Electronic Supplementary Material (ESI) for Materials Advances.

SUPPORTING INFO

Microwave-assisted methacrylation of chitosan for 3D printable hydrogel in tissue engineering

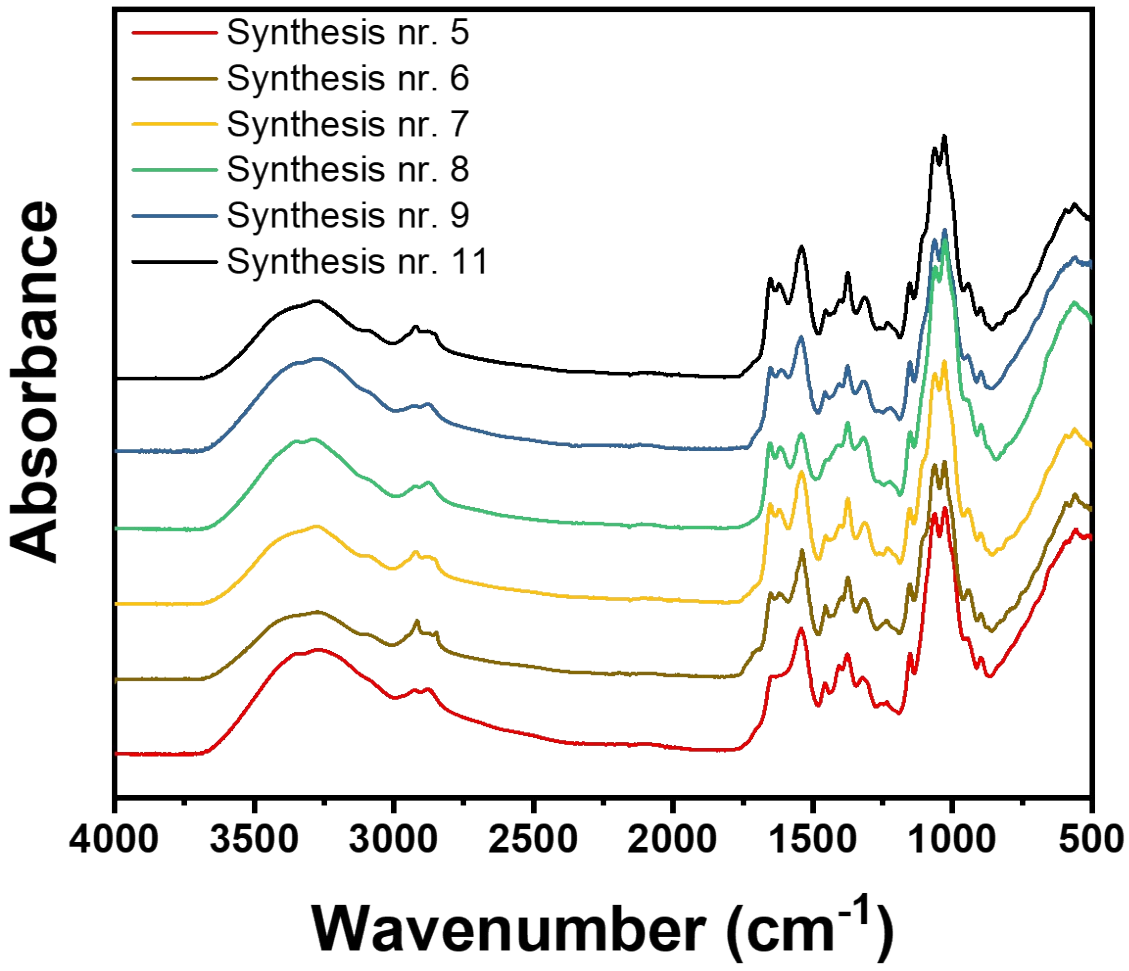
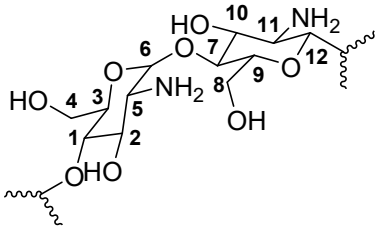


Figure S1: FT-IR of various synthesis

^{1}H-NMR



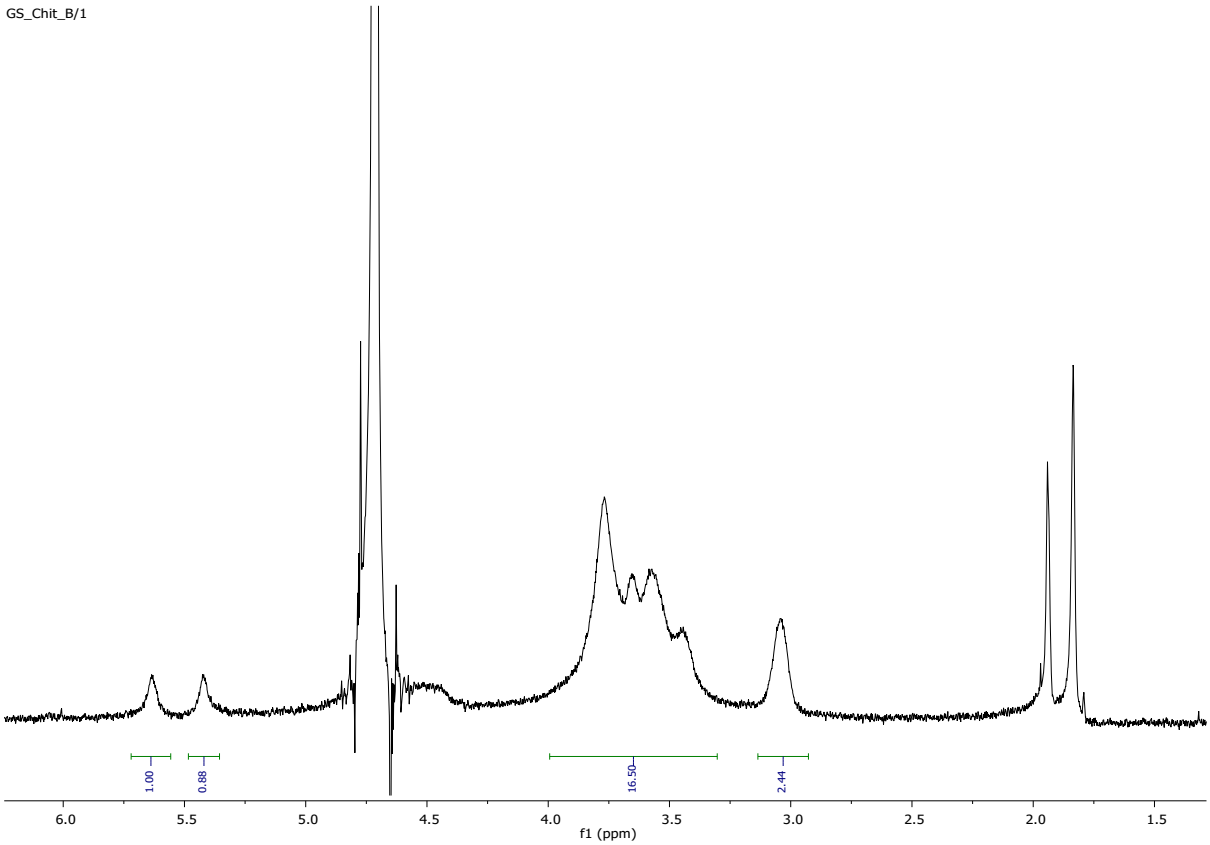
Protons 1-4; 6-11; 12: broad signal at ~3,6 ppm.

