Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information for

Mechanical Reinforcement of C_2-Phenyl-Derived Hydrogels for Controlled Cell Adhesion

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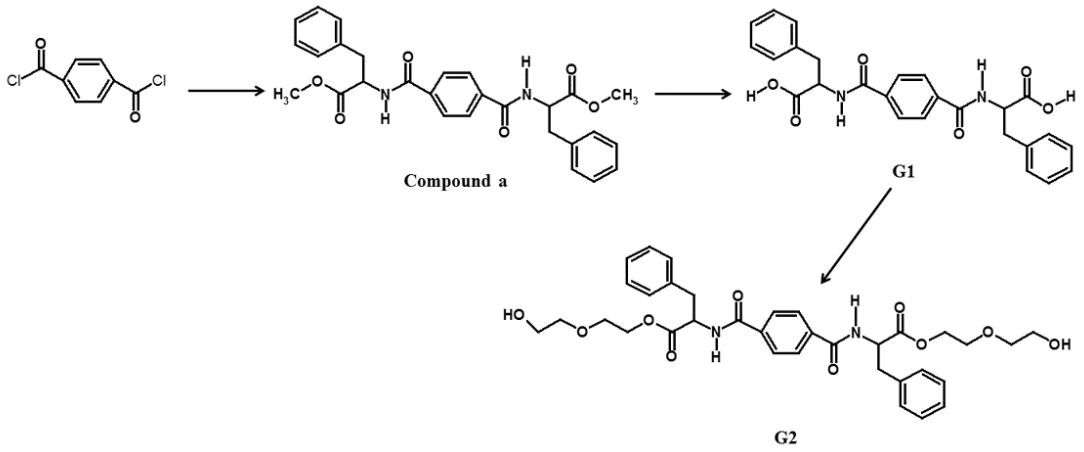
1. Gelator synthetize

Material: L-phenylalanine methylester hydrochloride, 1, 4-benzenedicarbonyl dichloride, diglycol and Sodium Alginate were purchased from Aladdin Chemicals.
Gelators G1 and G2 Synthesis: Gelators G1, G2 were synthesized with high yields through conventional liquid phase reaction in three steps according to Scheme S-1.



Scheme S-1. Synthetic route of gelators G1 and G2.

1, 4-benzenedicarbonyl dichloride (2.60 g, 13 mmol) in dry dichloromethane (DCM) (20 ml) was added dropwise to a solution of L-phenylalanine methyl ester hydrochloride (6.00 g, 26.1 mmol) and Et3N (8 ml, 58.3 mmol) in dry DCM (100 ml, T=0 ℃). The solution was stirred at room temperature for 24 h. All the solvents were evaporated upon vacuum, and the residue was subsequently dissolved in ethanol (100 ml). After filtration, undissolved substance was collected and dried to give compound *a* as demonstrated in Figure S-1a (5.31 g, 10.9 mmol, 84%). For the hydrolysis, aqueous NaOH (10 ml, 2 M) was added to a cooled (0 ℃) suspension of compound *a* (3.00 g, 6.14 mmol) in MeOH (20 ml). The mixture was slowly brought back to room temperature and stirred for 24 h, and a clear solution was obtained. The solution was then acidified with 3M HCl to pH < 3, and a gel-like precipitate formed. The gel phase was filtered, washed with deionized water and finally dried in the vacuum oven to give Gelator G1 shown in Figure S-1b (2.57 g, 5.59 mmol, 91%).

Overall yield of Gelator G1: 76.44%; 1H NMR (400 MHz, DMSO-d6, δ): δ=3.2 (d, 4H, CH2), 4.6 (s, 2H, CH), 7.3 (q, 10H, Ar H), 7.8 (s, 4H, Ar H), 8.8 (d, 2H, NH), 12.8 (s, 2H, OH) ppm; EI-MS for C26H24O6N2 calcd. 460.49; found 460.17 [M+]

Gelator G1 (2.80 g, 6.1 mmol) was dissolved in diglycol (80 ml). Three or four drops of concentrated HCl were then added into the solution. The mixture solution was stirred at 145 ℃ for 3.5 hours until it became clear. The clear solution was dropped into a water/ice mixture (350 ml) and a gel-like precipitate formed. After collecting the gel by using a filter, they were subsequently washed by water, dried in a vacuum oven for overnight to give G2 shown in Figure S-1c (3.00 g, 4.72 mmol, 77.3%).

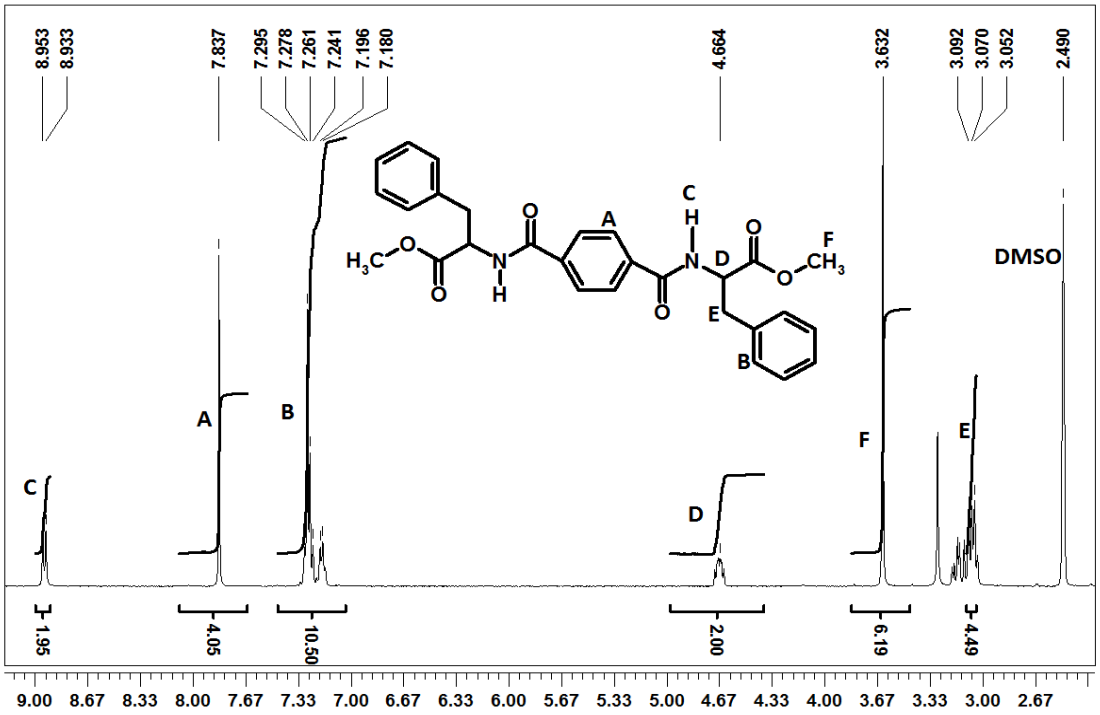
Overall yield of gelator G2: 59.1%; ^{1}H NMR (400 MHz, DMSO-d6, δ): δ=3.1 (m, 4H, CH2), 3.4 (m, 12H, CH2), 4.2(q, 4H, CH2), 4.7 (q, 2H, OH), 7.3 (m, 10H, Ar H),

