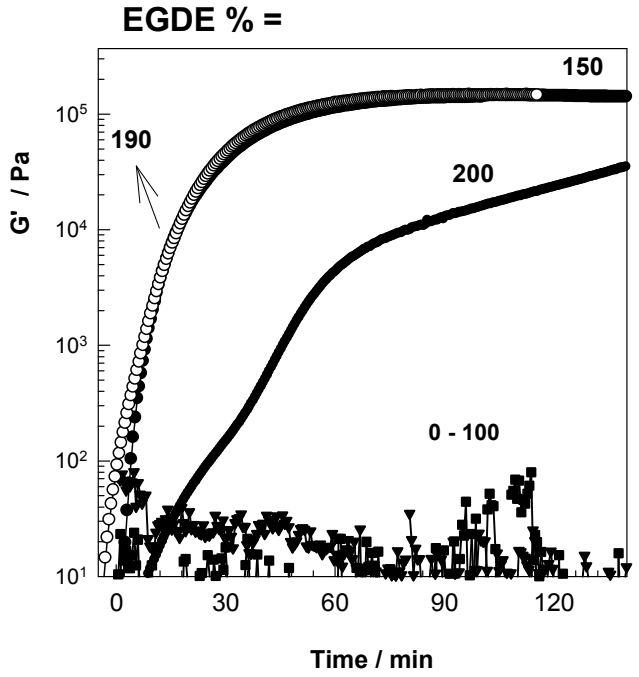

Figure S4. Elastic modulus *G' vs* reaction time (except the lag phase) plots during the cross-linking of silk fibroin at 50°C in the presence of various amounts of EGDE indicated. pH = 9.0. ω = 1 Hz. γ_o = 0.01.

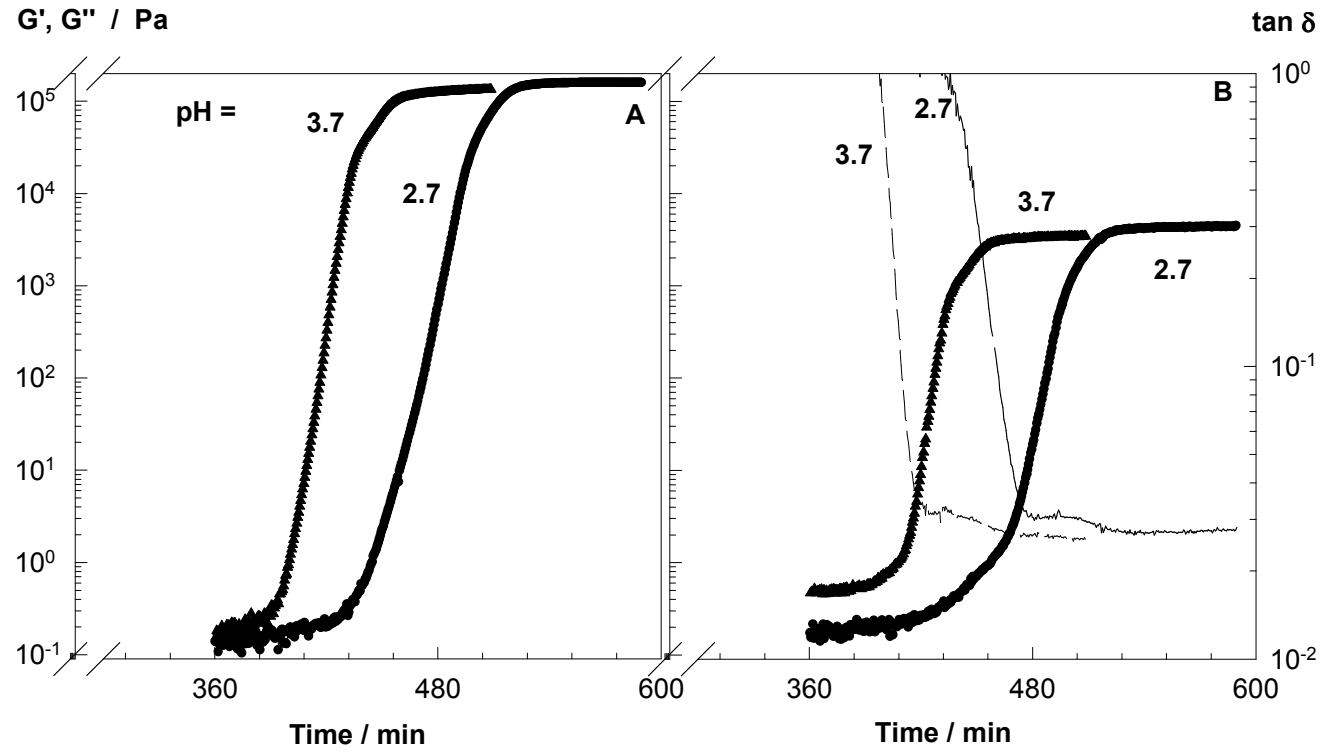

Figure S5. *G'* (A), *G''* (B, symbols) and *tan* δ (B, curves) during the cross-linking of silk fibroin at 50°C in the presence of 150 % EGDE. pHs indicated. $\omega = 1$ Hz. $\gamma_o = 0.01$.