

**A Comprehensive Study on Rheological Properties of Photocrosslinkable Gallol-Metal
Complexed Hyaluronic Acid-Based Biomaterial Inks**

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1. Synthesis of hyaluronic acid methacrylate

The hyaluronic acid methacrylate (HAMA) was synthesised, as shown in Figure S-1. Briefly, 400 mg of sodium hyaluronate was dissolved in 100 mL of deionised water, and the pH was adjusted to 9. Methacrylic anhydride (MA, 750 μ L) was added dropwise, and the reaction was carried out for 7 hours at 4 $^{\circ}$ C with pH \sim 8. The mixture was dialysed against deionised water for 72 hours using a lyophilised 3.5 kDa molecular weight cut-off (MWCO) membrane to obtain the pure product. The degree of modification of methacrylation was quantified by 1 H NMR at room temperature. The conjugation of the methacrylate group on hyaluronic acid (HA) was confirmed by the presence of distinctive olefinic peaks at 6.13 and 5.70 ppm against the methyl peak of the N-acetyl of HA at 1.95 ppm in the 1 H NMR spectrum. The degree of modification was ascertained to be 30 mol% with respect to the repeated disaccharide units of HA.

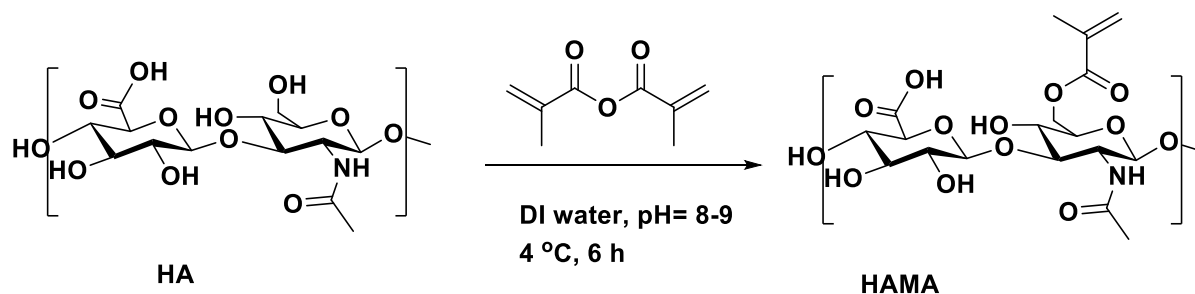


Figure S-1: Synthesis of hyaluronic acid methacrylate (HAMA).

2. Synthesis of hydrazone derivative of gallic acid

The hydrazone derivative of gallic acid (GH) was synthesised in two steps, as shown in Figure S-2. Briefly, 4 g of gallic acid was dissolved in 100 mL of methanol in a 250 mL flask. 12 drops of sulfuric acid were added, and the mixture was refluxed for 8 hours. After cooling to RT, methanol was removed using a rotary evaporator under reduced pressure. The remaining product was extracted with ethyl acetate, dried with anhydrous Na₂SO₄, and dried with a rotary

evaporator. The GA methyl ester intermediate was dissolved in 60 mL of methanol with 2 drops of triethanolamine (TEA). Then, 2 mL of 80% hydrazine monohydrate was added, and the mixture was stirred for 48 hours at RT. The resulting white solid product was filtered twice with methanol and water. The GH was characterised by ^1H and ^{13}C NMR spectroscopy (Figure S-4 to Figure S-8).

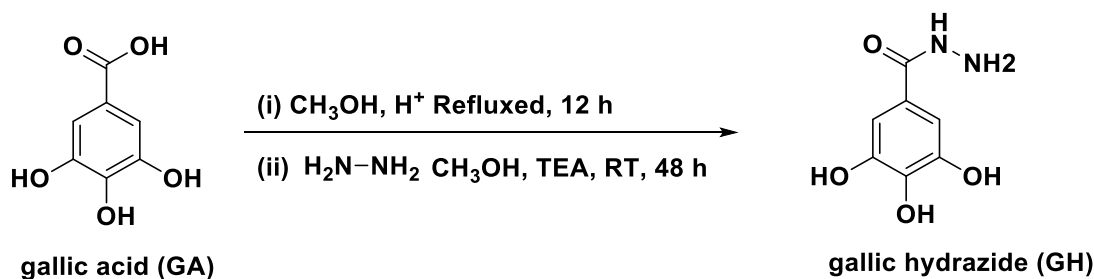


Figure S-2: Synthesis of gallic hydrazide (GH).

3. Synthesis of gallic acid conjugated hyaluronic acid methacrylate

The GA functionalised HAMA (HAMA-GA) was synthesised, as shown in Figure S-3. The conjugation of GA in the HA was confirmed by the presence of distinctive peaks at 6.99 ppm due to aromatic protons of GH in the ^1H NMR spectrum. The degree of GA modification was ascertained to be 10 mol% with respect to the repeated disaccharide units of HA.