Protons 5, 11: peak at ~3,0 ppm.

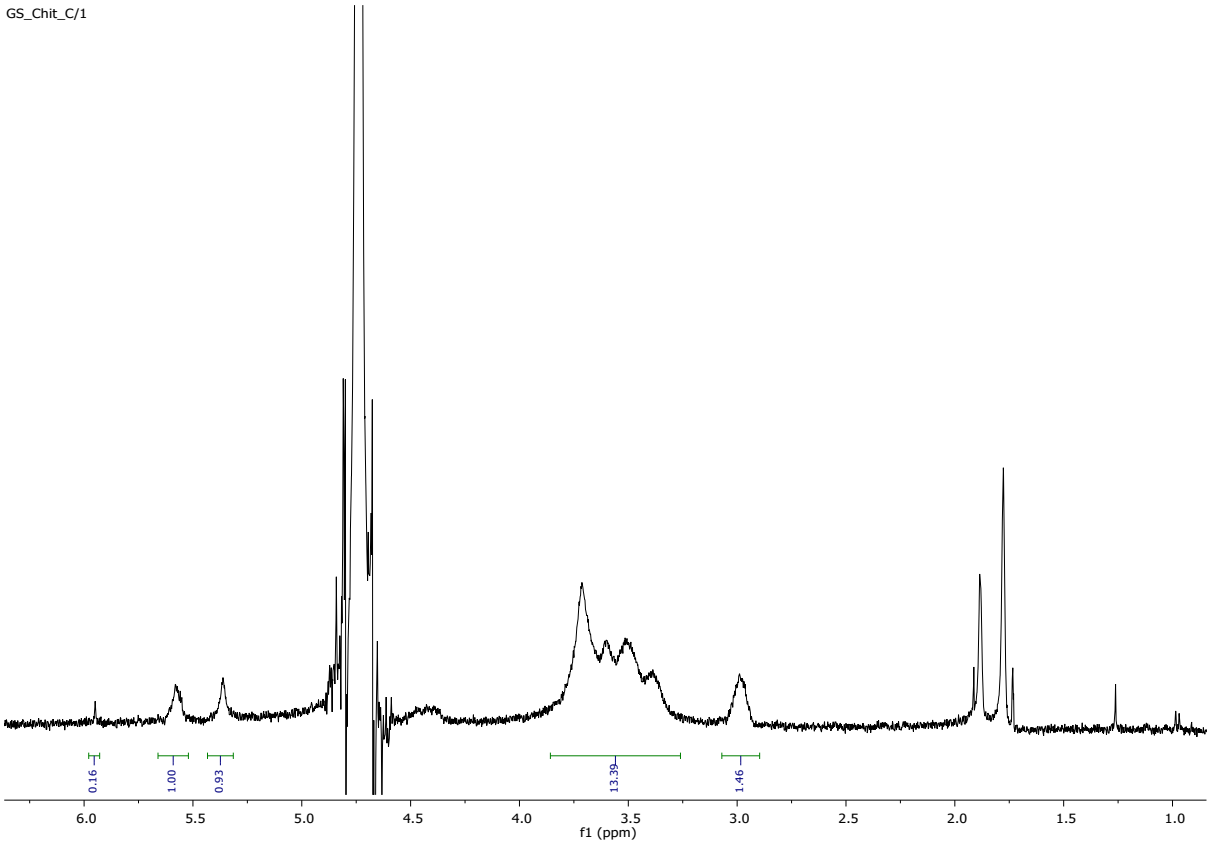
Methylene proton of acrylates bonded to NH_2 groups: peaks at ~5.6 and ~5.4 ppm.

Methylene proton of acrylates bonded to OH groups: peaks at ~6.0 and ~ 5.6 ppm.

