Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Dual mode gelation behavior of silk fibroin microgel embedded poly(ethylene glycol) hydrogel

S. Ryu,[a] H. H. Kim,[a] Y. H. Park,[a] C.-C. Lin,[b] I. C. Um,[c] C. S. Ki[a]*

[a.] Department of Biosystems and Biomaterials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea

[b.] Department of Biomedical Engineering, Purdue School of Engineering and Technology, Indiana University-Purdue University Indianapolis, Indianapolis, Indiana 46202, USA

[c.] Department of Bio-fibers and Materials Science, Kyungpook National University, Daegu 41566, Republic of Korea

(*Supplementary information*)

* Corresponding author

Chang Seok Ki

Email: ki.cs@snu.ac.kr

Table S1. Formulation for SF-PEG hybrid hydrogel fabrication.

Gel formulation	0% SF-4% PEG	1% SF-4% PEG	2% SF-4% PEG	3% SF-4% PEG	4% SF-4% PEG	4% SF-3% PEG	4% SF-5% PEG
PEG4NB (wt%)	4.0	4.0	4.0	4.0	4.0	3.0	5.0
$[NB_{PEG4NB}]$ (mM)	8.0	8.0	8.0	8.0	8.0	6.0	10.0
SF-NB (wt%)	0	1.0	2.0	3.0	4.0	4.0	4.0
$[NB_{SF-NB}]$ (mM)	0	0.8	1.6	2.5	3.3	3.3	3.3
[SH] of DTT (mM)	10.0	10.0	10.0	10.0	10.0	8.0	12.0

The photoinitiator LAP of 1 mM was added into the precursor solution.

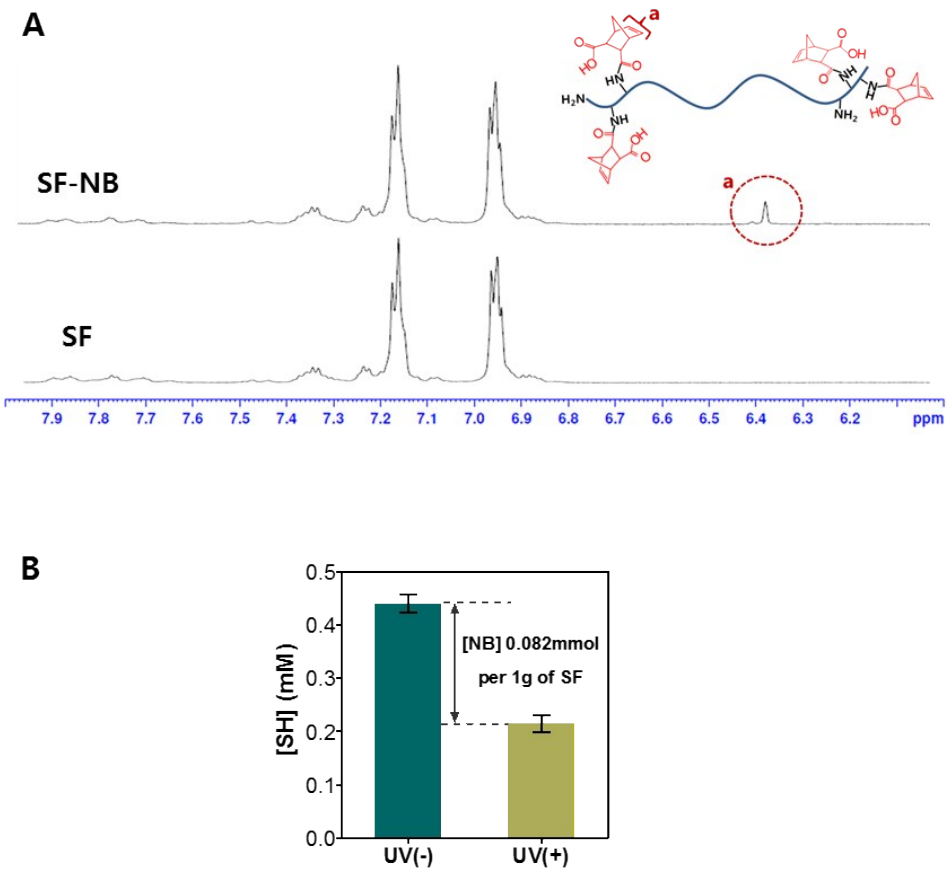

Fig. S1. (A) 600 MHz ^{1}H NMR spectrum of norbornene-functionalized silk fibroin (SF-NB). CF_3COOD was used as a solvent. (B) Thiol group consumption by SF-NB under UV irradiation (5 mW/cm^2, 365 nm, 5 min) with 1 mM LAP. Thiol group concentrations were measured by Ellman's assay (n = 3, mean ± SD). The amount of immobilized norbornene groups on SF was calculated as 0.082 mmol/g.