7.8 (s, 4H, Ar H), 8.9 (d, 2H, NH) ppm; EI-MS for C34H40O10N2 calcd. 636.71; found 637.28 [M+H]+

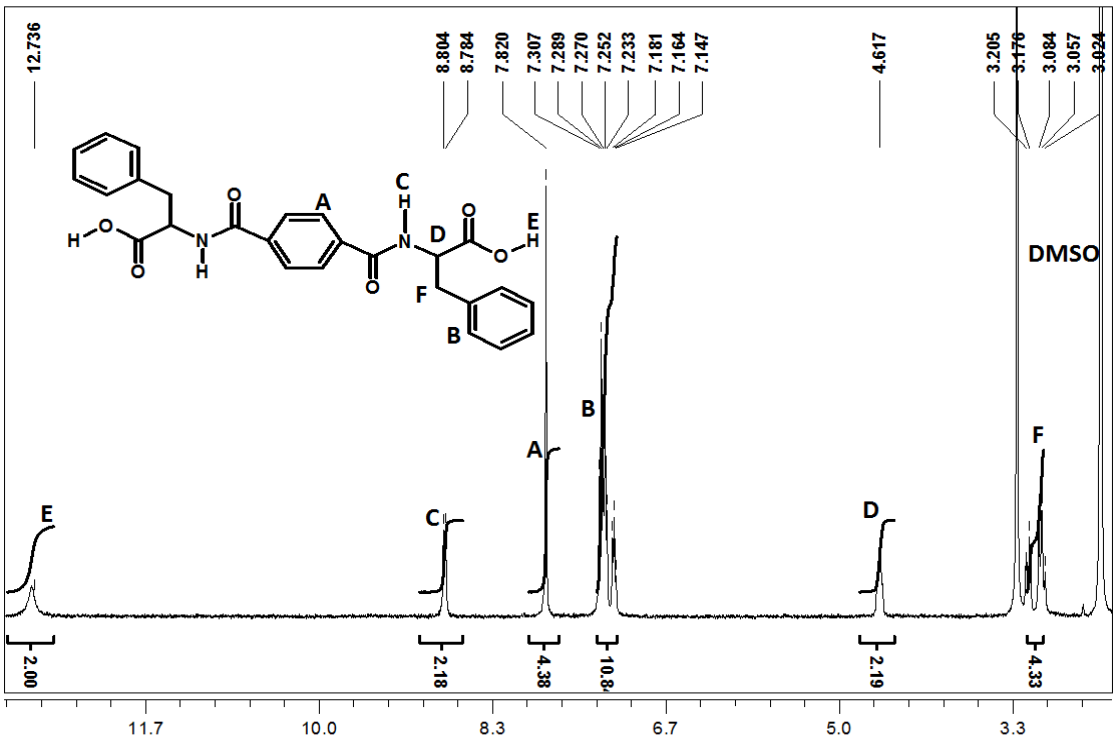
Mass experiments: Mass spectra were recorded on a Waters Q-Tof Mass Instrument by positive mode electrospray ionization. Methanol was used as the solvent.

2. ^{1}H NMR and Mass spectra of the compounds

(a)



(b)



(c)

