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Supporting Information for:

Enzymatic Synthesis of Hyaluronic Acid Vinyl Esters for Two-photon Microfabrication of Biocompatible and Biodegradable Hydrogel Constructs

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Table S1. Comparative analysis of cytotoxic effects: polyacrylates versus polyvinylesters.

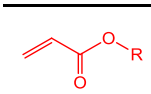
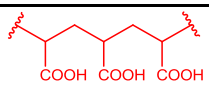
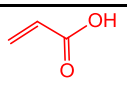
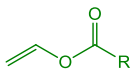
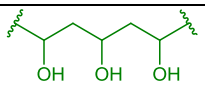
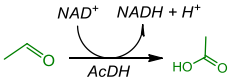
Monomers	Degradation products	Hydrolyzed product
		 irritant
Acrylates	high MW poly(acrylic acid)	acrylic acid
		
Vinyl esters	poly(vinyl alcohol)	Metabolizable

Table S2. Influence of Reaction Time and Stoichiometry on the Degree of Substitution (DS).

Entry	Stoichiometry *	Reaction Time (h)	DS
1	1:1	24	0.13
2	1:1	48	0.21
3	1:1	72	0.34
4	3:1	24	0.33
5	3:1	48	0.71
6	3:1	72	1.04
7	3:1	96	1.25

*Stoichiometry: the molar ratio between DVA and HA repeating unit

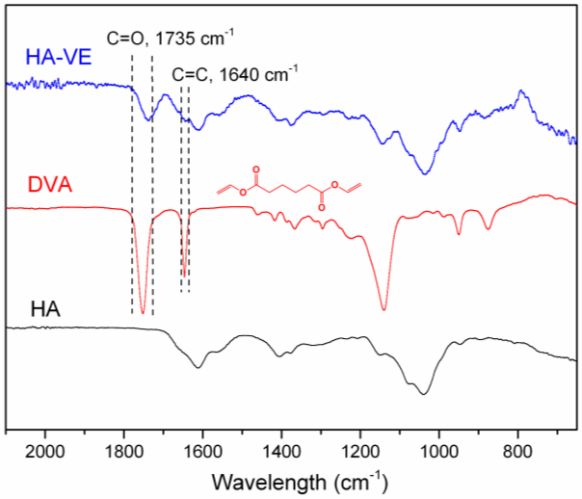


Figure S1. Comparative ATR-FTIR spectra of HA, DVA and HA-VE.

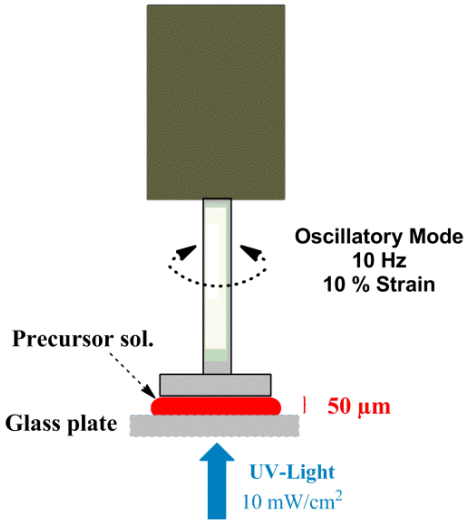


Figure S2. Schematic showing the photo-rheometer setup.

Table S3. Influence of DS on gel points, $G'_{plateau}$ and $G''_{plateau}$ values.

DS	Gel point (s)	G´plateau (kPa)	G´´plateau (kPa)
0.15	45	11.5	0.03
0.20	20	23.2	0.1
0.53	16	36.4	3.0

Table S4. Influence of macromer content on gel points, $G'_{plateau}$, and $G''_{plateau}$ values.

wt %	Gel point (s)	$G'_{plateau}$ (kPa)	$G''_{plateau}$ (kPa)
10	45	11.5	0.03
7	66	3.8	0.04
6	80	1.7	0.01
5	103	0.6	0.01
4	123	0.2	0.01

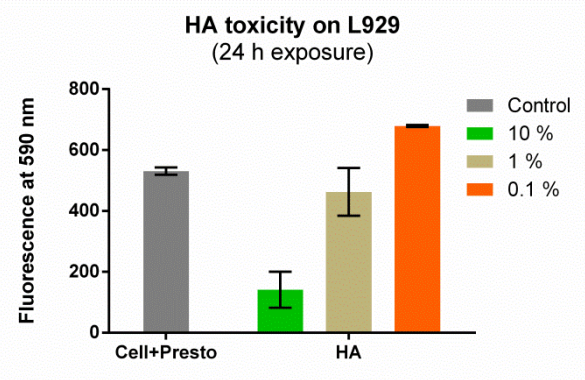


Figure S3. Influence of HA macromer concentration on cell metabolic activity.