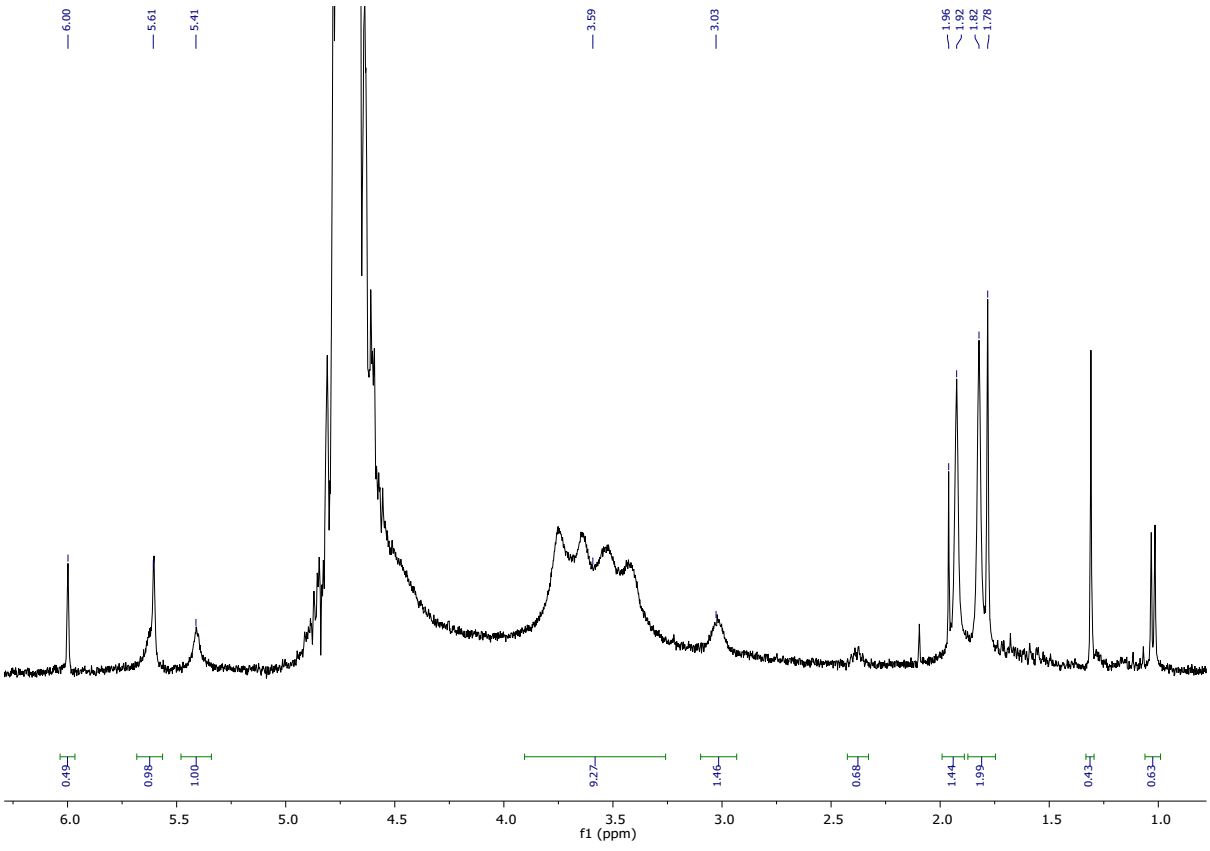
Synthesis 1 %DS: ~ 10 %



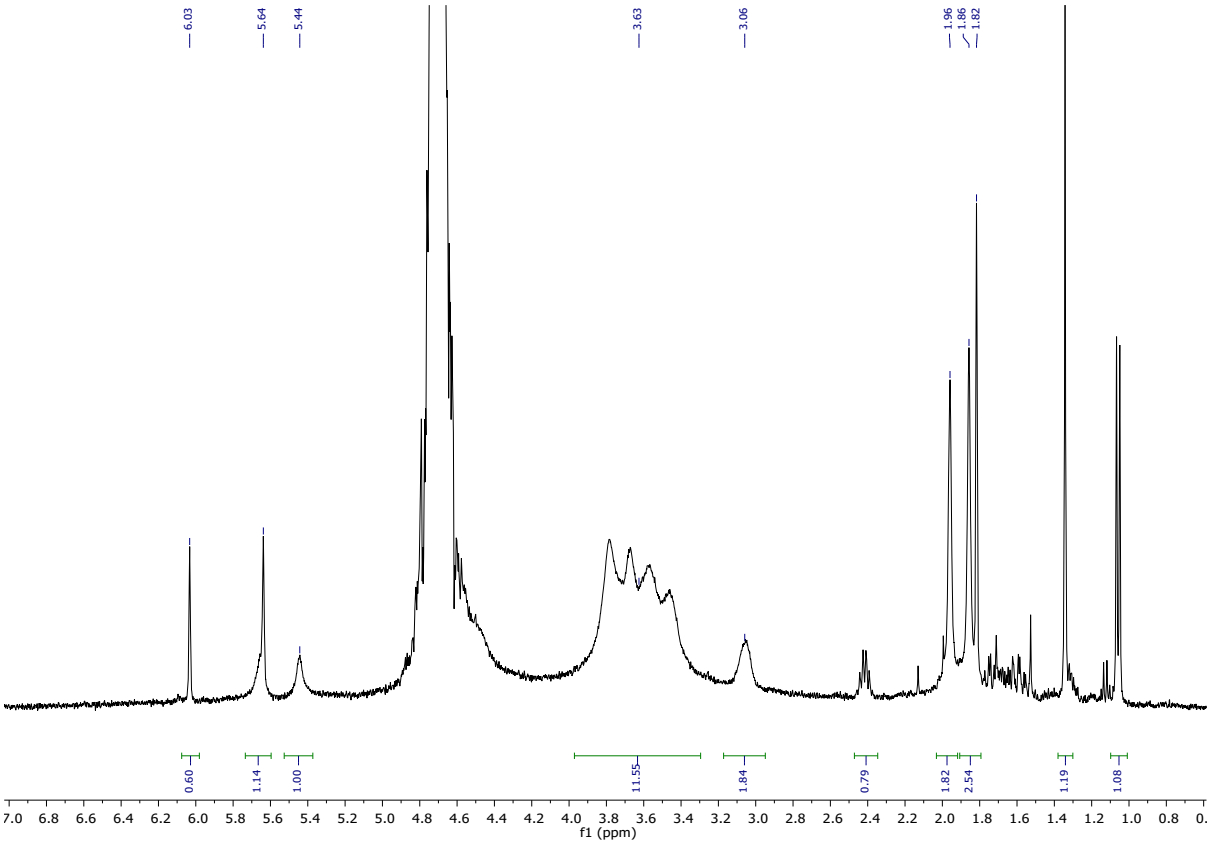
Synthesis 2 %DS: ~ 16 %



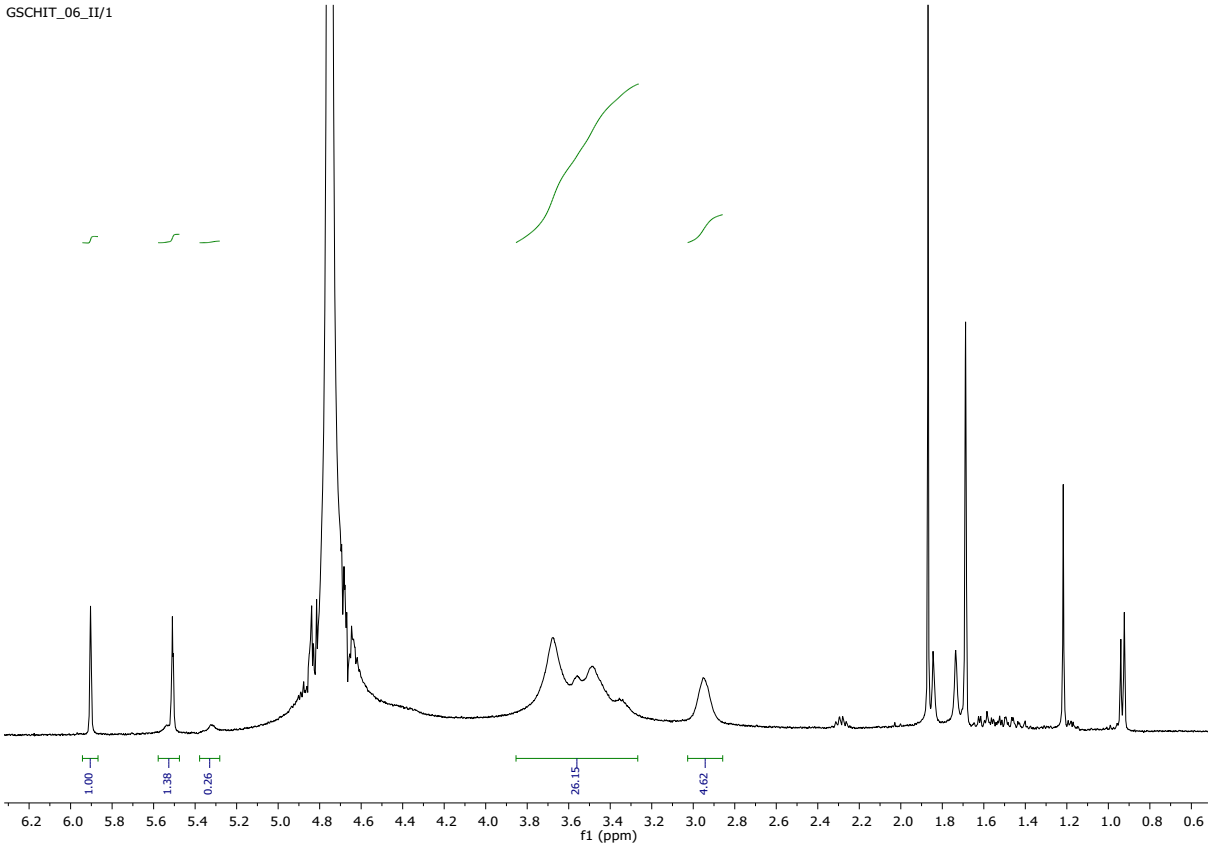
Synthesis 3 %DS: ~ 27 %



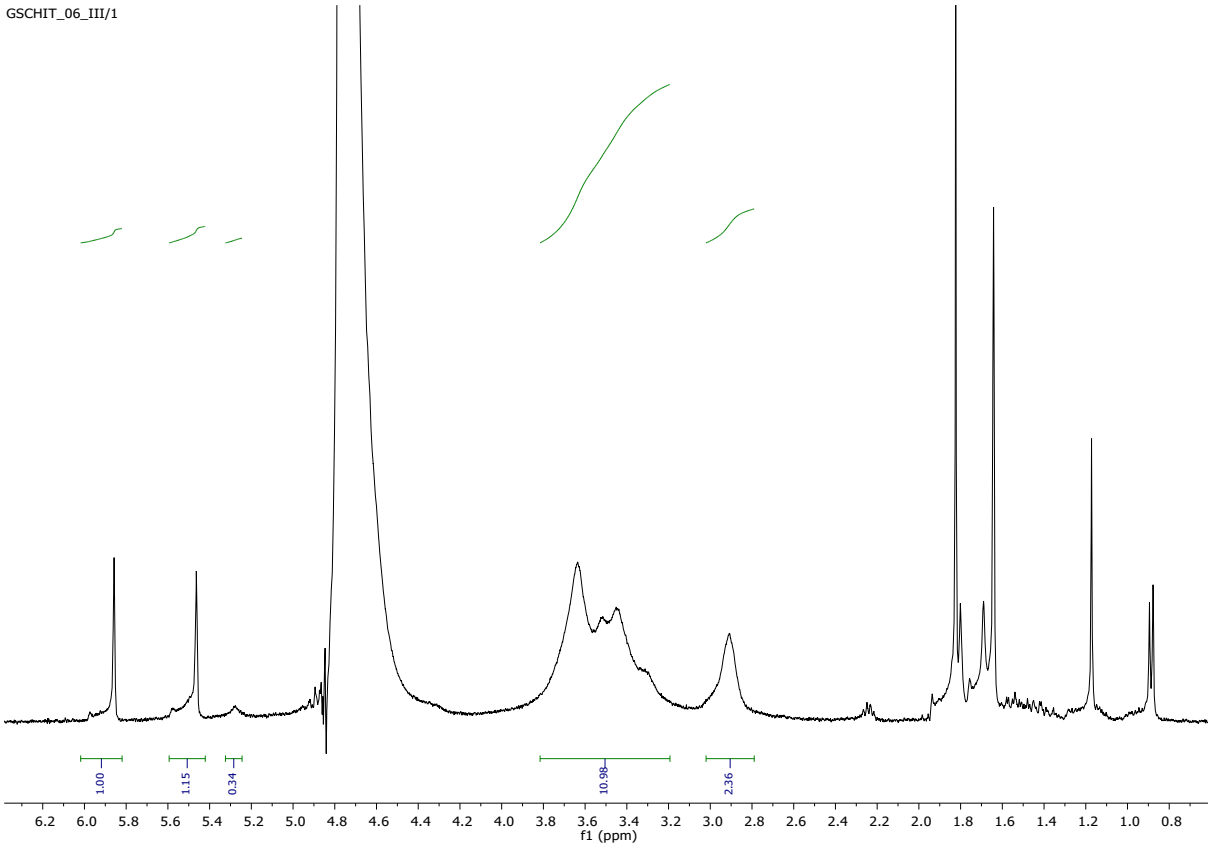
Synthesis 4 %DS: ~ 24 %