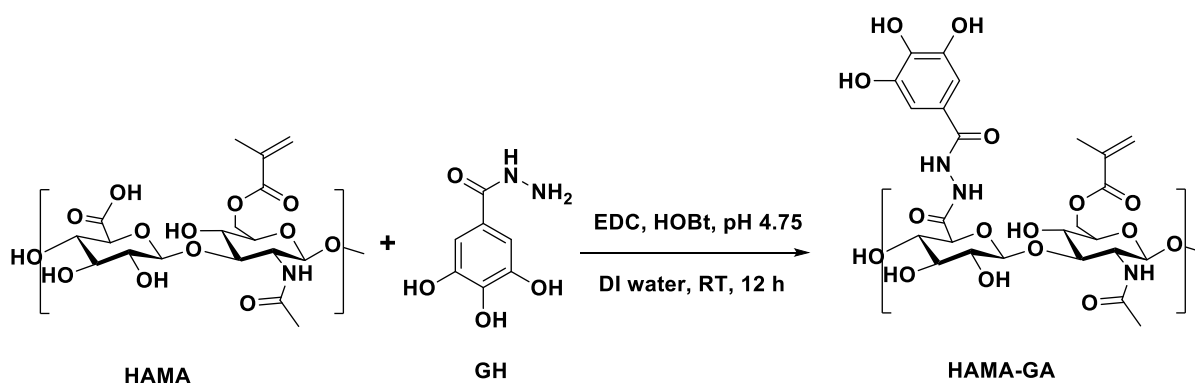


Figure S-3: Conjugation of gallic acid on hyaluronic acid methacrylate (HAMA-GA).

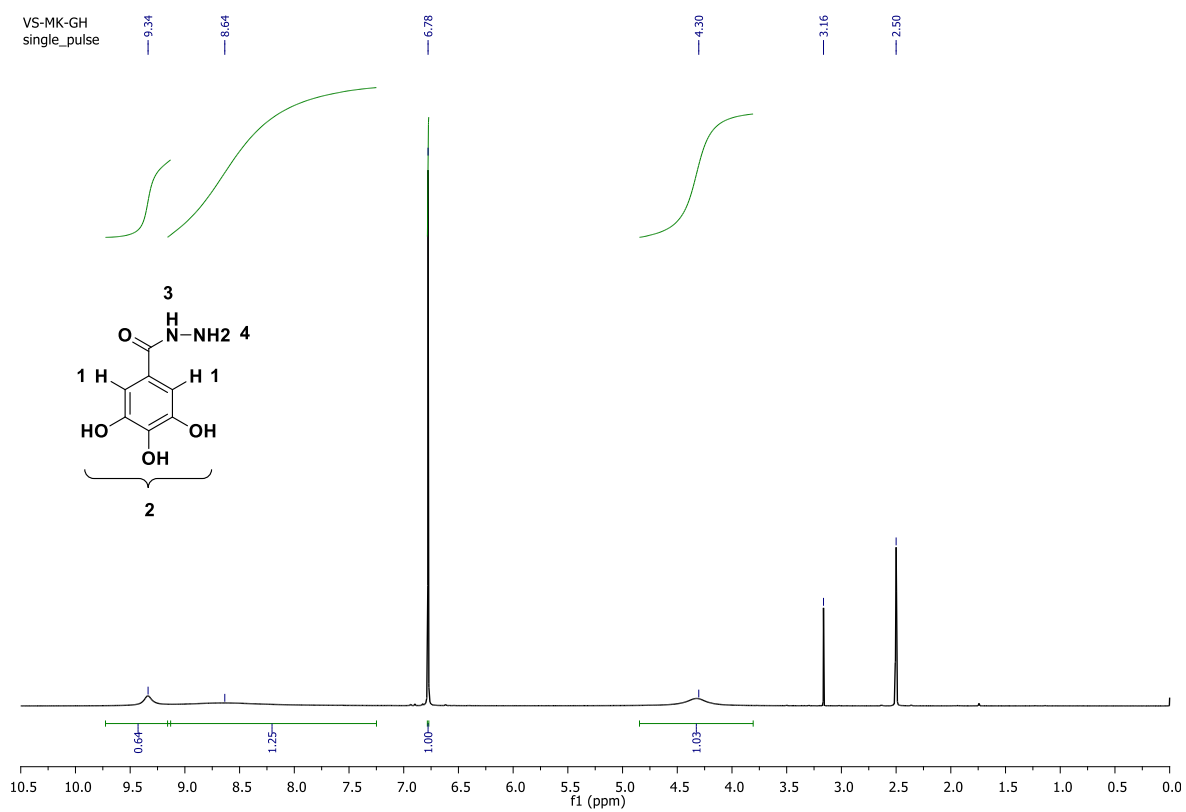


Figure S-4: ^1H -NMR (500 MHz) spectra of gallic hydrazide (GH) recorded in DMSO- d_6 .