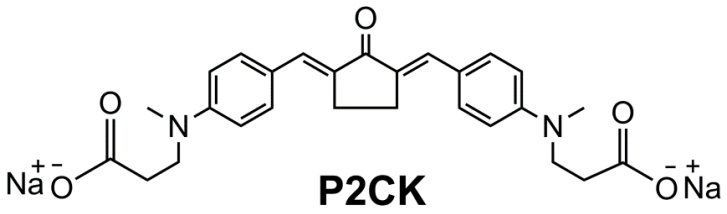


Figure S4. Chemical structure of P2CK (two-photon cross section: 176 GM at 800 nm).[1]

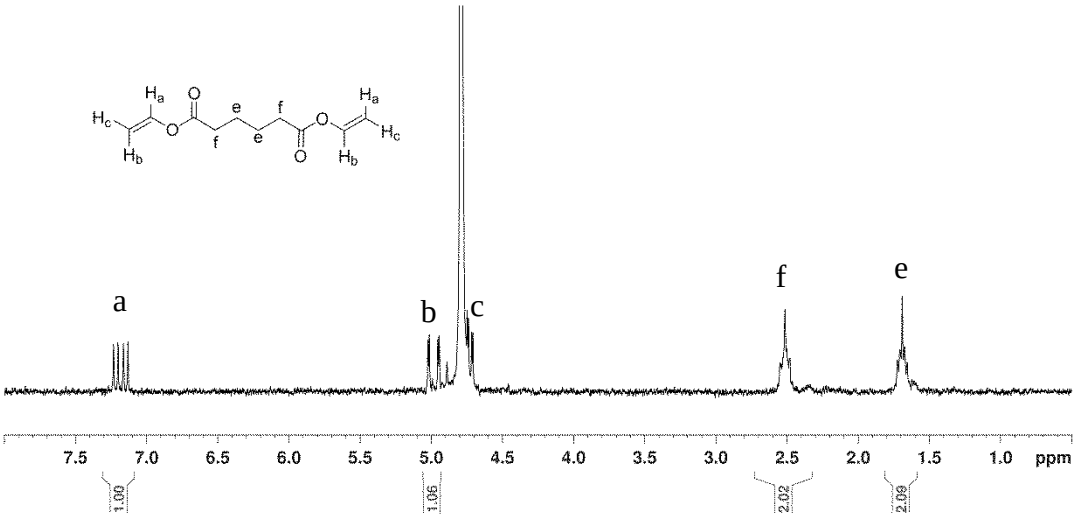


Figure S5. ^{1}H-NMR spectrum of DVA (D_2O, 200 MHz).

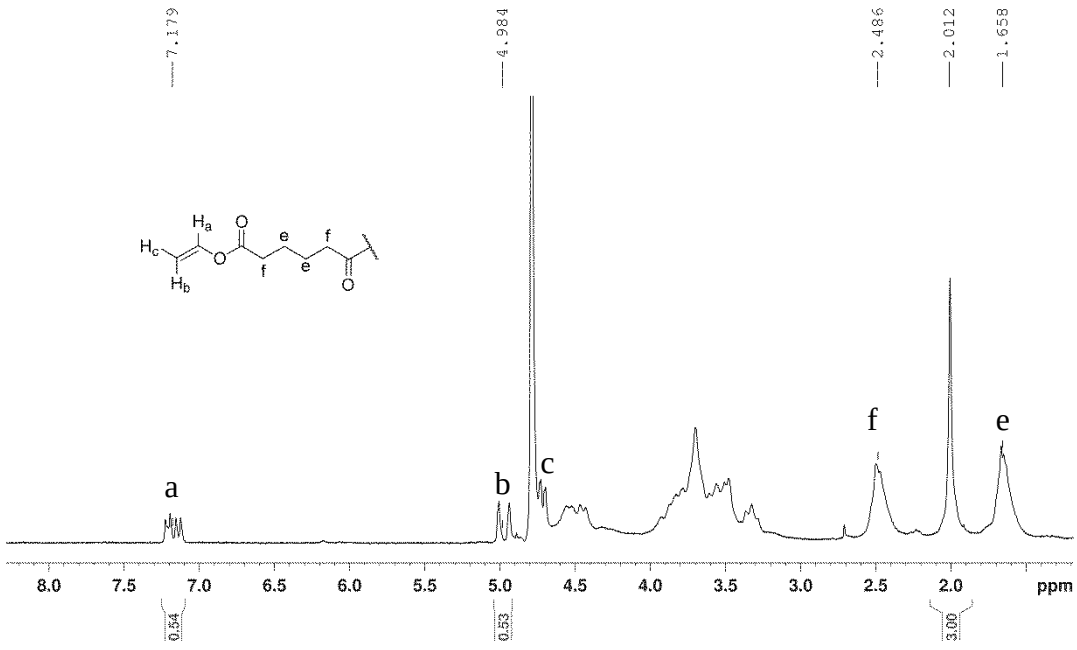


Figure S6. ^{1}H-NMR spectrum of HA-VE (D_2O, 200 MHz).