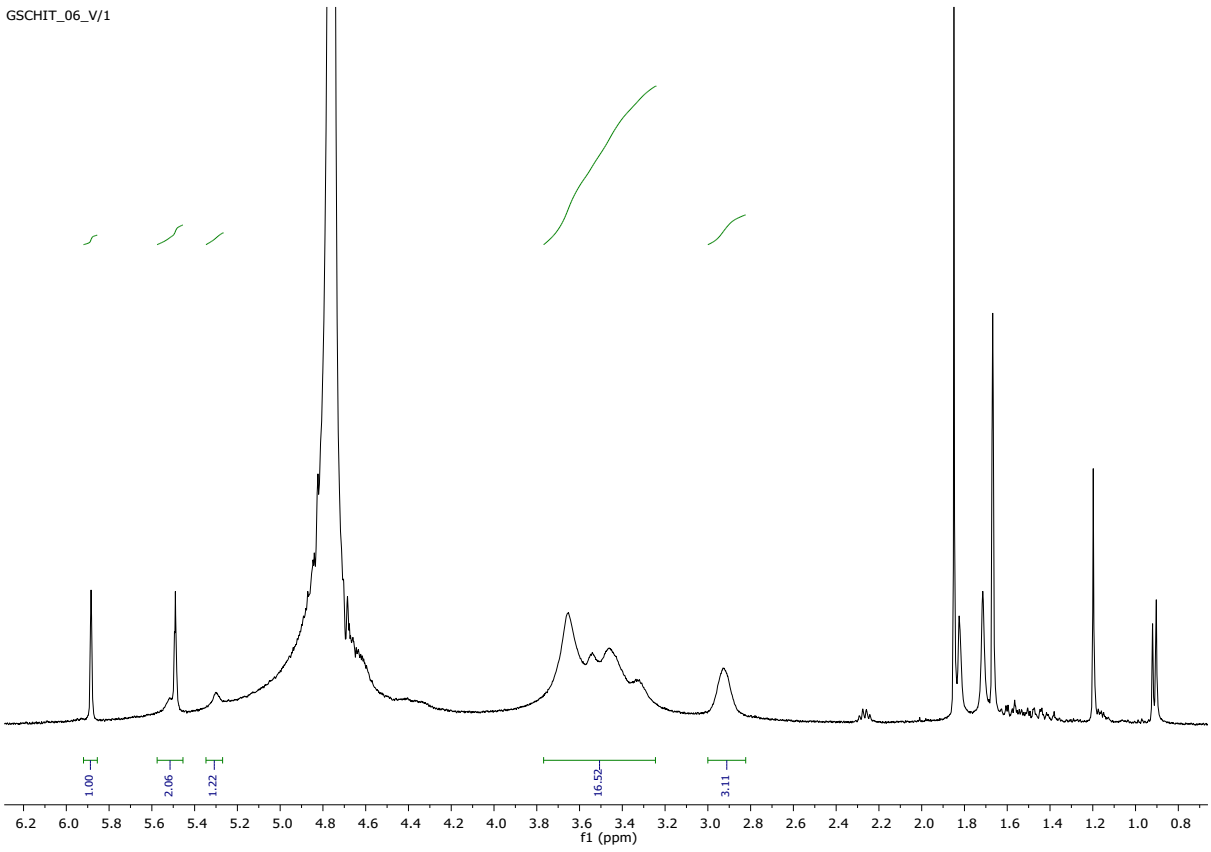
Synthesis 5 %DS: ~ 8 %



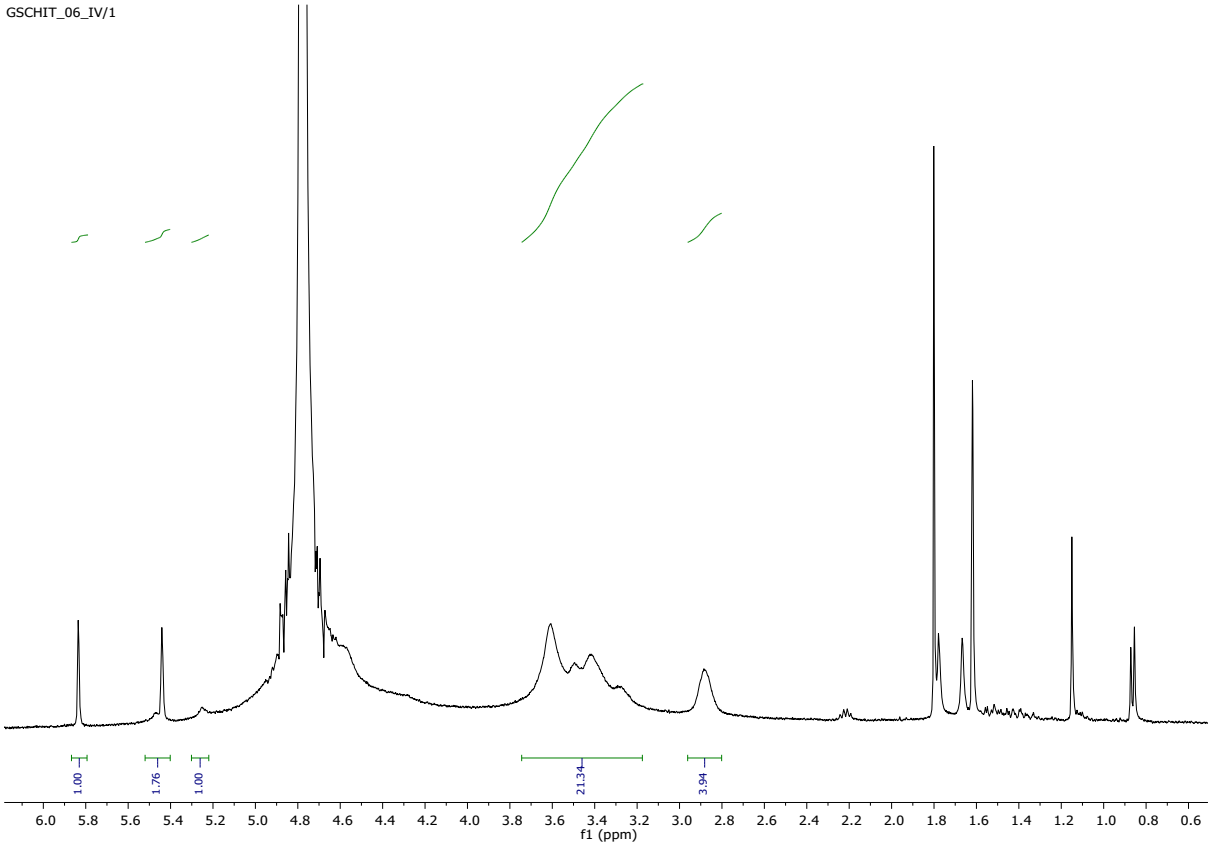
Synthesis 6 %DS: ~ 21 %



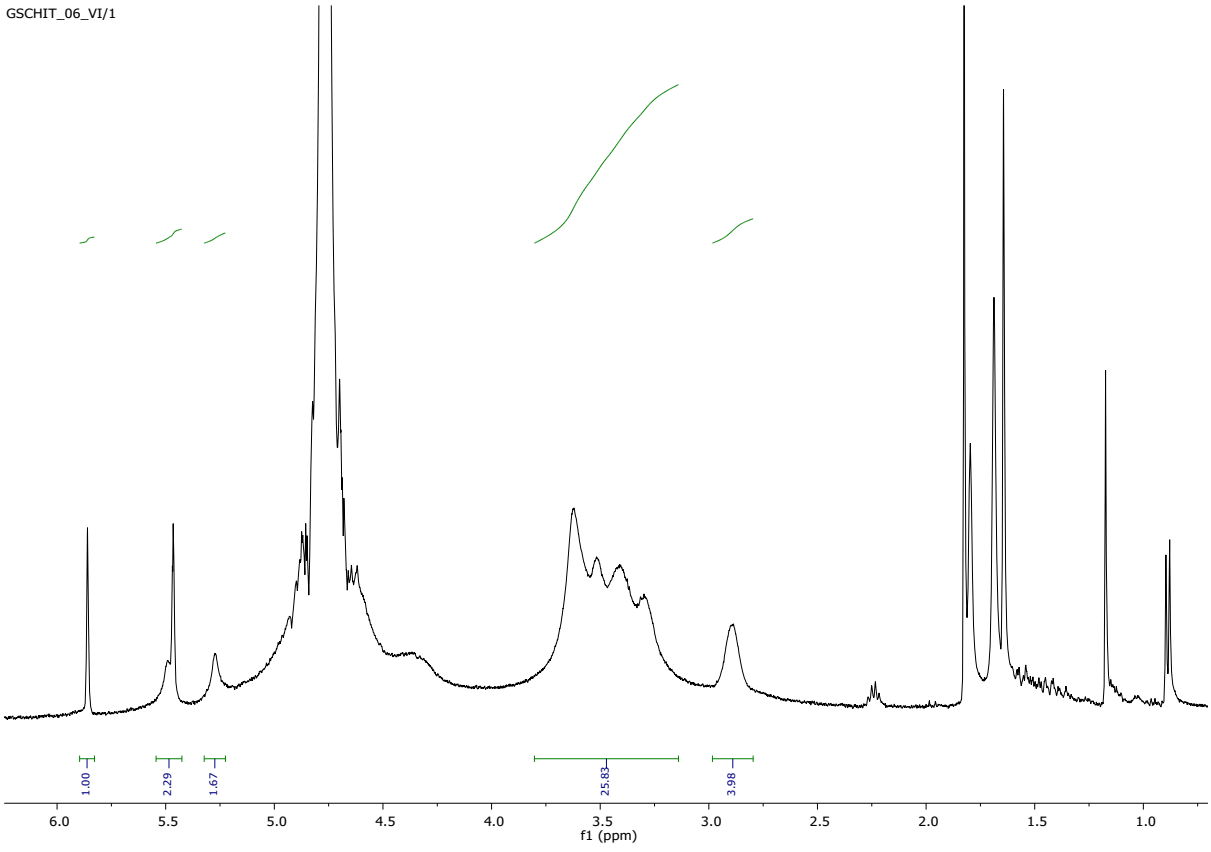
Synthesis 7 %DS: ~ 25 %



Synthesis 8 %DS: ~ 17 %



Synthesis 9 %DS: ~ 19 %



Synthesis 11 %DS: ~ 24 %