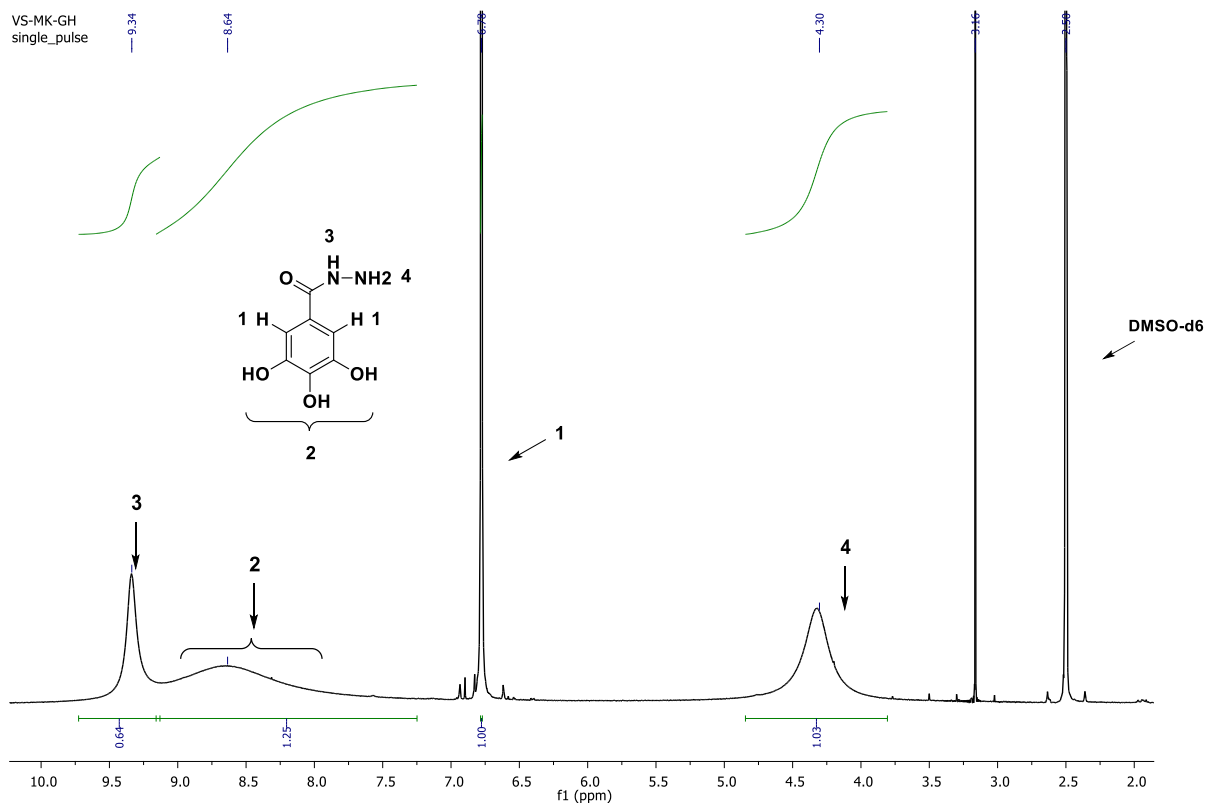


Figure S-5: $^1\text{H-NMR}$ (500 MHz) spectra of gallic hydrazide (GH) in DMSO-d₆. (Expanded)