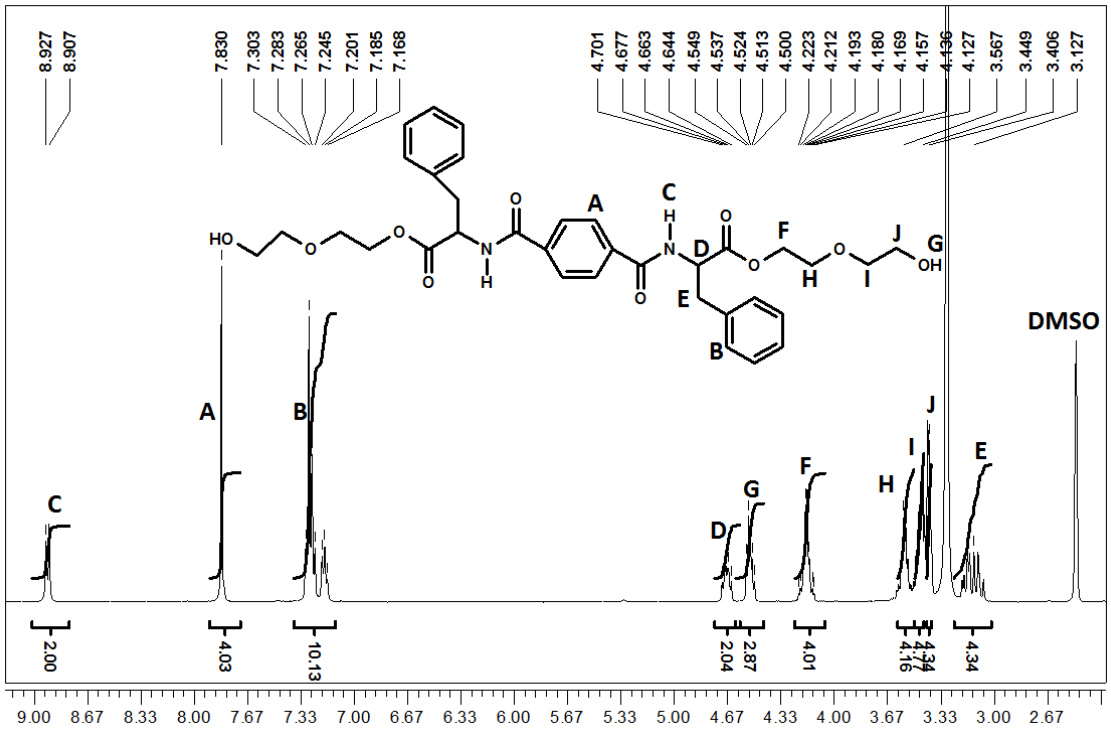
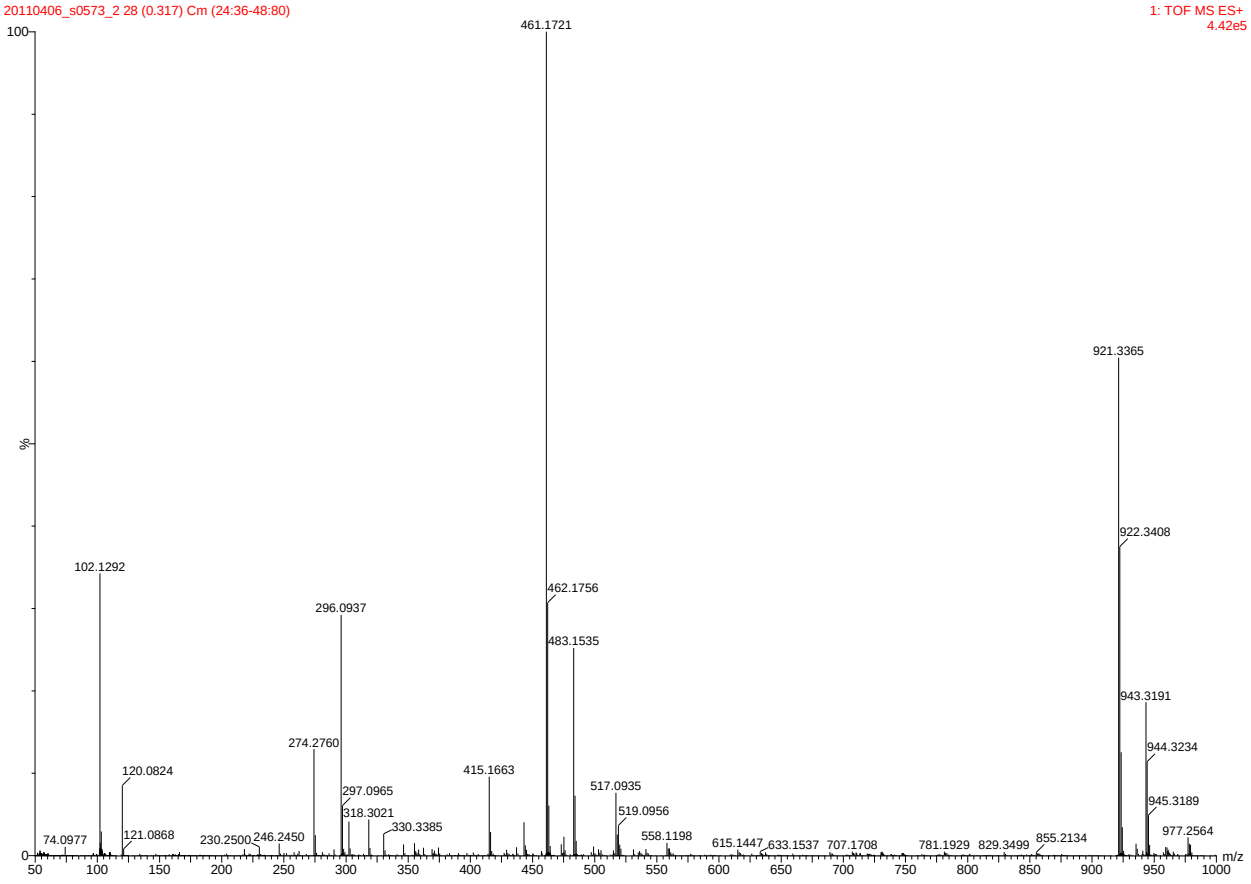


Fig. S-1 ^{1}H-NMR spectra of (a) compound *a*, (b) gelator G1 and (c) gelator G2.

(a)



(b)

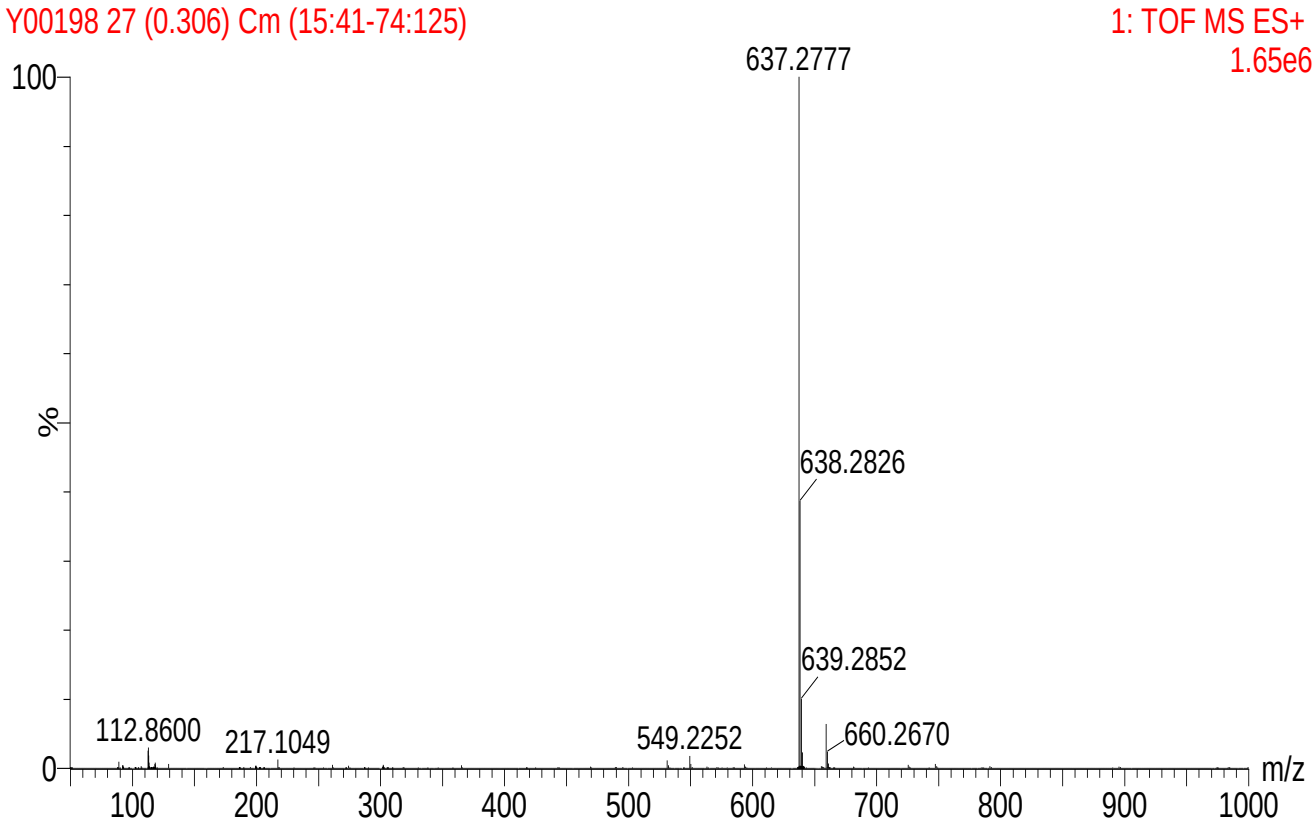


Fig. S-2 Mass spectra of (a) gelator G1, (b) gelator G2.

