

Supporting Information:

Alginate gels crosslinked with chitosan oligomers — A systematic investigation into alginate block structure and chitosan oligomer interaction

Georg Kopplin^a, Anders Lervik^b, Kurt I. Draget^a and Finn L. Aachmann^{*a}

^a *Norwegian Biopolymer Laboratory (NOBIPOL), Department of Biotechnology,
Norwegian University of Science and Technology, 7491 Trondheim, Norway*

^b *Department of Chemistry, Norwegian University of Science and Technology, 7491
Trondheim, Norway*

*Corresponding author. E-mail finn.l.aachmann@ntnu.no

Supporting Information

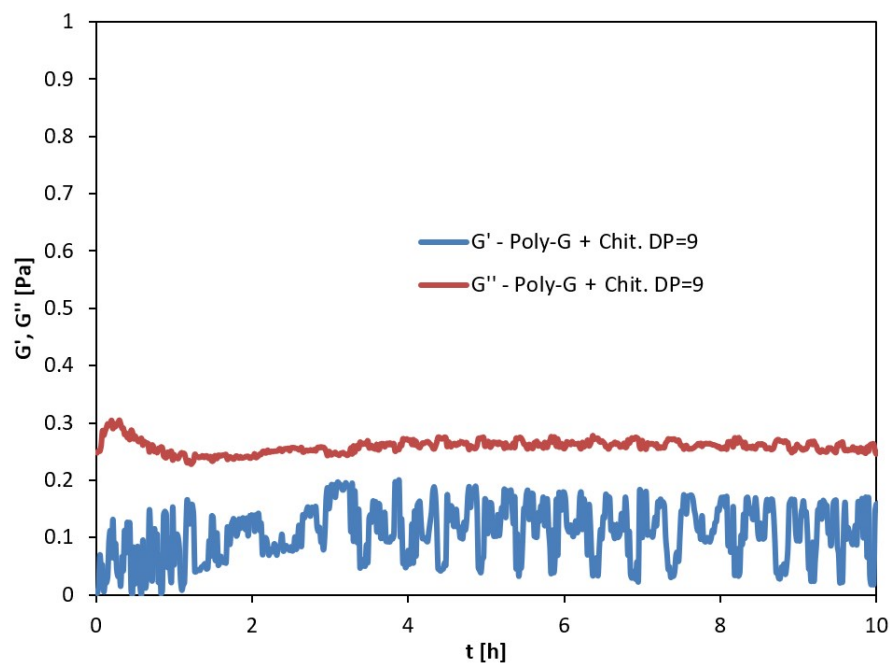


Figure S1: Kinetics of gelation of poly-G alginate concentration at 10 g/L (1%) with chitosan oligomers DP = 9 and concentration at 3 g/L (0.3%). GDL concentration 2 g/L. G' (blue line) and G'' (red line), was determined as a function of time.