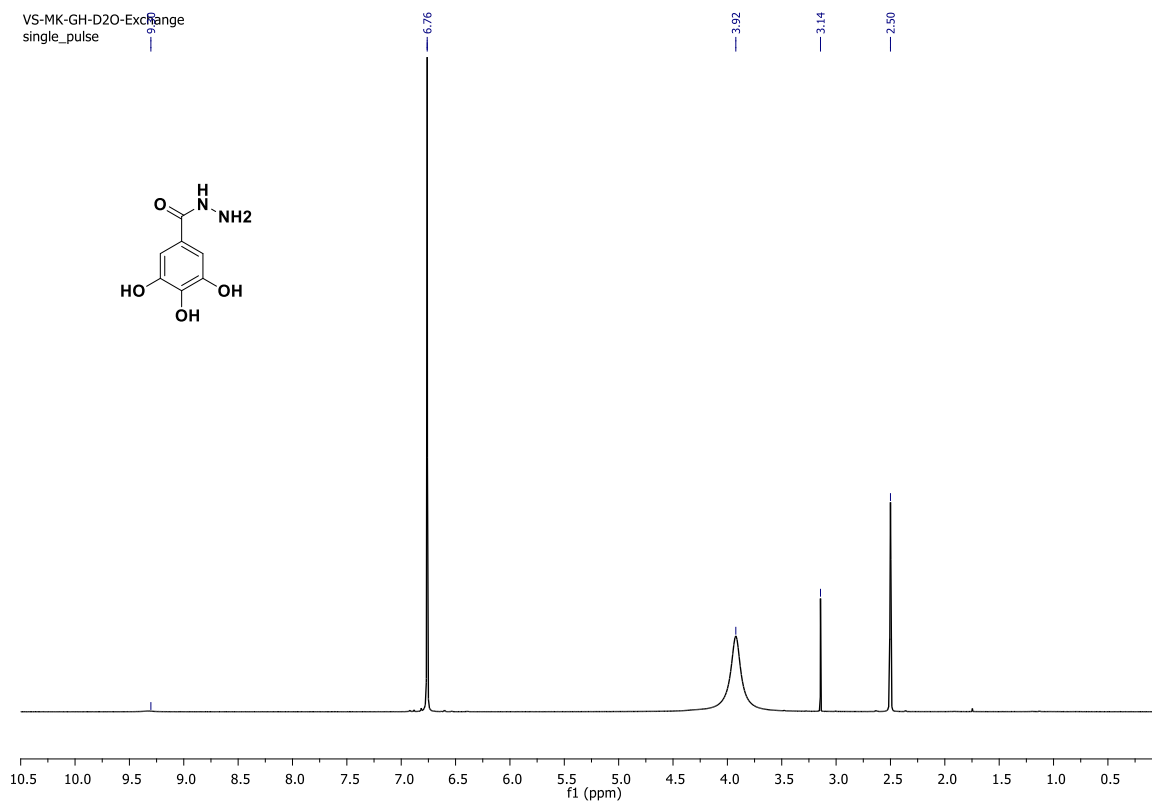


Figure S-6: $^1\text{H-NMR}$ (500 MHz) spectra of GH in DMSO- d_6 : D_2O (7:1), D_2O Exchange.

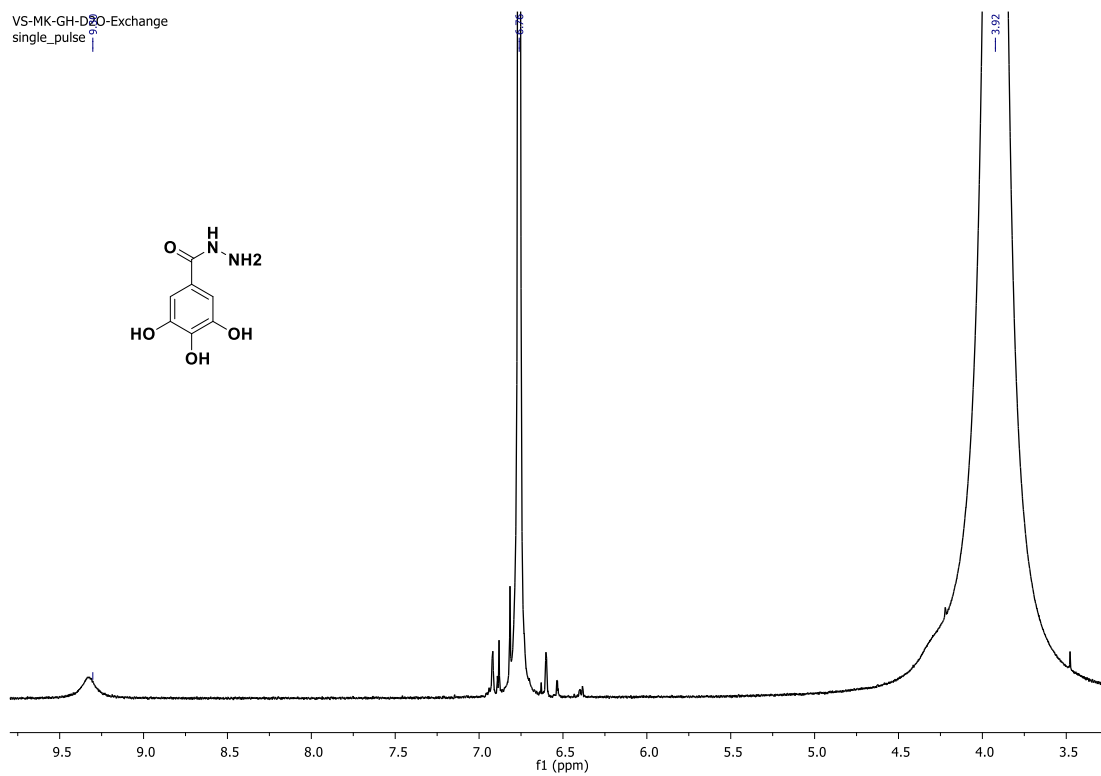


Figure S-7: $^1\text{H-NMR}$ (500 MHz) spectra of GH in DMSO- d_6 : D_2O (7:1), D_2O Exchange.