3. Stability of G1 and G2 hydrogels

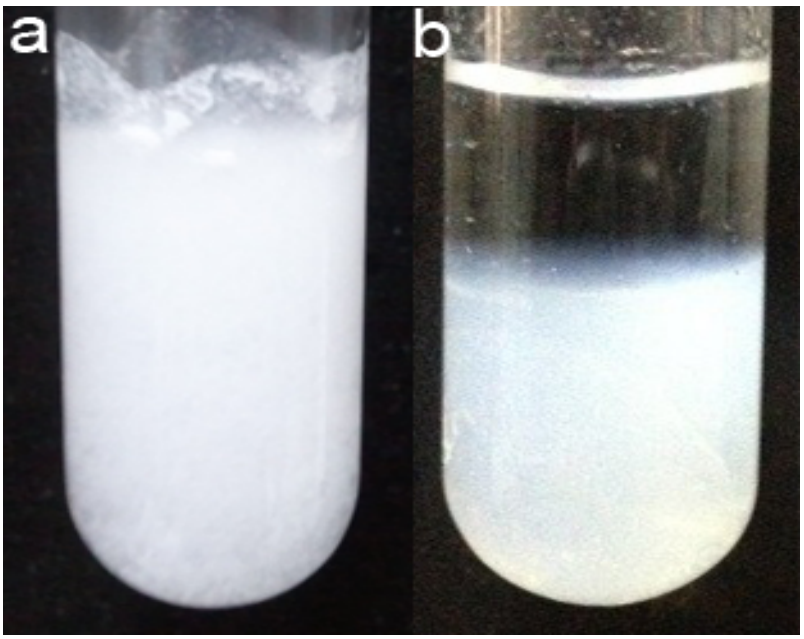


Fig. S-3 Photograph of (a) G1 hydrogels immersed in PBS after 2 hours and (b)G2 hydrogels immersed in PBS after 28 days .

4. Photographs of G2-SA-Ca hydrogels

Fig. S-4 Photograph of G2-SA-Ca hydrogels.

5. X-ray powder diffraction (XRD) spectrum for G2-SA gels

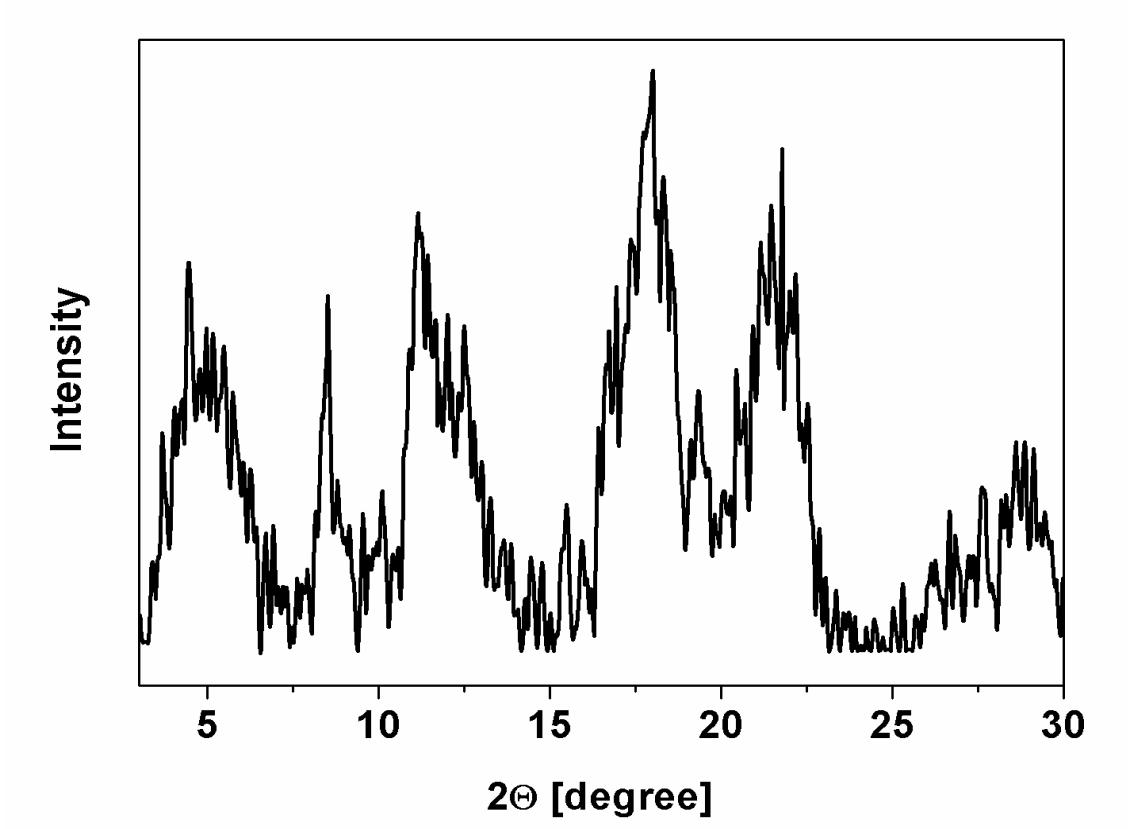


Fig. S-5 XRD spectrum of G2-SA hydrogels.