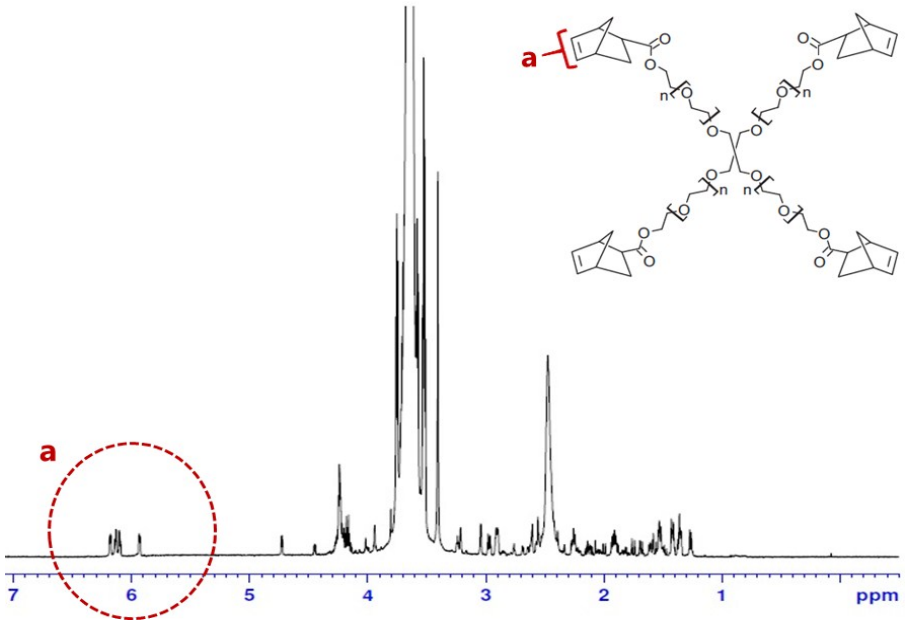

Fig. S2. 600 MHz ^{1}H NMR spectrum of norbornene-functionalized tetra-arm poly(ethylene glycol) (PEG4NB). $CDCl_3$ was used as a solvent.

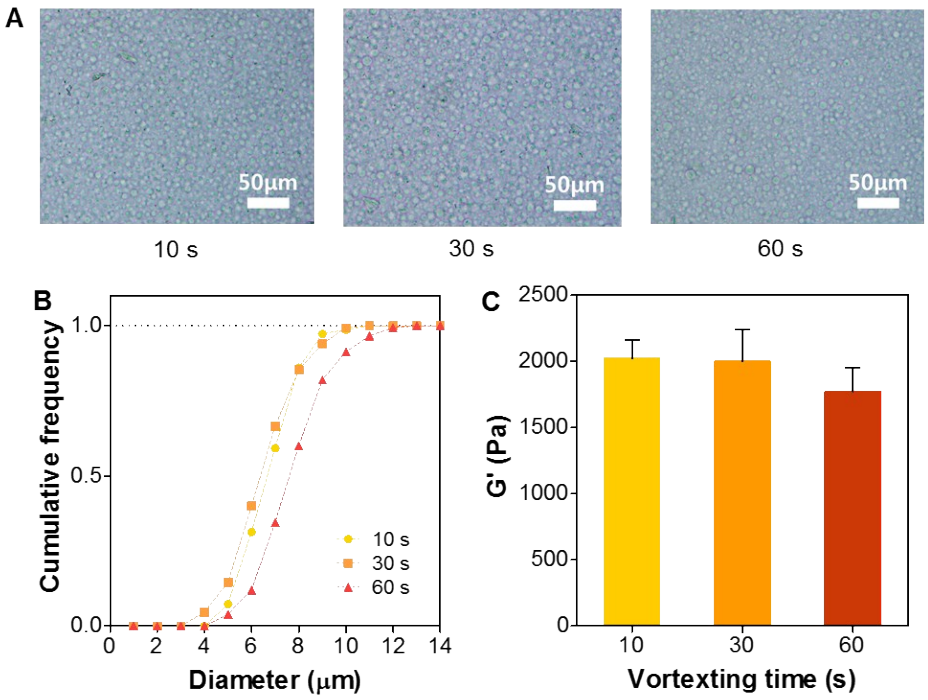

Fig. S3. (A) Phase-contrast images and (B) cumulative frequencies of diameters of SF-NB particles in PEG hydrogels fabricated with 4 wt% SF-NB and 4 wt% PEG4NB. The hydrogels were formed after vortexing of different times (10, 30, and 60 s) for precursor solution mixing. (C) Shear elastic moduli (G') of SF microgel embedded PEG hydrogels formed after different vortexing times at day-1 (n = 3, mean ± SD).