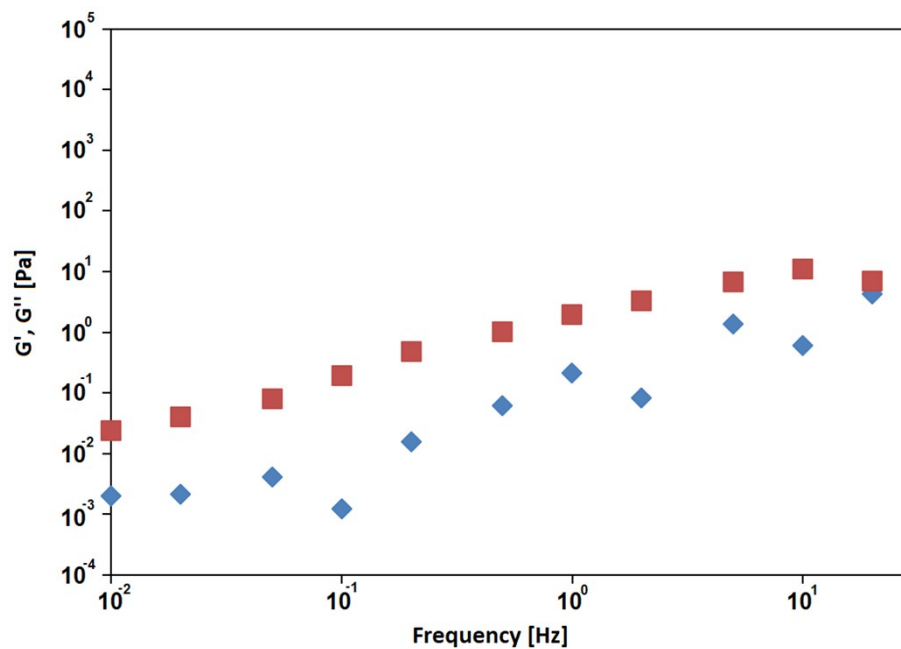


Figure S2: Frequency sweep of poly-MG (1.0%) and CHOS DP = 9 (0.3%), without GDL. G' (blue diamonds), G'' (red squares). All measurements performed at 20°C.

Table S1: Complete composition of alginate hydrogels, used for rheological experiments. Alginate was ionically crosslinked with chitosan oligosaccharides (CHOS) at various CHOS/Alginate monosaccharide unit ratios. The amounts of NaOH was adjusted to reach pH to 8 when mixing CHOS and Alginate. The amount of Glucono δ -lactone (GDL) was adjusted to reach a final pH of 4.35 ± 0.05 . For calculations based on the monosaccharide ratio, the molar masses 199.12 g/mol and 197.62 g/mol were assigned to the sodium alginate unit and to the glucosamine chloride unit respectively.

SAMPLE	1	2	3	4	5	Unit
Monosacch. unit ratio: CHOS/Alginate	0.2	0.3	0.4	0.5	0.6	
Alginate solution (30 g/L) added	1.00	1.00	1.00	1.00	1.00	g
Alginate amount	30.00	30.00	30.00	30.00	30.00	mg
Alginate concentration (final)	10.00	10.00	10.00	10.00	10.00	g/L
CHOS amount	6.08	9.12	12.16	15.20	18.24	mg
CHOS solution (100 g/L) added	60.8	91.2	121.6	152.0	182.4	μ l
CHOS concentration (final)	2.03	3.04	4.05	5.07	6.08	g/L
NaOH (1 M) added	14.9	22.4	29.8	37.3	44.7	μ l
GDL amount	5.32	7.98	10.63	13.29	15.95	mg
GDL concentration (final)	1.77	2.66	3.54	4.43	5.32	g/L
H ₂ O added (final Vol. 3 mL)	1924	1886	1849	1811	1773	μ l