6. Fourier transform infrared (FT-IR) spectrum for G2-SA gels

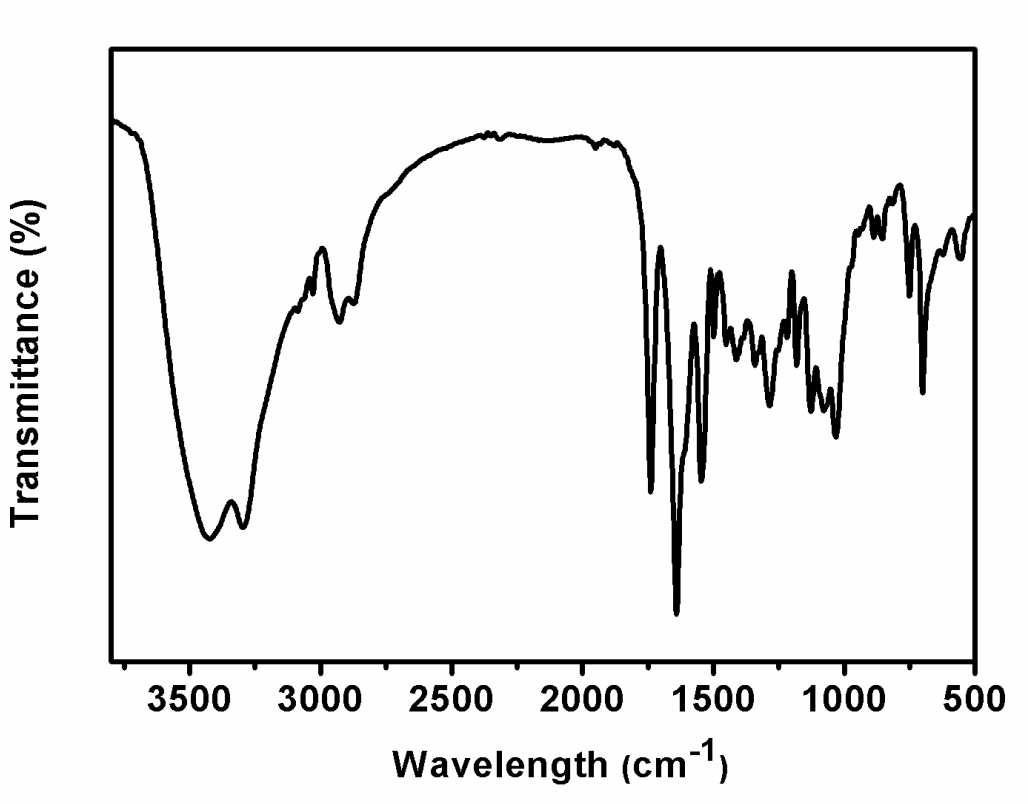


Fig. S-6 FT-IR spectrum of G2-SA hydrogels.

7. Circular dichrosim (CD) spectra

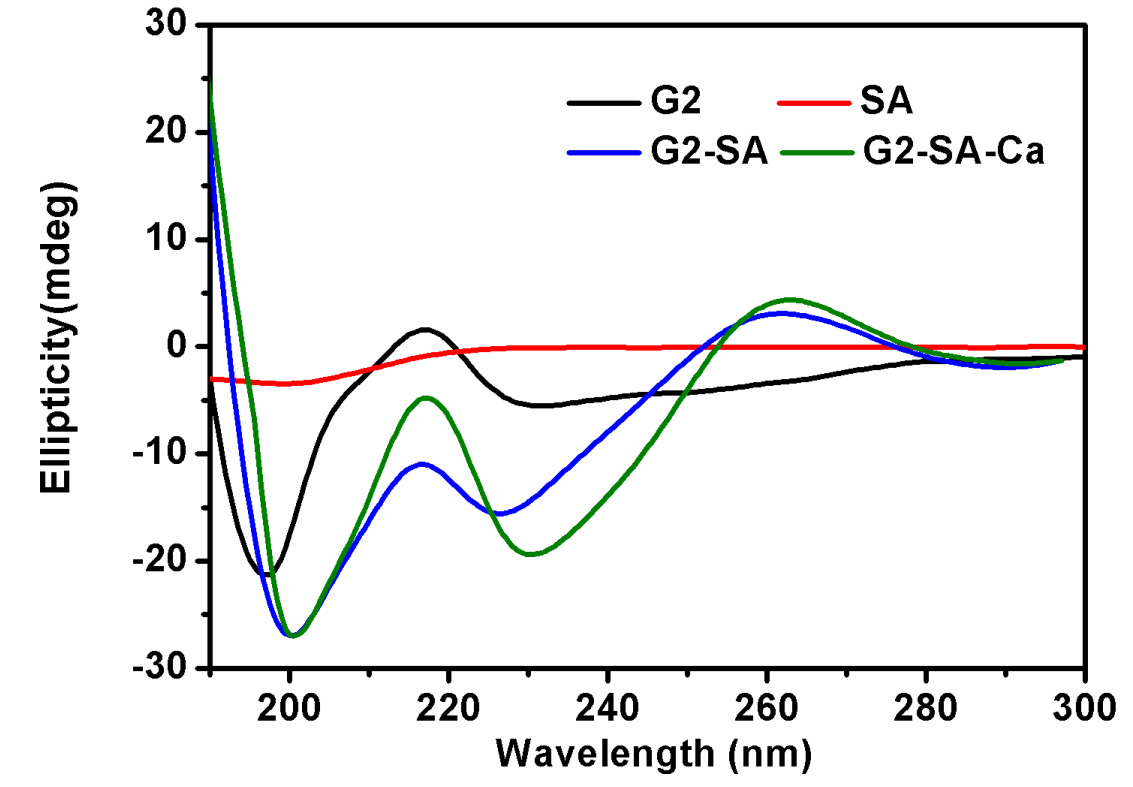
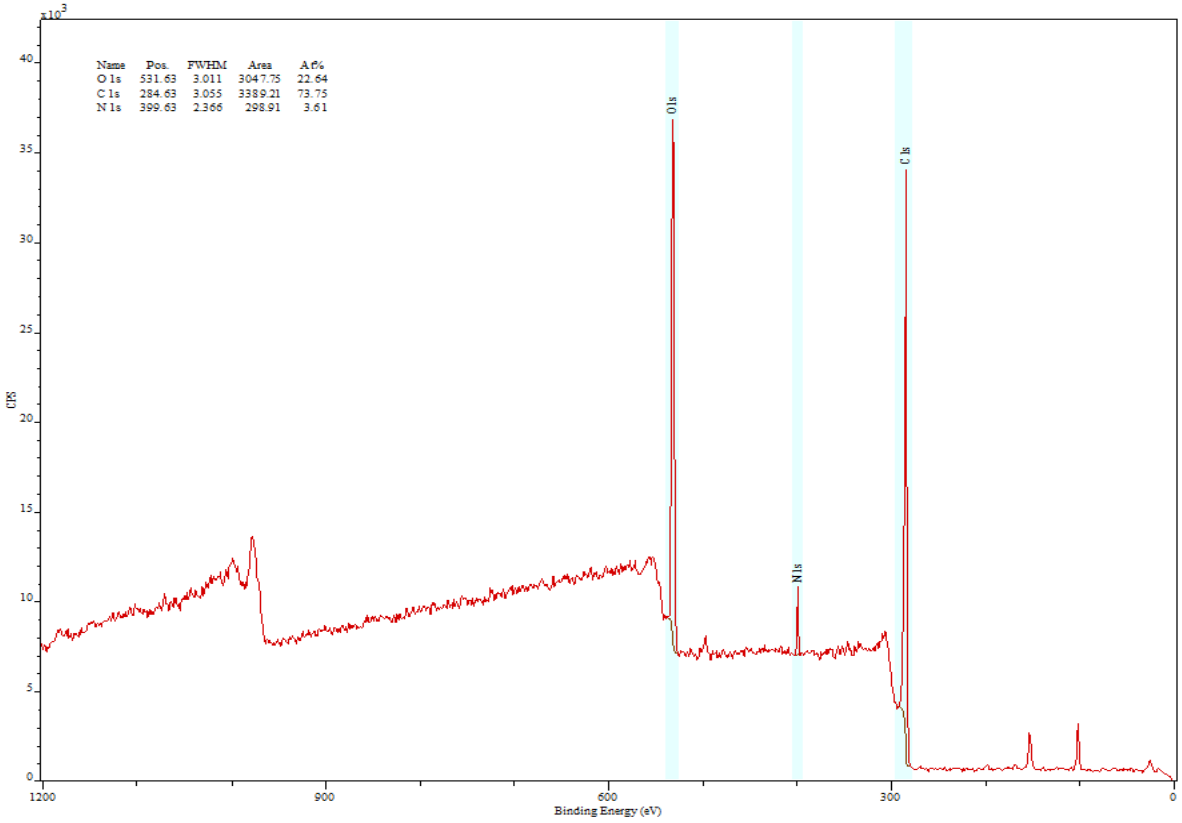