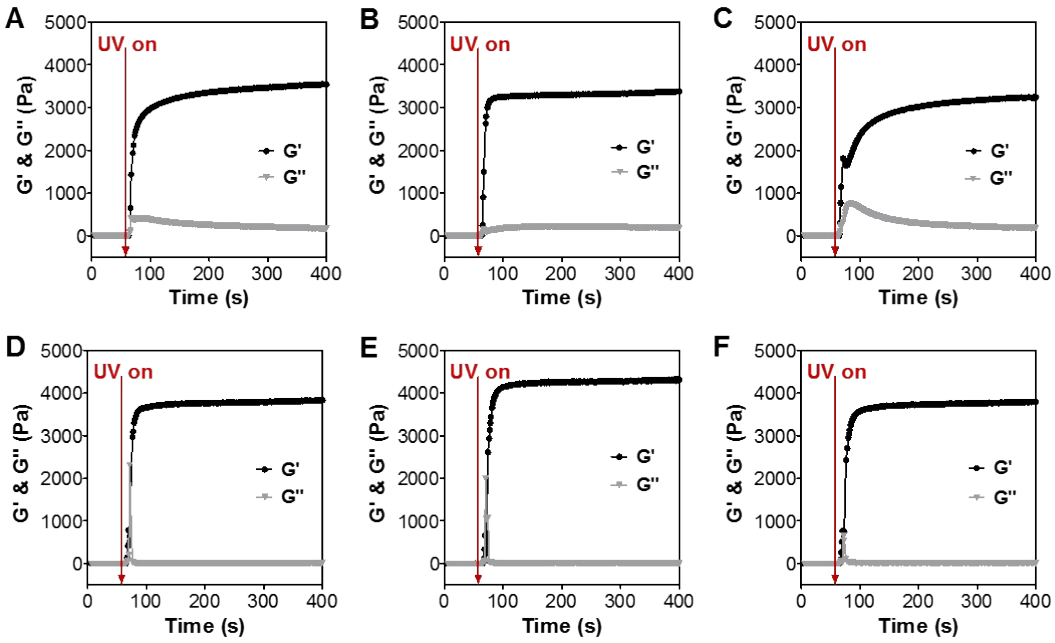

Fig. S4. In situ photo-rheometry results showing gelation kinetics of SF-PEG hybrid hydrogels formed with 1-3 wt% SF (A-C) and 1-3 wt% SF-NB (D-E) with 4 wt% PEG4NB in precursor solutions. UV light source was turned on at 60 seconds after the onset of measurement.

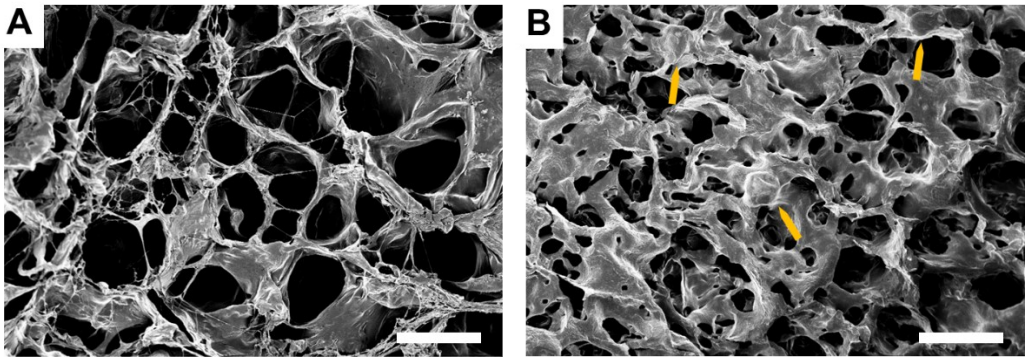

Fig. S5. Field-emission scanning electron microscopic images of (A) pure PEG hydrogel prepared from 4 wt% PEG4NB and (B) SF-PEG hybrid hydrogel (4 wt% SF-NB; 4 wt% PEG4NB) 5-day post-gelation. Yellow arrows indicate SF domain in SF-PEG hybrid hydrogel. (scale: 50 µm)