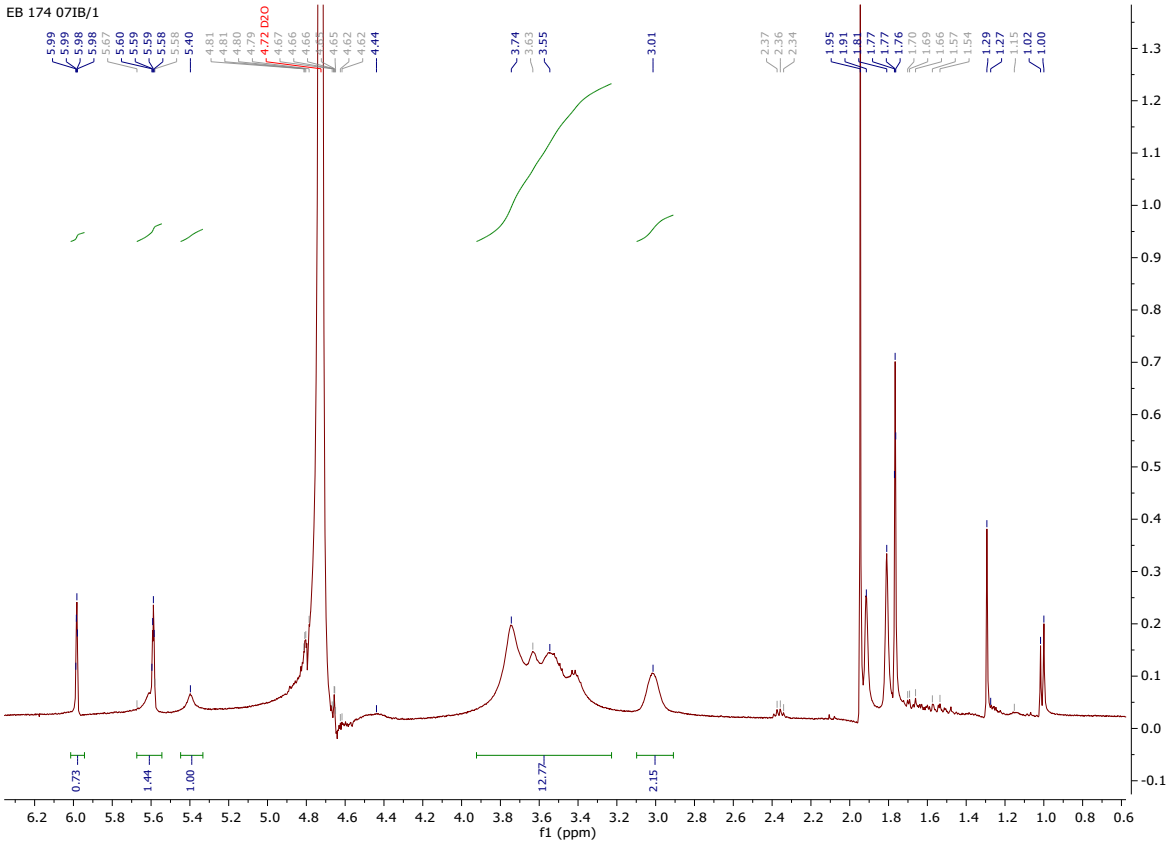


Figure S2: NMR Spectra obtained from the different synthesis

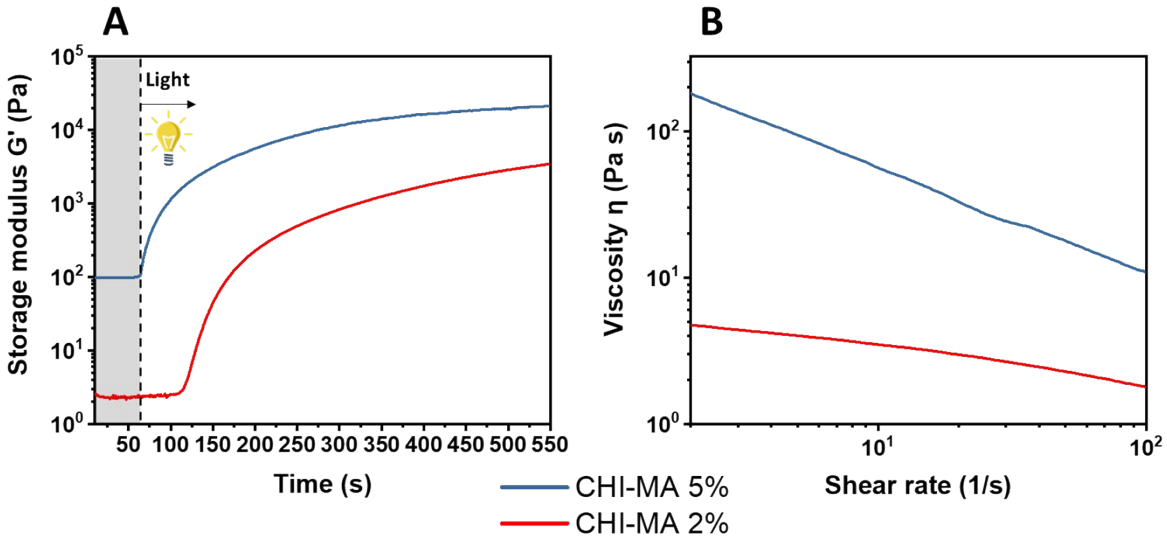


Figure S3: Photo-rheology (A) and viscosity (B) of CHI-MA DS 24 at different concentrations.

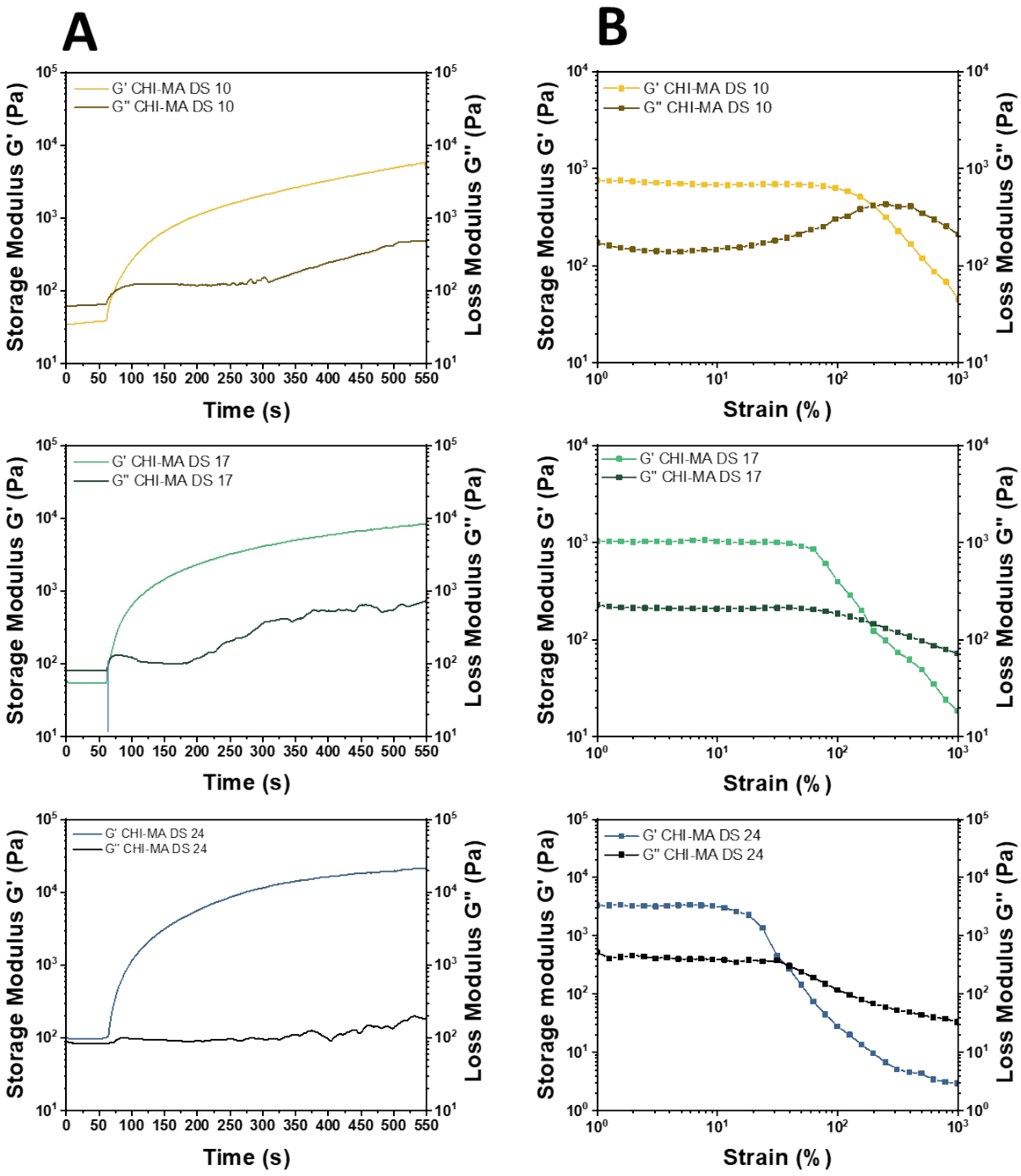


Figure S4: Photo-rheology (Column A) and Amplitude sweep (column B) of the three different CHI-MA batches. Both the Storage Modulus (G') and Loss Modulus (G'') are reported. Tan δ values calculated as G''/G' from the amplitude sweep plots are: CHI-MA DS10= 0.25, CHI-MA DS17= 0.22, CHI-MA DS24= 0.13.