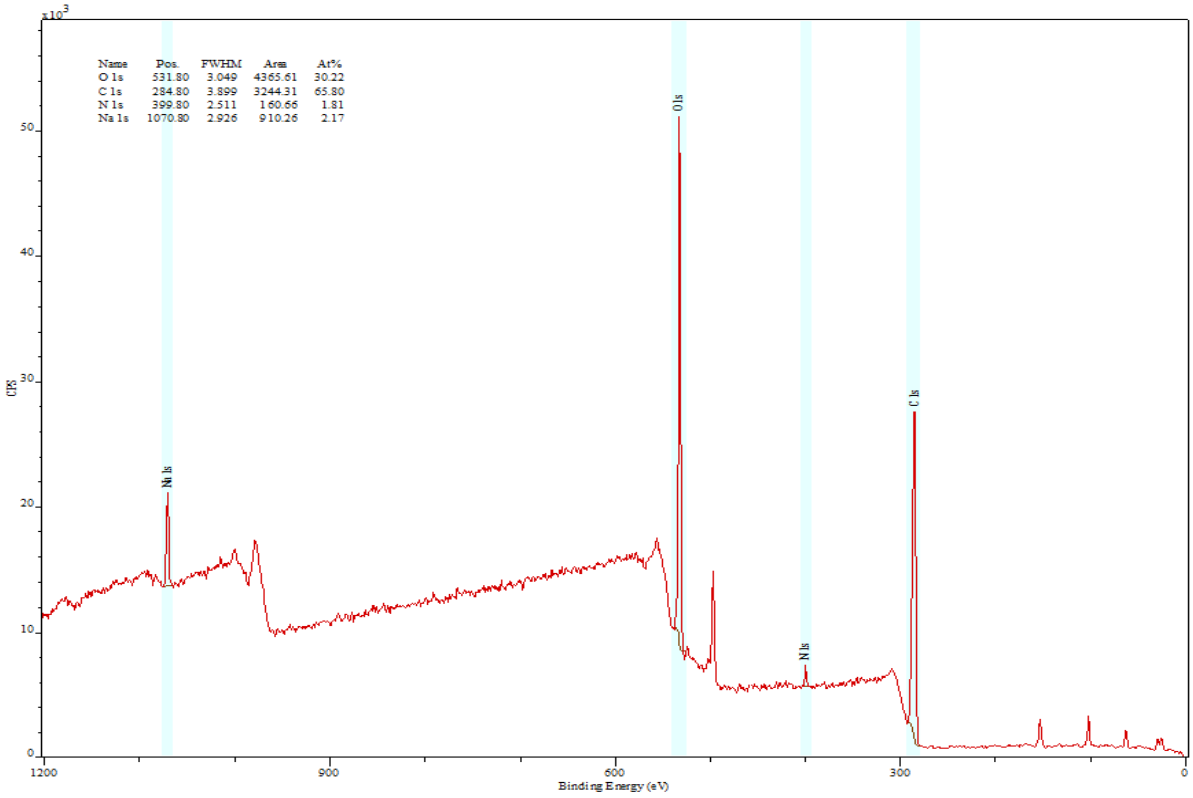
Fig. S-7 CD spectra of G2, SA, G2-SA and G2-SA-Ca diluted hydrogels.

8. X-ray photoelectron spectroscopy

(a)



(b)



(c)