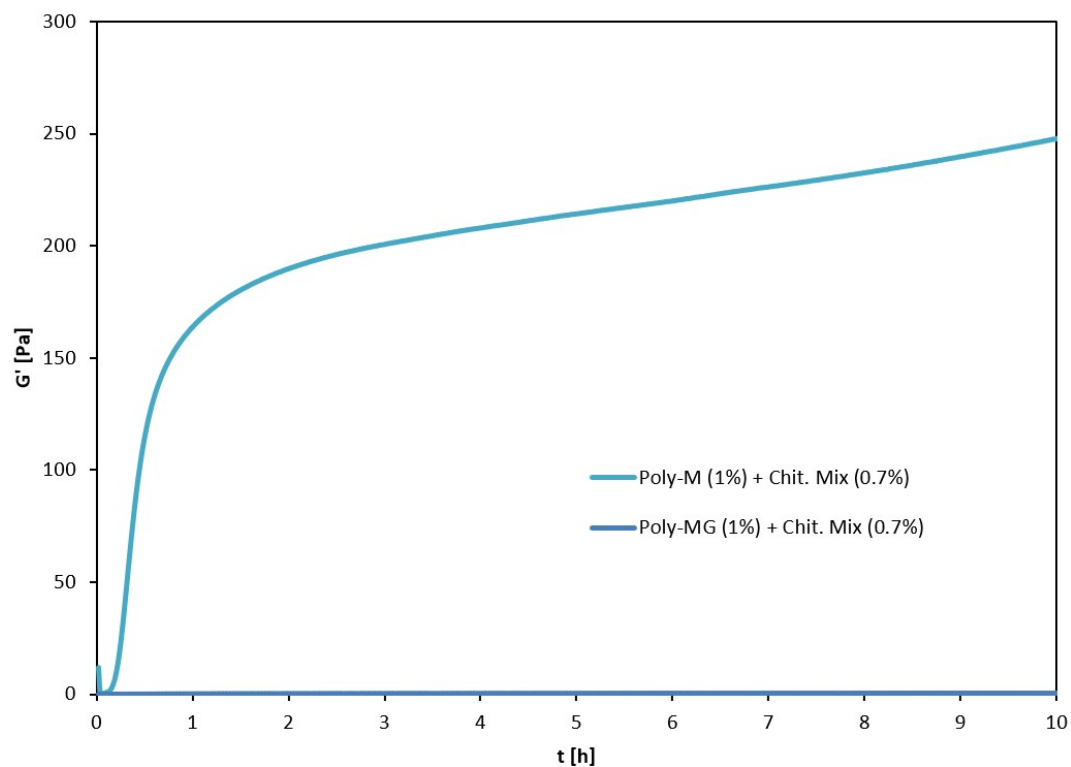


Figure S3: Kinetics of gelation as a function of time. Alginate concentration (poly-M: light blue, poly-MG: dark blue) at 10 g/L (1%). Chitosan oligomer mix ($DP_n = 3.96$, $FA = 0.045$) concentration at 7 g/L (0.7%). GDL at 2 g/L. G' was determined as a function of time. G'' and $\Delta\epsilon$ are not shown in the Figure for reasons of clarity.