SWELLING KINETICS MODELS

The equations used to describe the two swelling kinetics models are:

1) Fickian diffusion or Peppas-Korsmeyer model.

$$F = \frac{SwR_t}{SwR_e} = k_1 t^n \quad \text{(S1)}$$

Where SwRe and SwRt are the swelling ratios at the swelling equilibrium and at the considered time t, n is the solvent diffusion index and k_1 is the swelling rate constants of the Peppas-Korsmeyer model. In Figure S5A the experimental data were fitted inside of the model while the obtained values are reported on Table S1 where the R^2 value is used to certificate the adhesion to the model (only valid for SwRt/SwRe < 60%). In fact, the Peppas-Korsmeyer model is used to investigate the swelling mechanism of polymeric hydrogels and in particular, the two characteristics of solvent molecules propagation inside of the network and polymeric chains mobility (especially their local relaxation). The n value indicates which of the two is prevalent. If n < 0.5 the diffusion is Fickian (i.e., the relaxation rate of the chains is predominant over the solvent diffusion), If 0.5 < n < 0.9 the diffusion is non-Fickian (i.e., the two mechanisms are equally predominant) while if n > 0.9 the diffusion of the solvent is faster than the relaxation of the polymer chains (with possible ruptures of the structure).

2) Schott's model.

$$\frac{t}{SwRt} = \frac{1}{k_2 (SwRe^2)} + \frac{t}{SwRe} \quad \text{(S2)}$$

Where SwRe and SwRt are the swelling ratios at the swelling equilibrium and at the considered time t and k_2 is the swelling rate constants of the Schott's model. In Figure S5B the experimental data were fitted inside of the model while the obtained values are reported on Table S1 where the R^2 value is used to certificate the adhesion to the model. The Schott's model is used to describe the swelling rate so if the rate is proportional to the product of the concentrations (in moles) of two of the reactans, or to the square of the molar concentration of the reactant if only one is present.

In conclusion CHI-MA follow both the models (considering the high values of R^2) and the n constant (n < 0.5 in all the samples) suggest a predominance of the chains' relaxation over the solvent diffusion and the hydrogel possibility to be employed in tissue engineering.

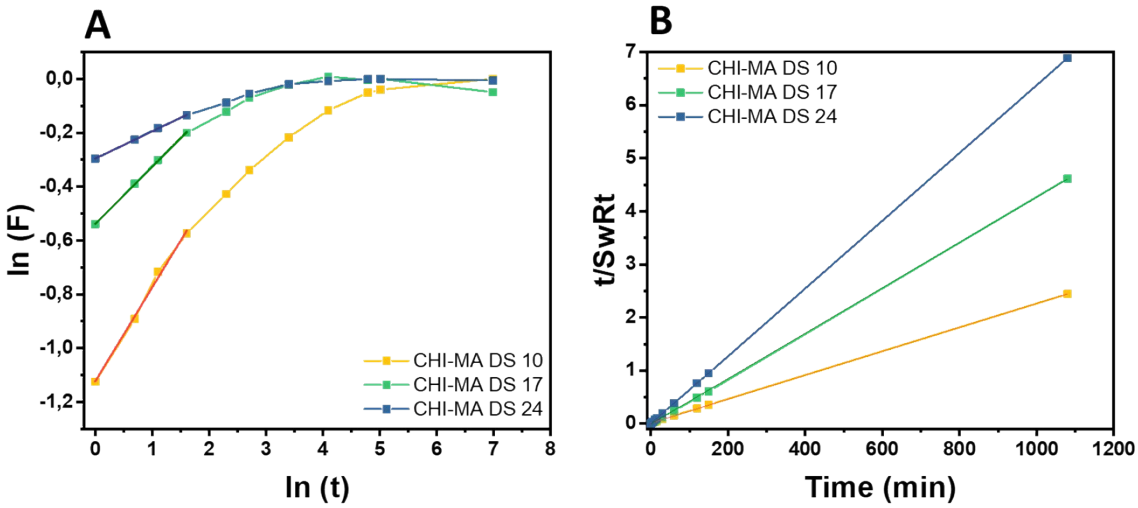


Figure S5: Peppas-Korsmeyer and Schott's model fittings.

	Peppas-Korsmeyer model		**Schott's model**
	R^2	**n**	**R^2**
CHI-MA DS 10	0,9953	0,34	0,9999
CHI-MA DS 17	0,9994	0,21	0,9999
CHI-MA DS 24	0,9995	0,1	1