(Expanded)

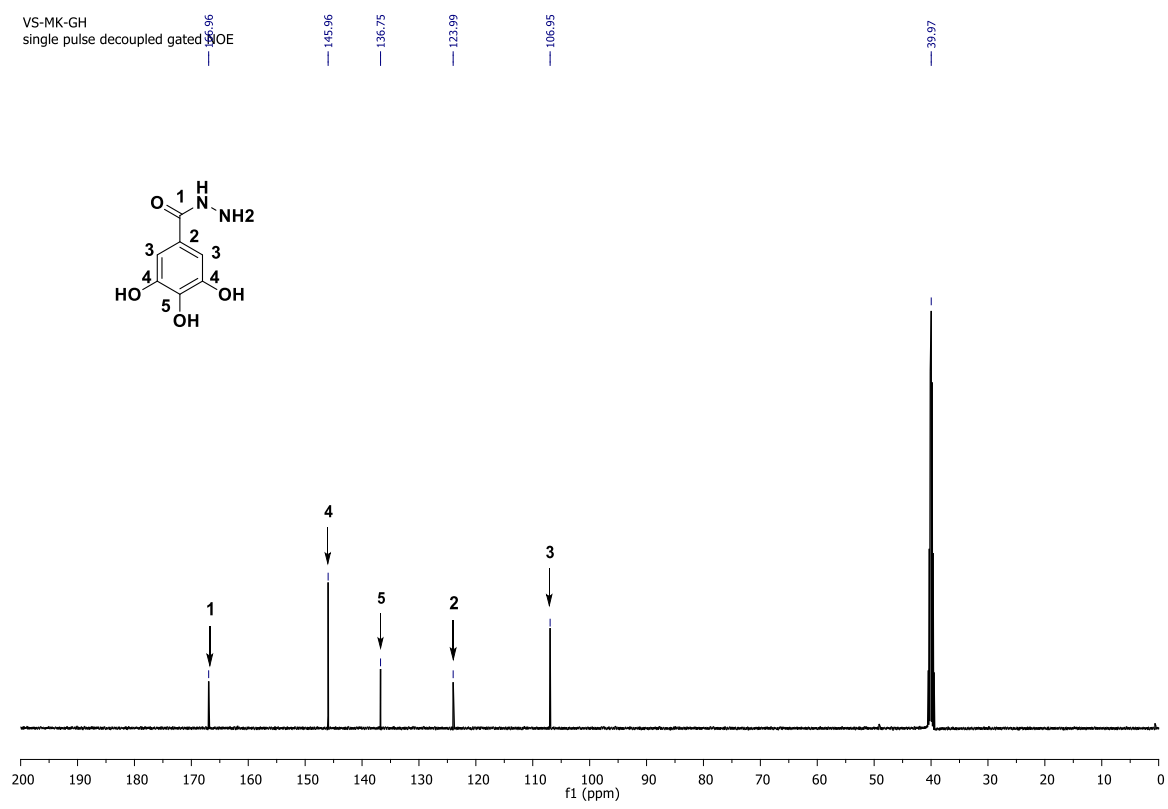


Figure S-8: ^{13}C -NMR (125 MHz) spectra of GH recorded in DMSO- d_6 .

