

## Self-assembly of Alginate Based Graft Copolymers into Nanoparticles

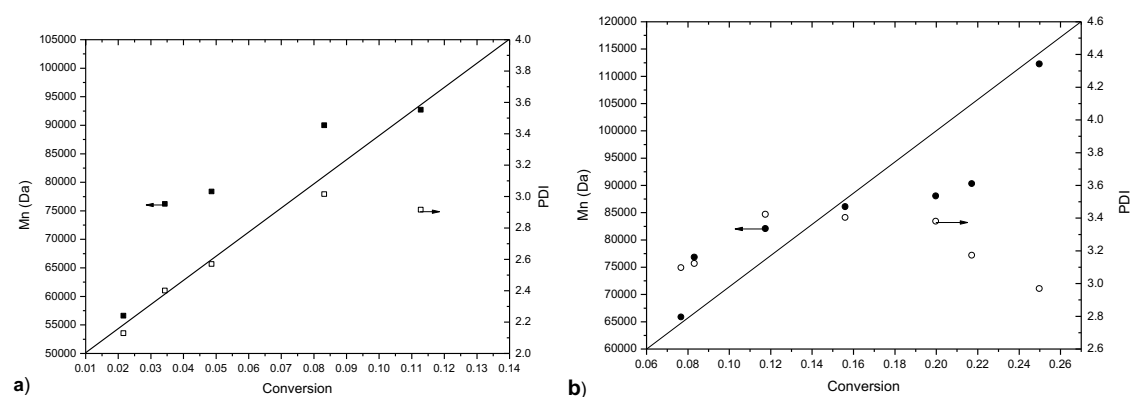
Jatin N Kumar\*, Victoria Y.T. Pang, Shalen X. L. Aik

### Supplementary Information

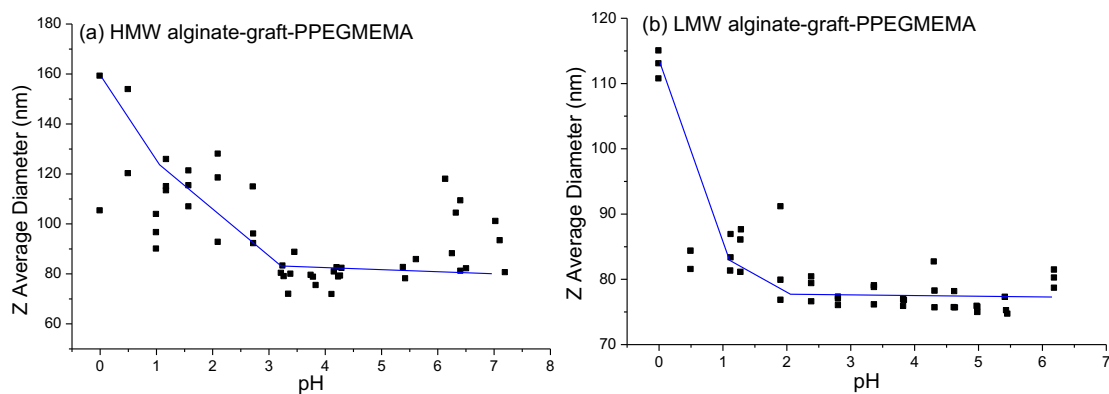
**Table S1:** Summary of reaction time, conversion and degree of polymerization (DP<sub>n</sub>) determined by <sup>1</sup>H NMR,  $M_n^{GPC}$  and its associated PDI (Đ) as determined by size exclusion chromatography with a single refractive index detector and PMMA calibration

	No.	Reaction Time	Conversion (%)	DP <sub>n</sub>	$M_n^{theo}$ (kDa)	$M_n^{GPC}$ (kDa)	Đ
HMW	1	45	2.17	5	267	56.5	2.13
	2	90	3.45	11	333	76.1	2.40
	3	135	4.88	16	387	78.3	2.57
	4	180	8.33	25	485	89.9	3.01
	5	225	11.29	35	594	92.6	2.91
	6	270	14.86	48	735	96.8	3.06
LMW	1	45	7.69	25	508	65.8	3.09
	2	60	8.33	35	682	76.7	3.12
	3	90	11.76	42	804	82.0	3.42
	4	105	15.63	50	943	86.2	3.40
	5	135	20.00	58	1,083	88.0	3.38
	6	150	21.74	62	1,152	90.2	3.17
	7	180	25.00	66	1,222	112.2	2.97

$M_n^{theo}$ :  $M_n^{GPC}$  of alginate + (DP<sub>n</sub> \* 300 \* no. of RAFT agents per backbone)