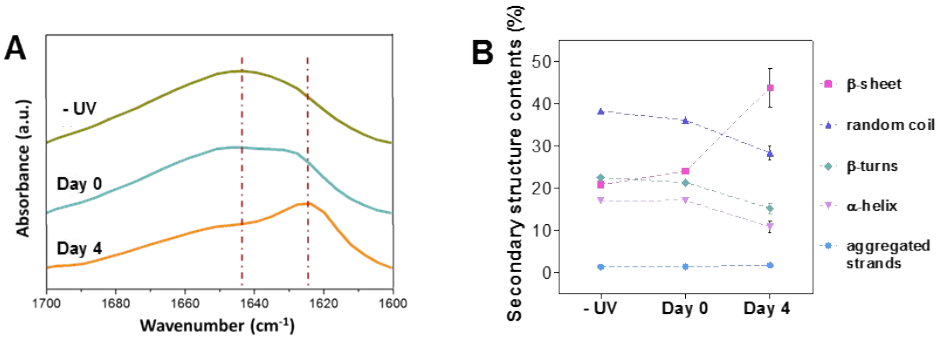

Fig. S6. (A) ATR-FTIR spectra of freeze-dried precursor solution (-UV), SF-PEG hybrid hydrogel right after the UV light irradiation (Day 0), and hydrogel after 4-day incubation in PBS (pH 7.4) at 37°C. All samples were prepared with 4 wt% SF-NB, 4 wt% PEG4NB, 5 mM DTT, and 1 mM LAP. (B) Changes of secondary structure composition of SF in hydrogel. Each fraction was obtained by integration of deconvoluted amide I band of IR spectrum (n = 3, mean ± SD).

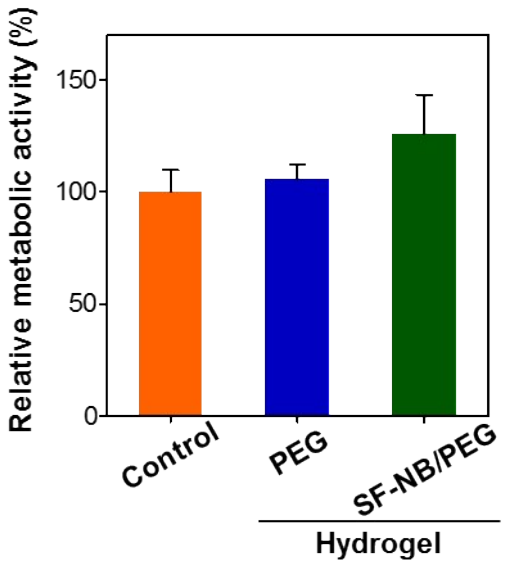

Fig. S7. Relative metabolic activities of NIH3T3 cells cultured with extracts of hydrogels. Metabolic activities were measured after cell incubation in extracts containing culture medium for 24 h by MTT assay. Control is the value obtained from non-treated cells (n = 5, mean ± SD).

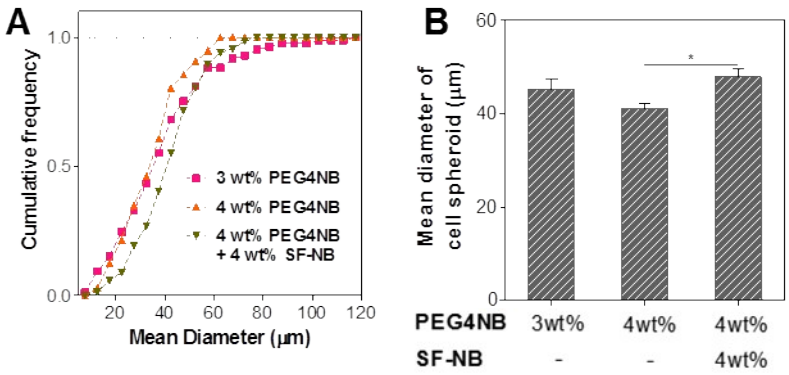

Fig. S8. (A) Cumulative frequencies of diameters and (B) mean diameters of A549 cell clusters in hydrogels 11-day post-encapsulation (n = 150, mean ± SEM).