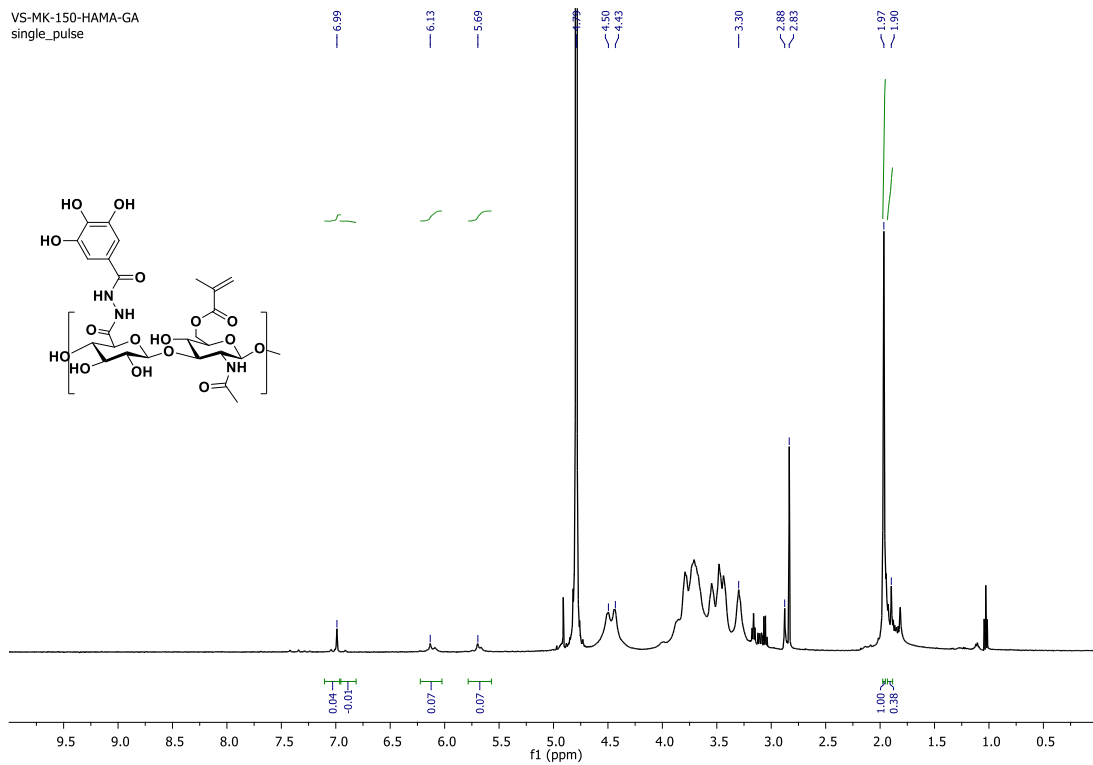


Figure S-9-A: $^1\text{H-NMR}$ (500 MHz, D_2O) spectra of GA-conjugated HAMA (HAMA-GA).

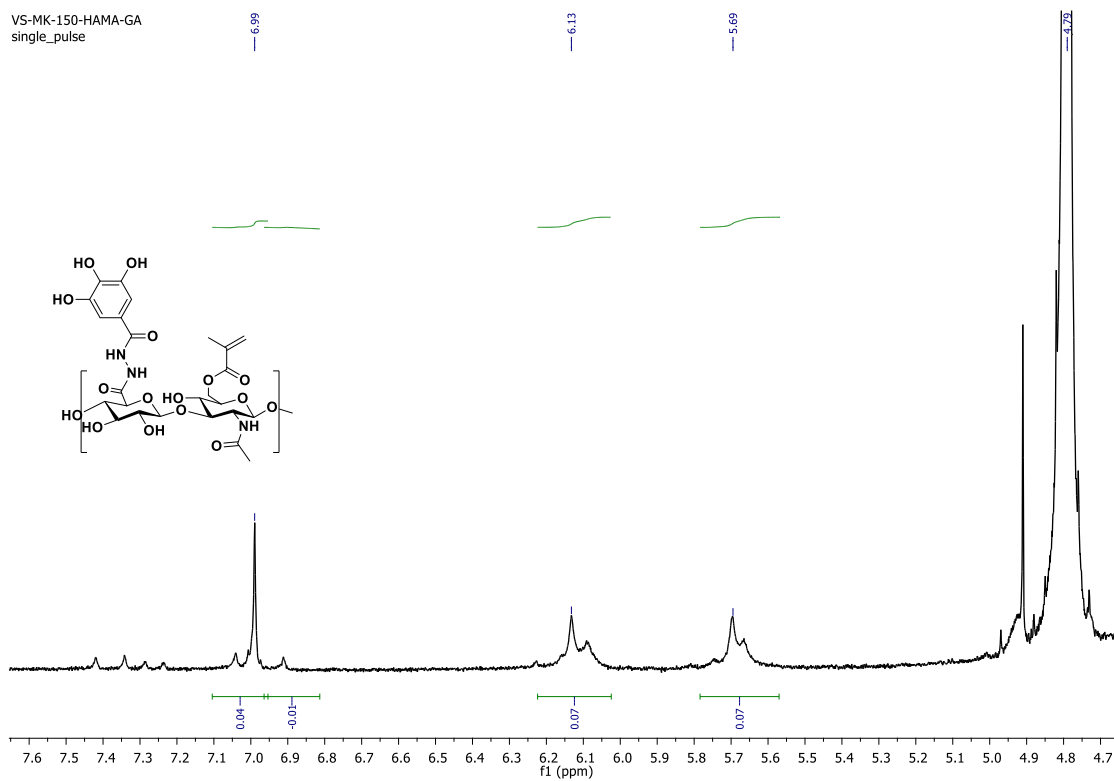


Figure S-9-B: $^1\text{H-NMR}$ (500 MHz, D_2O) spectra of GA conjugated HAMA (HAMA-GA)

Expanded.