Table S1: Peppas-Korsmeyer and Schott's models parameters

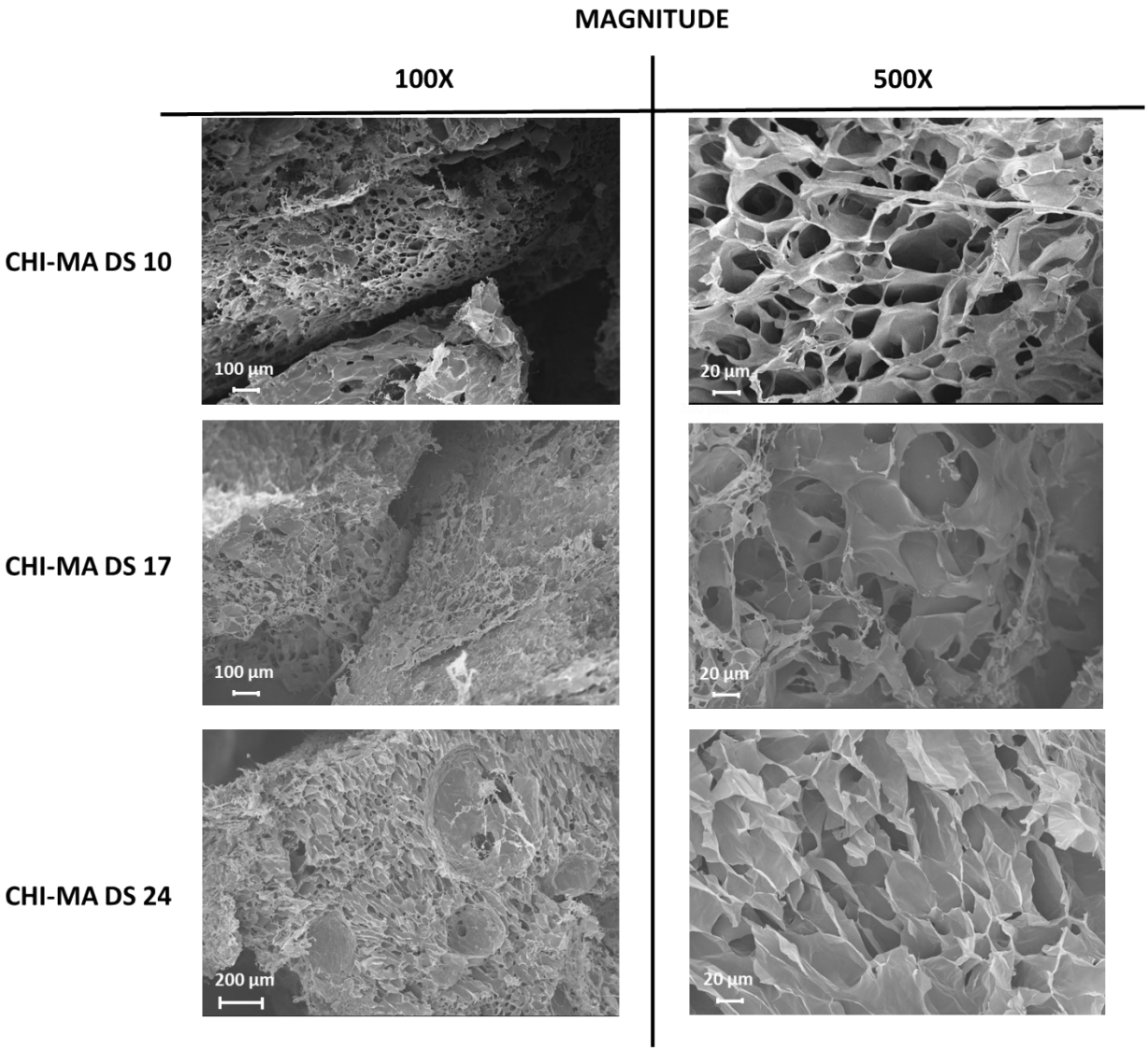


Figure S6: SEM Images at different magnification (scale bars on the images) for the samples at different DS%

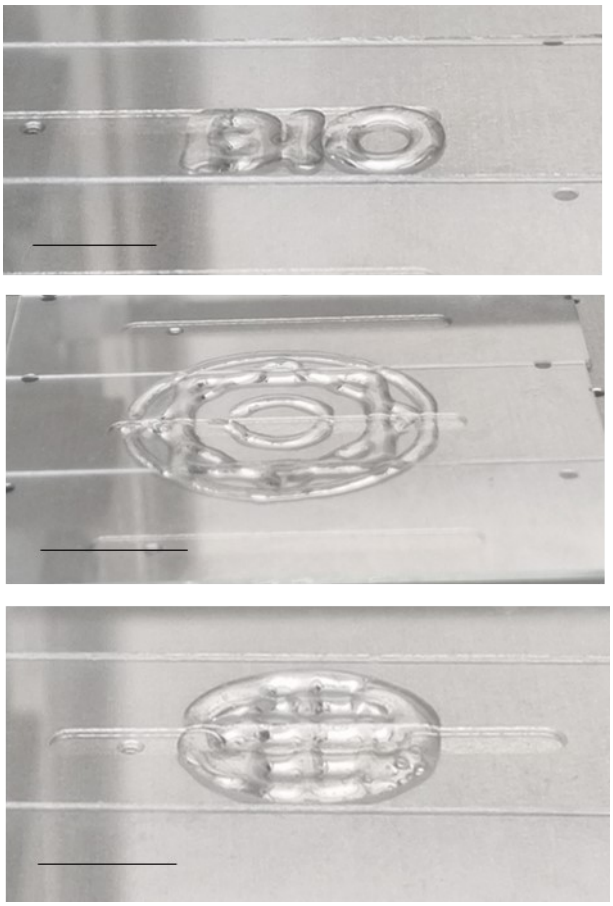


Figure S7: 3D printing optimization tests (scale bar 1cm)

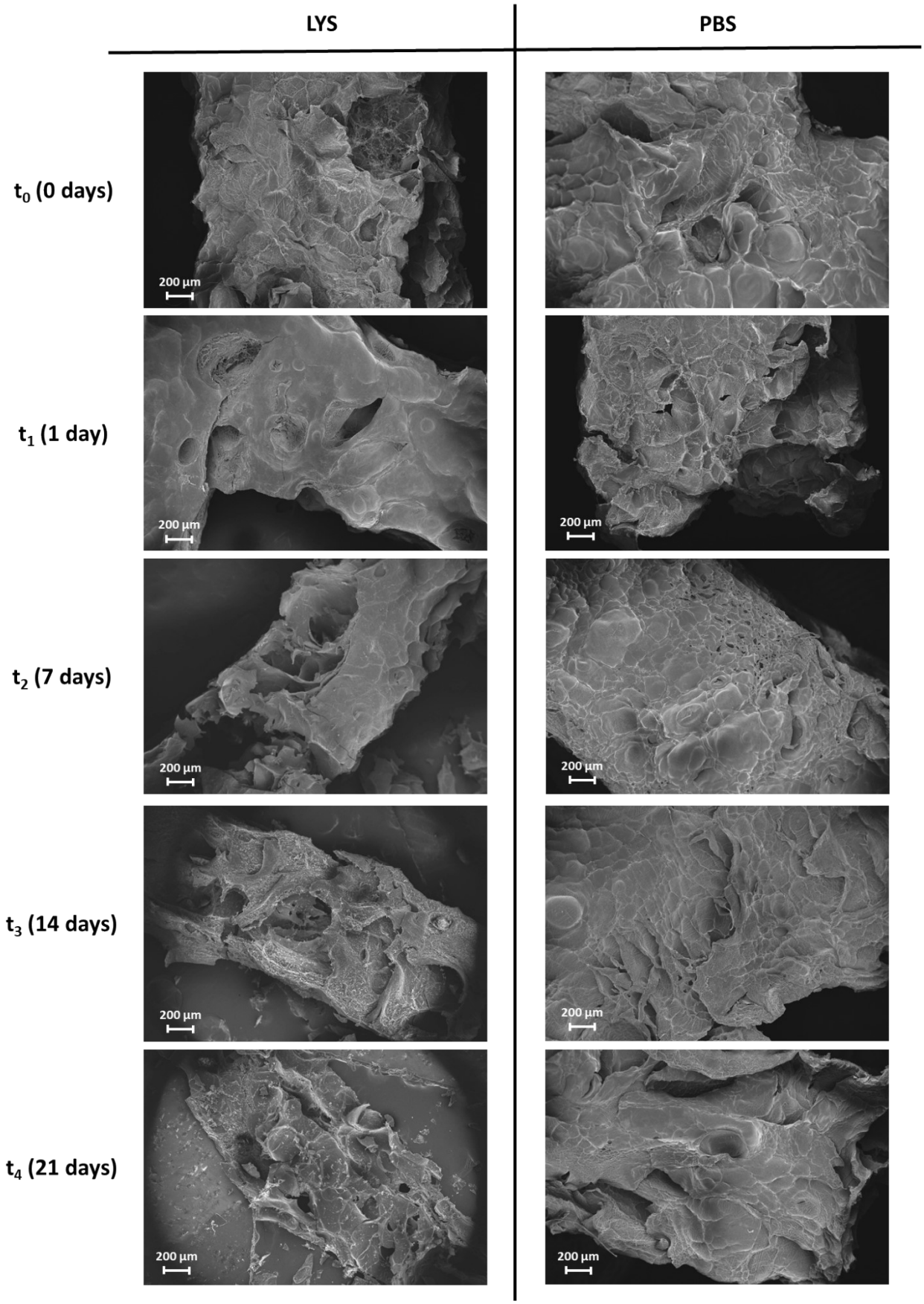


Figure S8: FESEM images of lysozyme (LYS) and hydrolysis (PBS) degraded samples. The scale bars denote 200 µm.