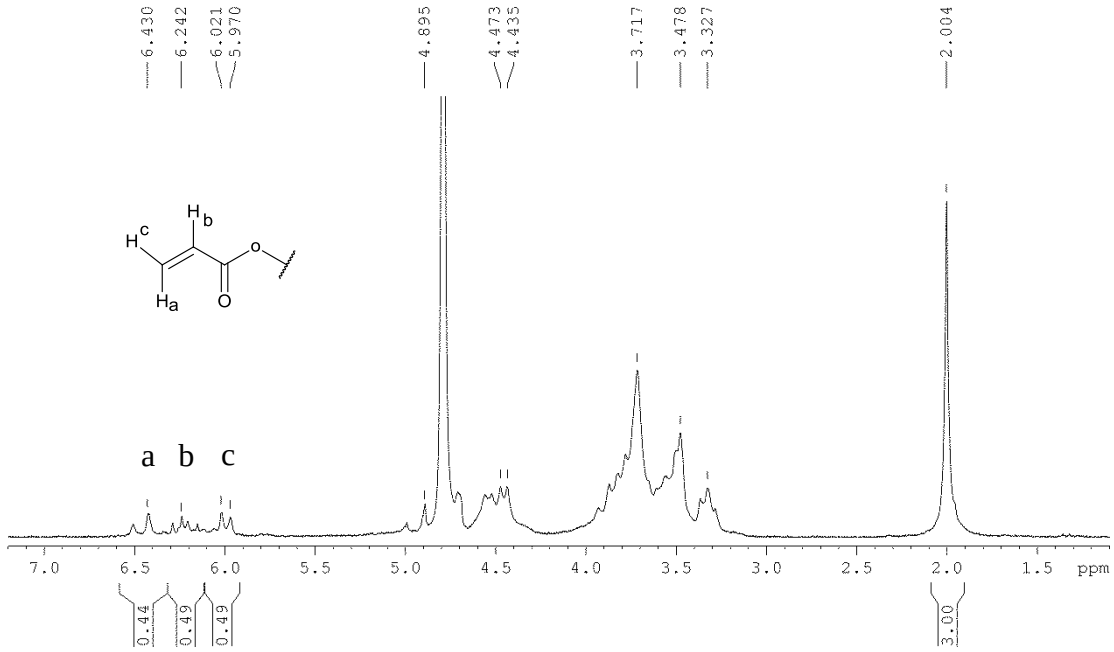


Figure S7. ^{1}H-NMR spectrum of HA-AC (D_2O, 200 MHz).

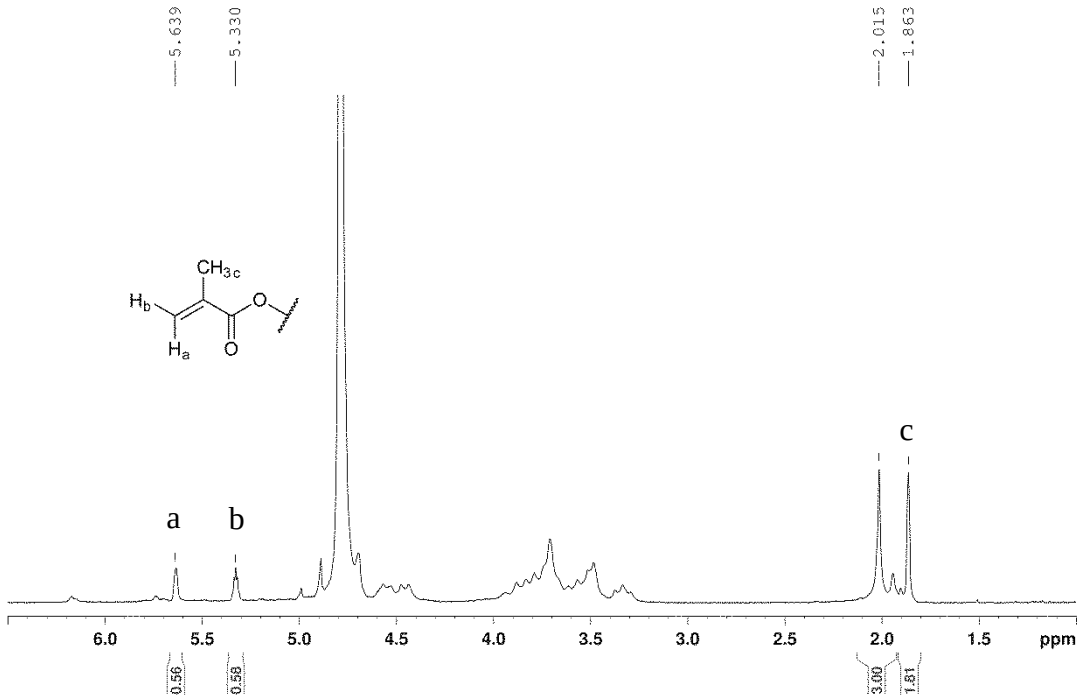


Figure S8. ^{1}H-NMR spectrum of HA-MA (D_2O, 200 MHz).

Reference

[1] Z. Li, J. Torgersen, A. Ajami, S. Muhleder, X. Qin, W. Husinsky, W. Holnthoner, A. Ovsianikov, J. Stampfl, R. Liska, RSC Advances 2013, 3, 15939.