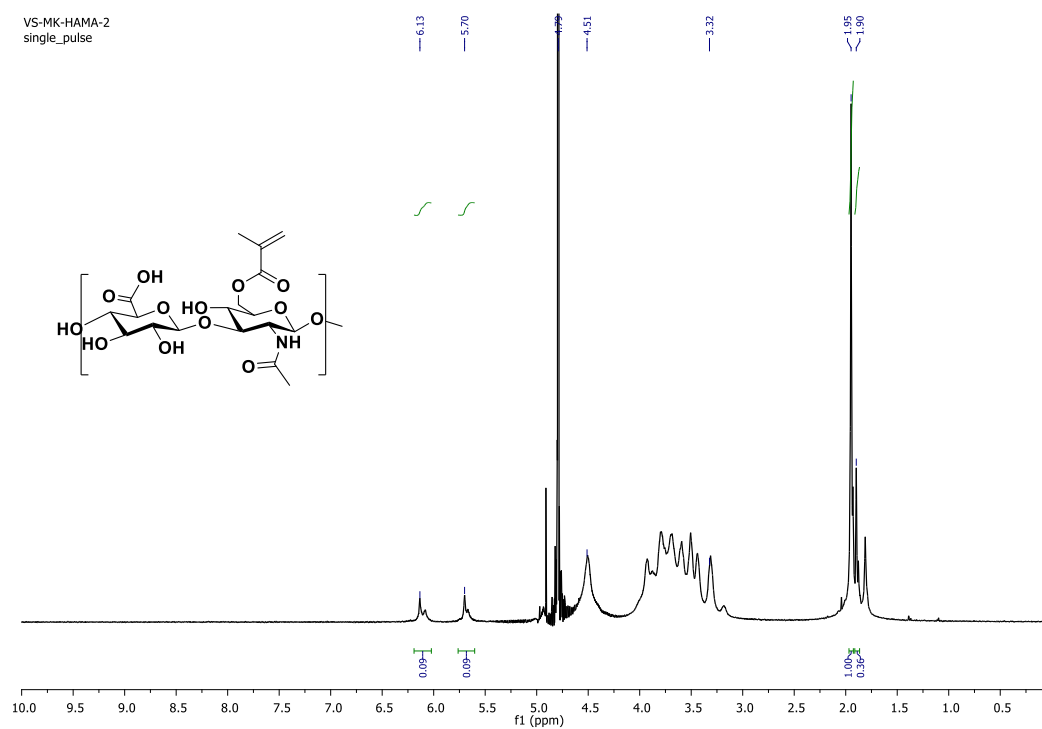


Figure S-10-A: $^1\text{H-NMR}$ (500 MHz, D_2O) spectra of hyaluronic acid methacrylate with 30% degree of modification (HAMA30).

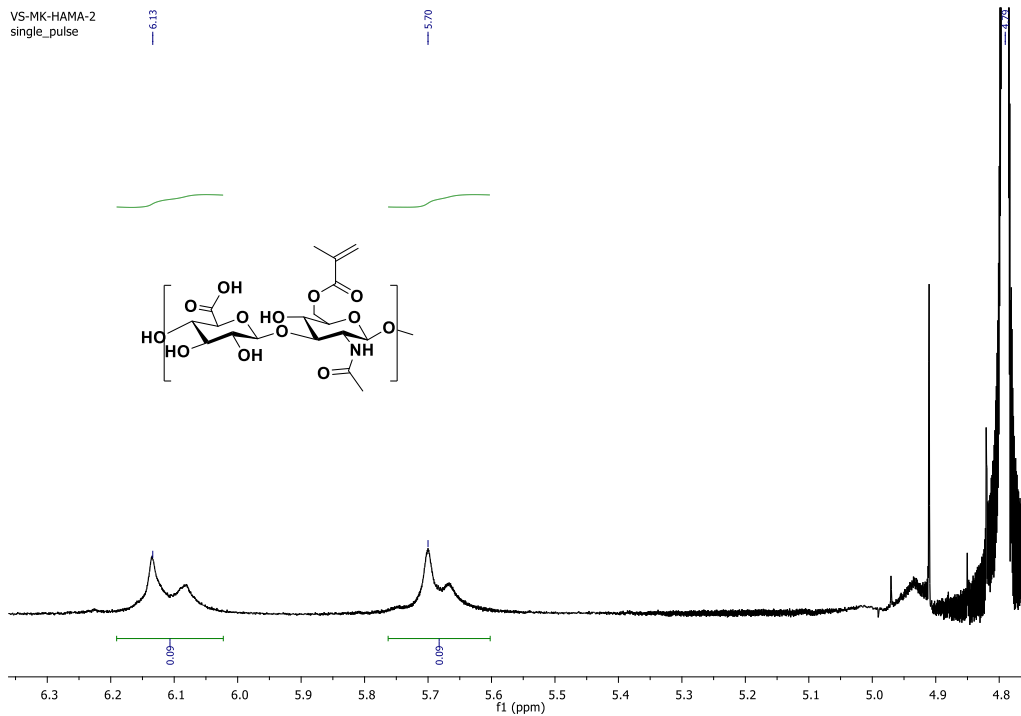


Figure S-10-B: $^1\text{H-NMR}$ (500 MHz, D_2O) spectra of hyaluronic acid methacrylate with 30% degree of modification (HAMA30) expanded.

5% w/v HAMA-GA	FeCl_3 0 %w/v	FeCl_3 0.125 %w/v	FeCl_3 0.25 %w/v	FeCl_3 0.5 %w/v
pH 3-5				
pH 7				
pH >9				

Liquid
 Weak gels
 True gels

Figure S-11: The prescreening of sol-gel phase transition. The tone of the yellow photo frame at 0% w/v of FeCl₃ indicates the level of gelation of hydrogels at each pH level in the absence of FeCl₃; the darker the tone, the more gelled hydrogel.