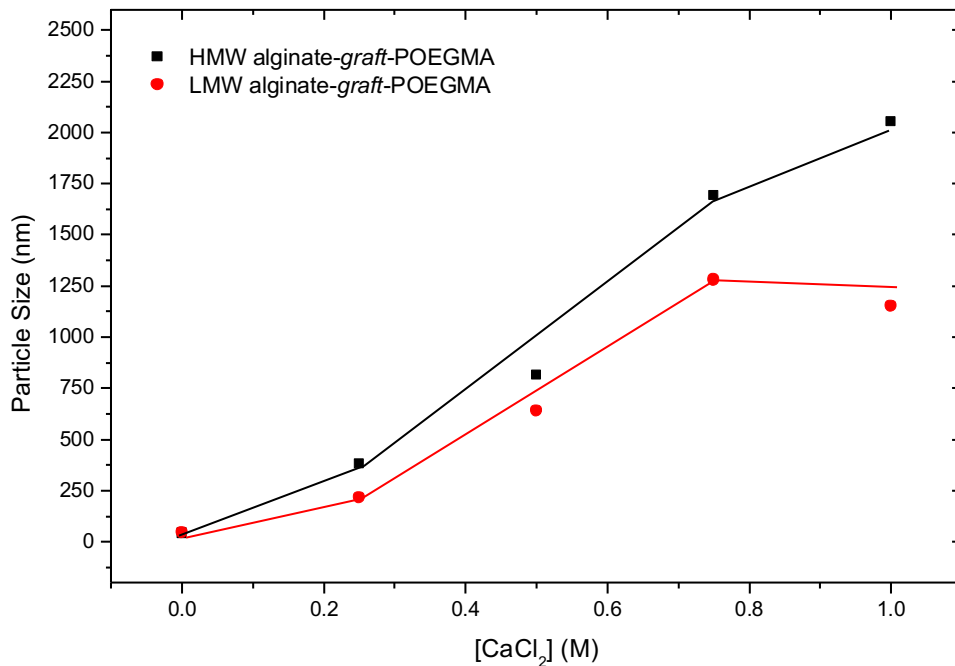
**Figure S1:** Molecular weight (closed symbols) and polydispersity index (open symbols) development with conversion of the polymerization of OEGMA for the (a) HMW alginate macroRAFT agent and (b) LMW alginate macroRAFT agent



**Figure S2:** Z-average diameter and the associated PDI of 2 mg/mL solution of (a) HMW alginate-graft-POEGMA; or (b) LMW alginate-graft-POEGMA titrated against HCl down to pH: 0

**Table S2:** Z-average particle size and polydispersity index (PDI) of the 2 polymers in different solvents

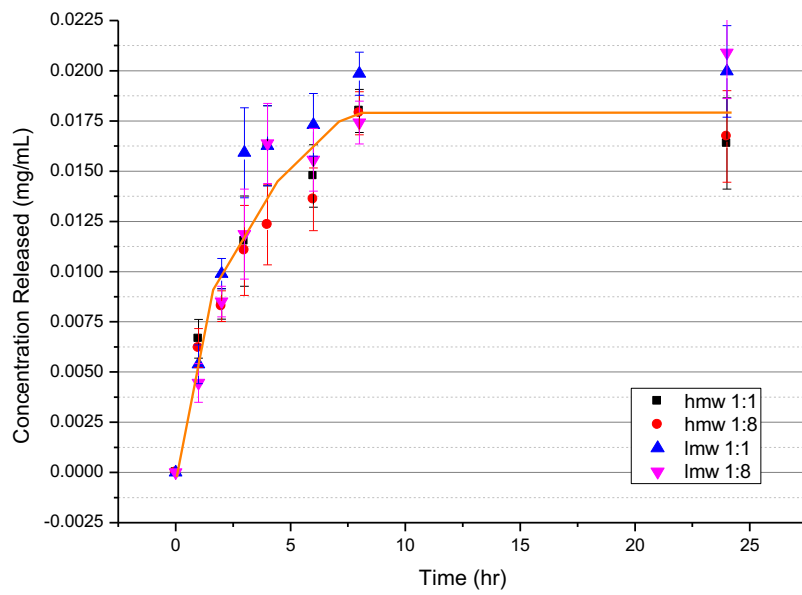
	Solvent	Z-average size (nm)	PDI
HMW Alginate-graft-POEGMA	Water	43.7	0.347
	Chloroform	64.9	0.110
	Methanol	37.8	0.251
	Acetone	44.4	0.373
LMW Alginate-graft-POEGMA	Water	43.6	0.381
	Chloroform	37.9	0.189
	Methanol	45.95	0.256
	Acetone	31.5	0.186



**Figure S3:** Z-average diameter recorded for 2 mg/mL of each polymer in methanol as a function of CaCl<sub>2</sub> concentration

**Table S3:** Encapsulation percentages for the various ratios of 4BR to HMW and LMW alginate-graft-POEGMA when CaCl<sub>2</sub> is introduced into the polymer solution

	Ratio of 4BR:poly	Encap (%)	Loading (%)
HMW	1:8	87	11
	1:4	68	17
	1:2	67	33
	1:1	64	64
	2:1	68	136
LMW	1:8	86	11
	1:4	84	21
	1:2	85	43
	1:1	87	87
	2:1	88	176



**Figure S4:** Concentration over time of the released 4BR showing a similar quantity of 4BR released over 24 hours irrespective of polymer size or polymer to 4BR ratio