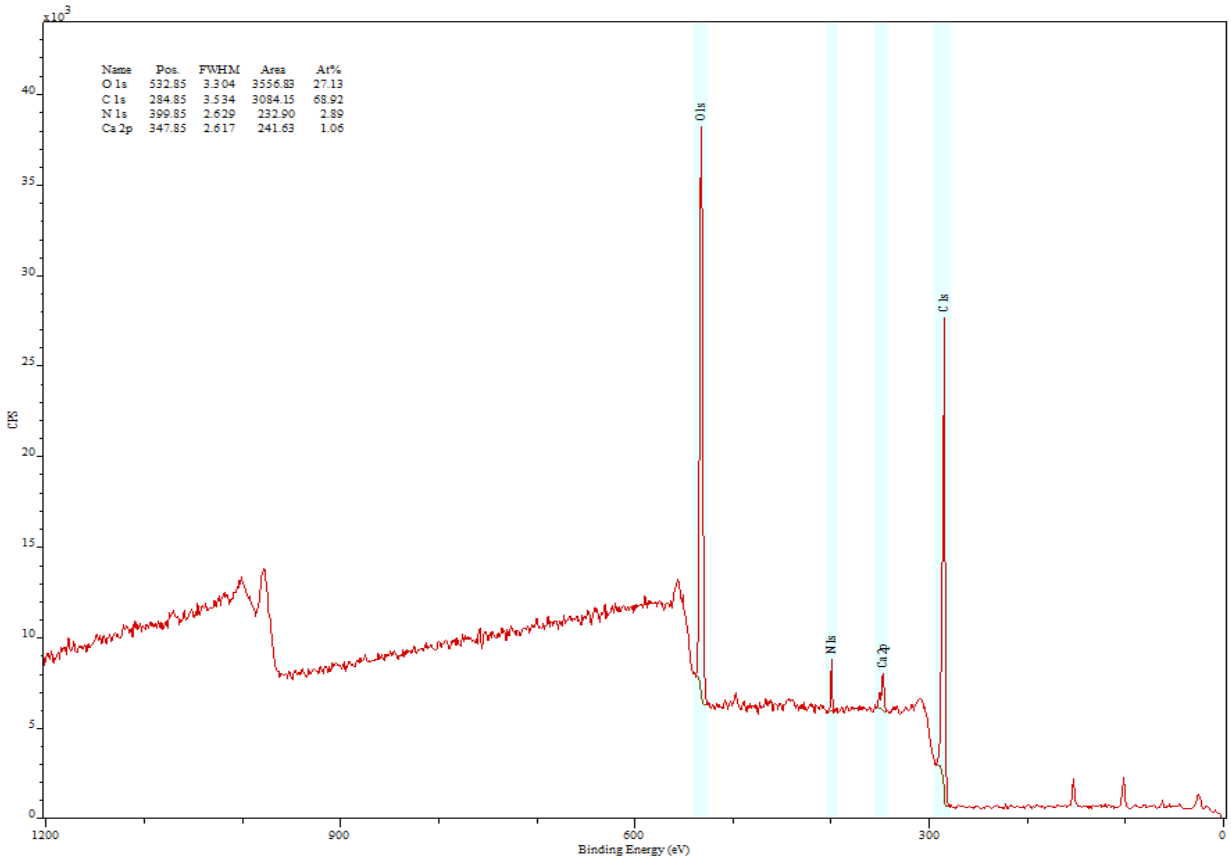


Fig. S-8 XPS of (a) G2, (b) G2-SA and (c) G2-SA-Ca gels.

9. Contact angles

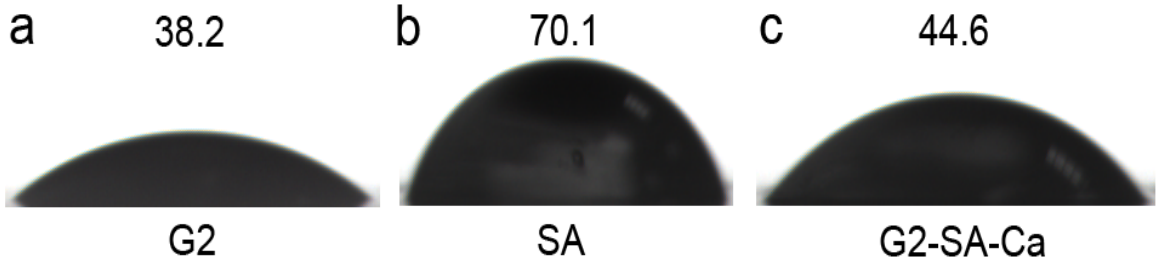


Fig. S-9 Contact angles of (a) G2, (b) SA and (c) G2-SA-Ca xerogels.

10. Rheology data of hydrogels

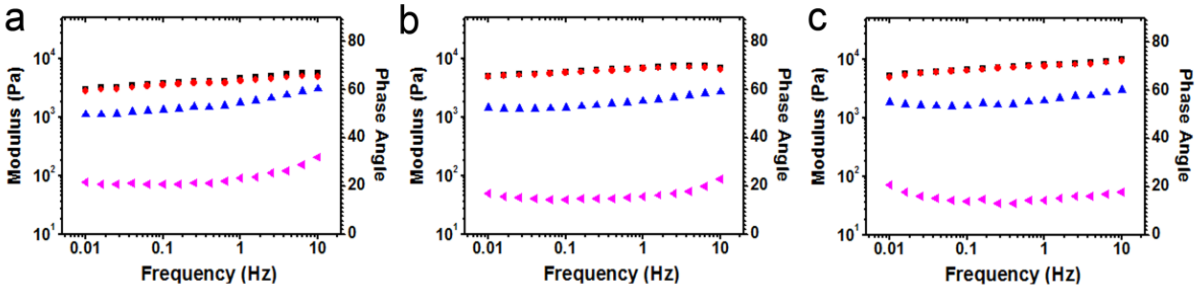


Fig. S-10 Complex modulus (■), elastic modulus (●), viscous modulus (▲) and phase angle (◀) of pure G2 hydrogels with (a) 2 mg/ml, (b) 3 mg/ml and (c) 6 mg/ml G2.

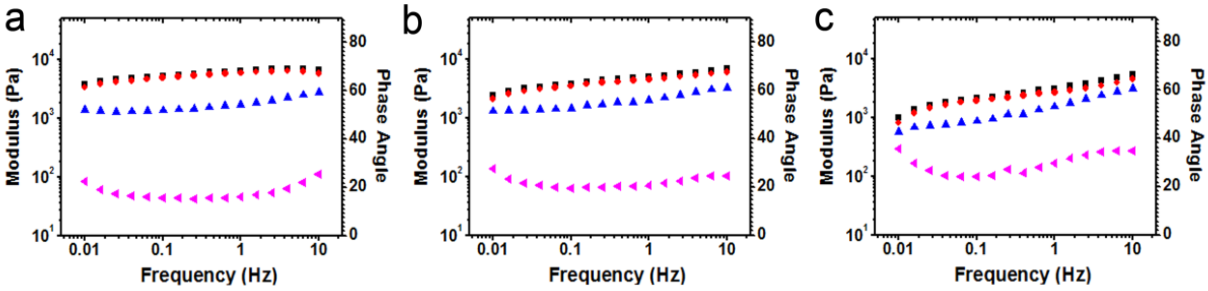


Fig. S-11 Complex modulus (■), elastic modulus (●), viscous modulus (▲) and phase angle (◀) of G2-SA hydrogels with 3mg/ml G2 and (a) 0.5 wt%, (b) 1 wt% and (c) 2 wt% SA.

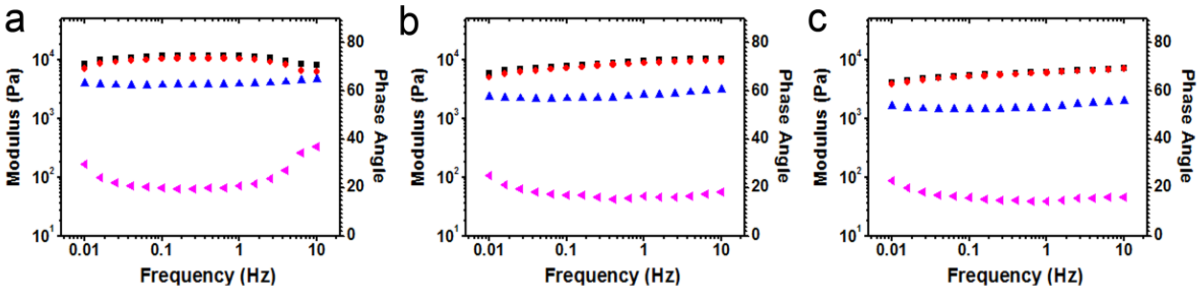


Fig. S-12 Complex modulus (■), elastic modulus (●), viscous modulus (▲) and phase angle (◀) of G2-SA-Ca hydrogels with 3mg/ml G2, 0.01 M calcium ion and (a) 0.5 wt%, (b) 1 wt% and (c) 2 wt% SA.