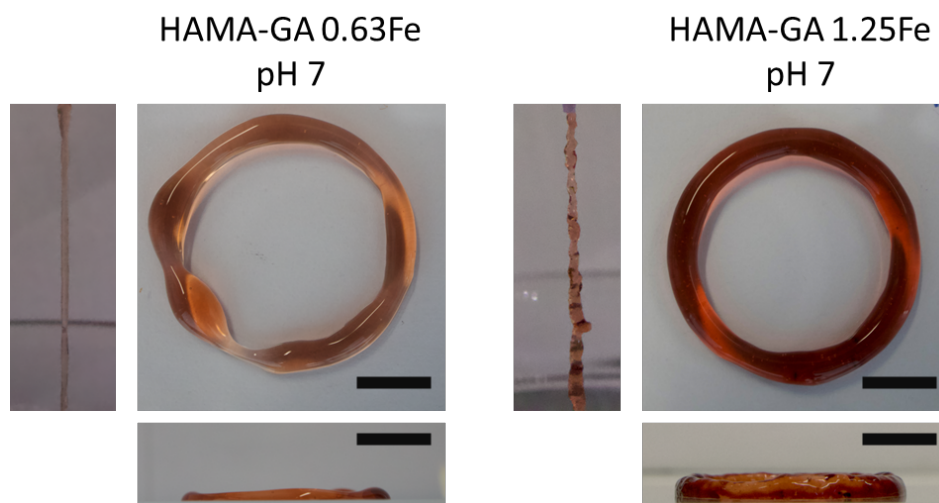


Figure S-12: HAMA-GA 0.63Fe and HAMA-GA 1.25Fe at pH 7 were selected for 3D printing of tubular structures, with a comparison made between single filament printing (in the air) and multi-layer printing in terms of their printability. Scale bar = 5 mm.

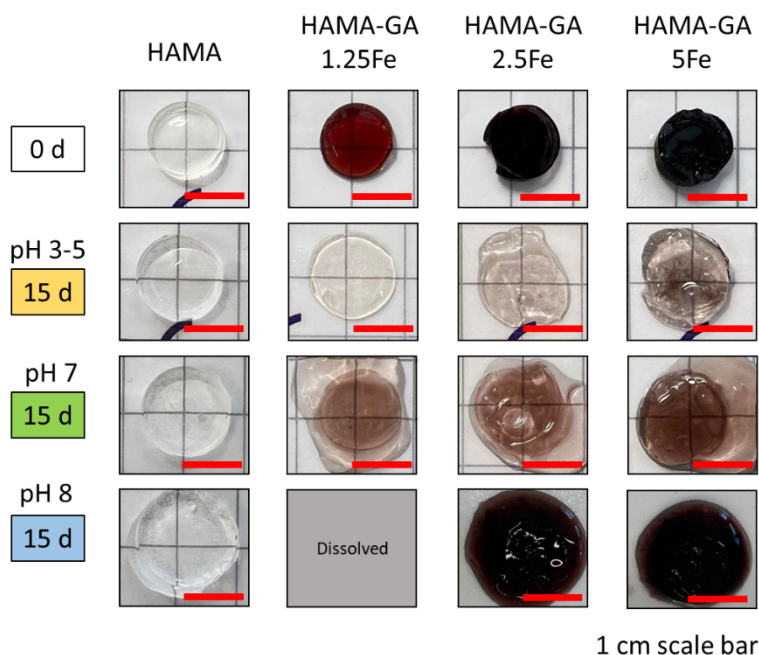


Figure S-13: The change of hydrogel samples (HAMA, HAMA-GA 1.25Fe, HAMA-GA 2.5Fe and HAMA-GA 5Fe) in volume at the zero time point and after 15 days of observation time. Scale bar = 1 cm.

Table S-1. The shear-thinning coefficients of catechol-metal coordination complexes: The pH conditions designate the degree of coordination: pH 3–5 mono, pH 7 bis and pH 8–9 tris.

Sample	Degree of coordination	FeCl ₃ [%w/v]	η_0 [Pa·s]	λ [s]	n	R ²
HAMA-GA	-	0	1.6	0	1	0.98
HAMA-GA 0.63Fe	Bis	0.063	41	0.3	0.2	0.98
HAMA-GA 1.25Fe	Bis	0.125	671	0.54	0.32	0.98
HAMA-GA 2.5Fe	Bis	0.25	2593	0.66	0.15	0.98
HAMA-GA 5Fe	Bis	0.5	2143	0.21	0.34	0.98
HAMA-GA 2.5Fe	Mono	0.25	147	15.85	0.40	0.98
HAMA-GA 2.5Fe	Tris	0.25	5407	0	0.07	0.98