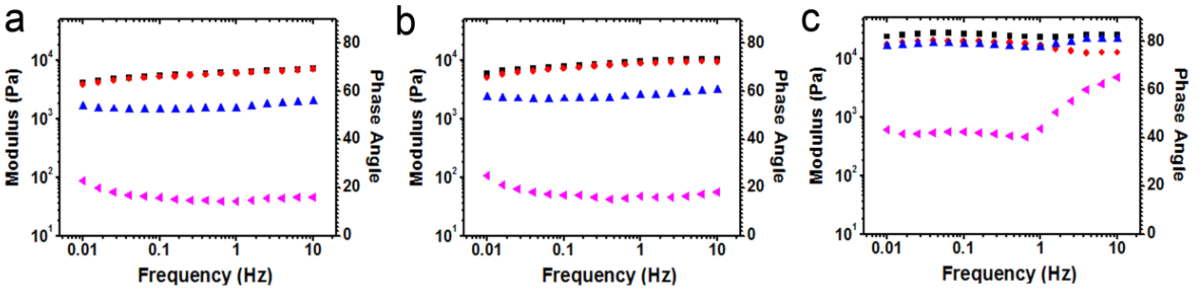


Fig. S-13 Complex modulus (■), elastic modulus (●), viscous modulus (▲) and phase angle (◀) of G2-SA-Ca hydrogels with 3mg/ml G2, 1 wt% SA and (a) 0.005

M (b) 0.01 M and (c) 0.02 M calcium ion.

11. Gel stablility

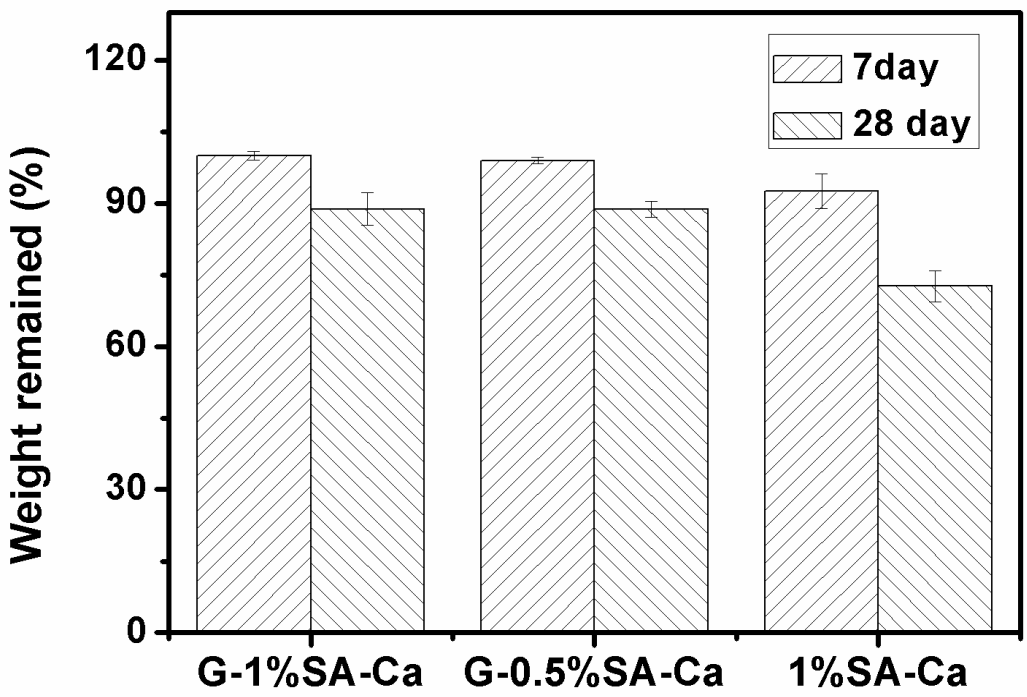


Fig. S-14 Weight remaining of G2-SA-Ca and SA-Ca hydrogels under PBS after 7, 28 days.

12. Live/ Dead cell counting

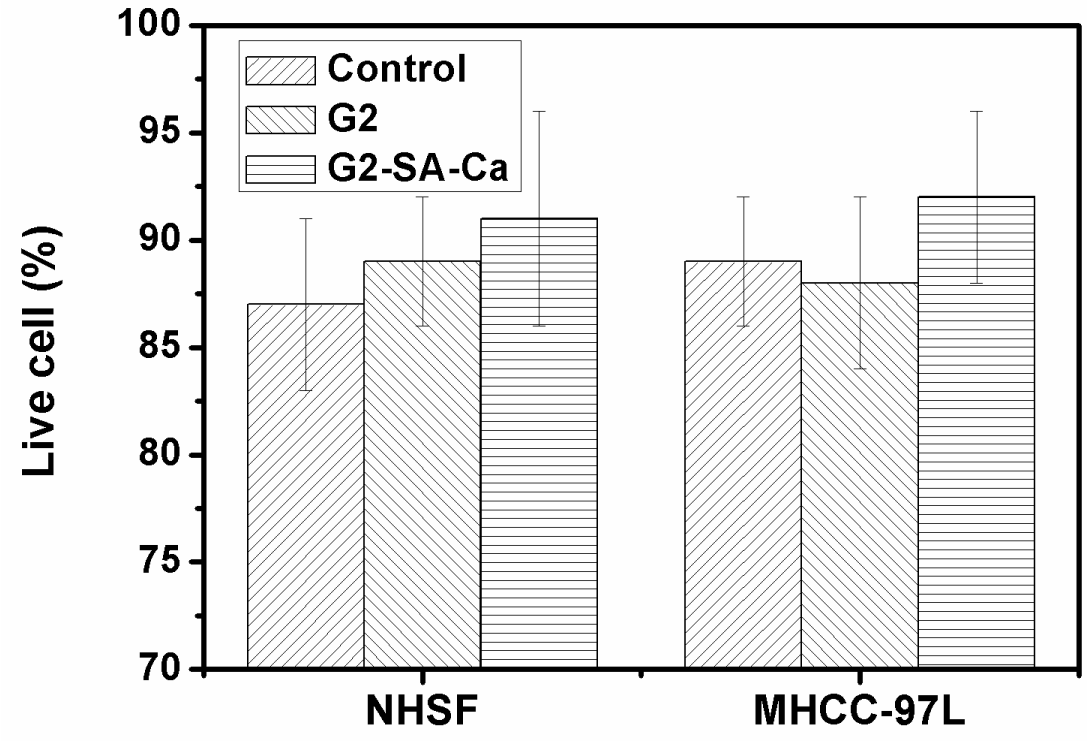


Fig. S-15 Normalized live cell percentages of cultured NHSF and MHCC-97L on

control, G2 and G2-SA-Ca hydrogels.