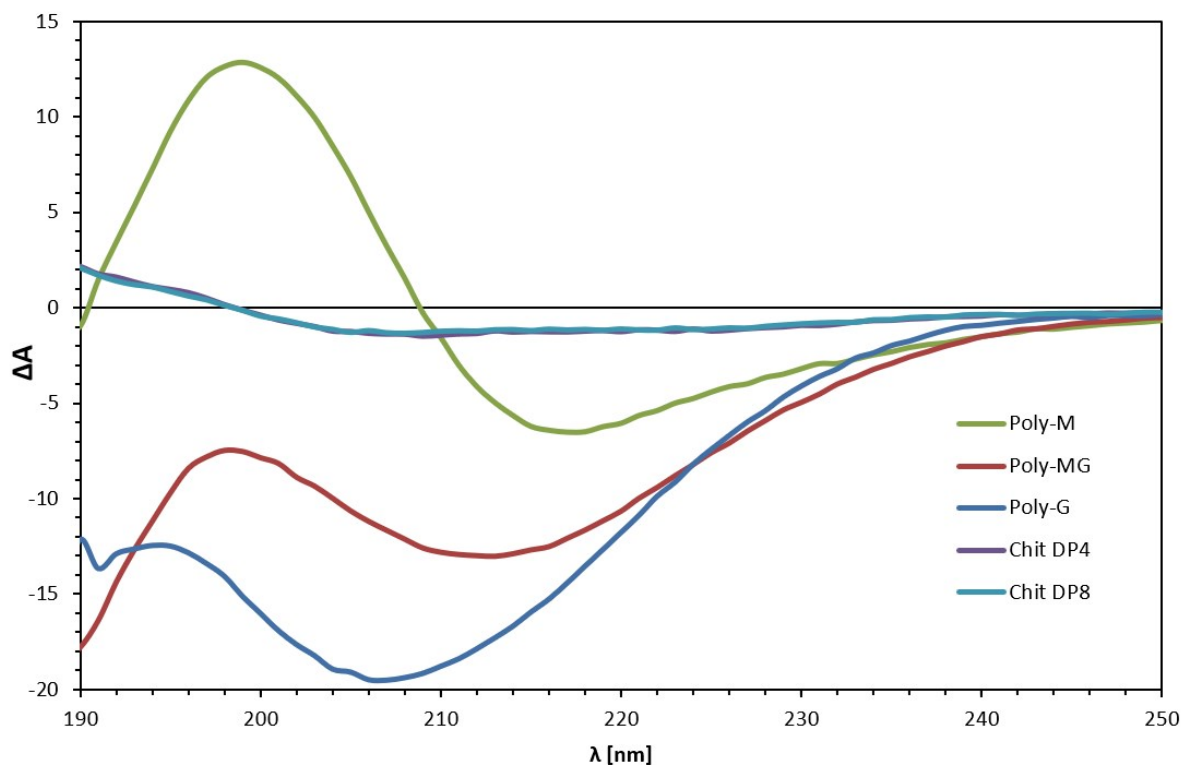


Figure S4: Circular dichroism spectra of poly-M (green), poly-MG (red), poly-G (blue) and chitosan DP = 4 (purple) and DP = 8 (light blue). All measurements were performed at pH = 4.5 and T = 25°C with a sample concentration of 0.4 g/L.

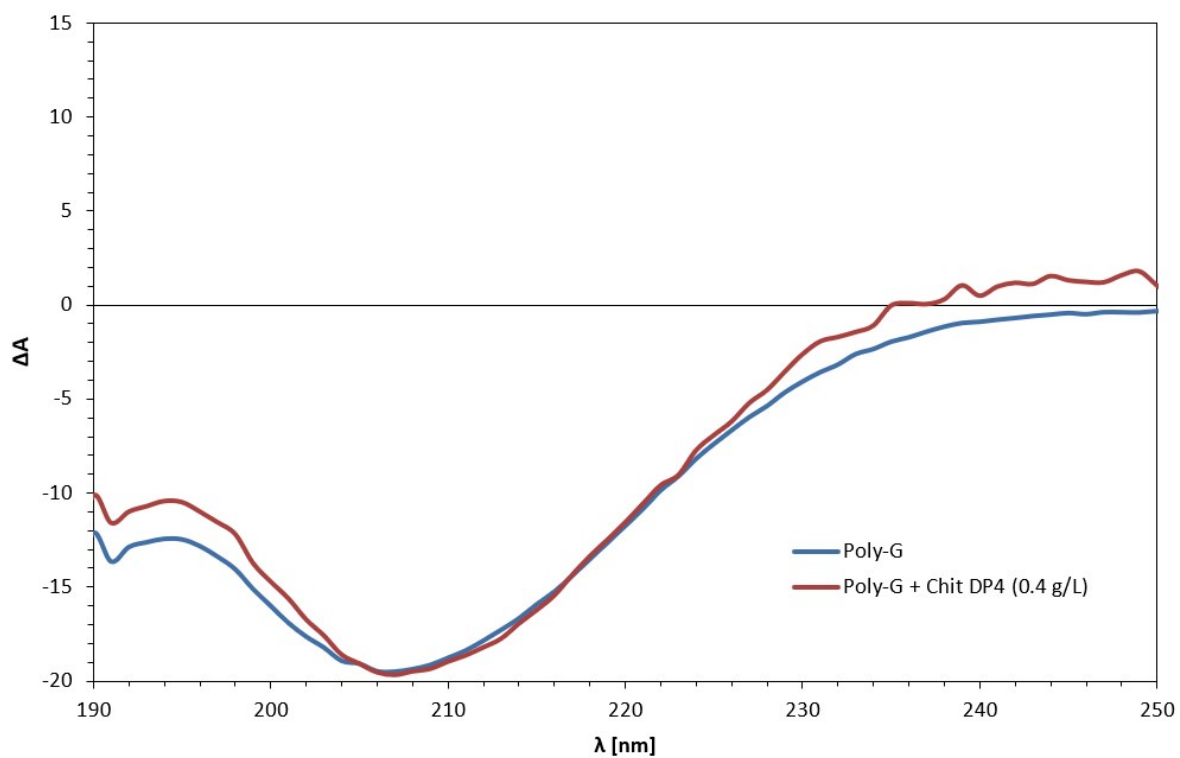


Figure S5: Circular dichroism spectra of poly-G (blue line) and poly-G upon addition of chitosan DP = 4 (red). The alginate and chitosan concentration was at 0.4 g/L. All measurements were performed at pH = 4.5 and T = 25°C.

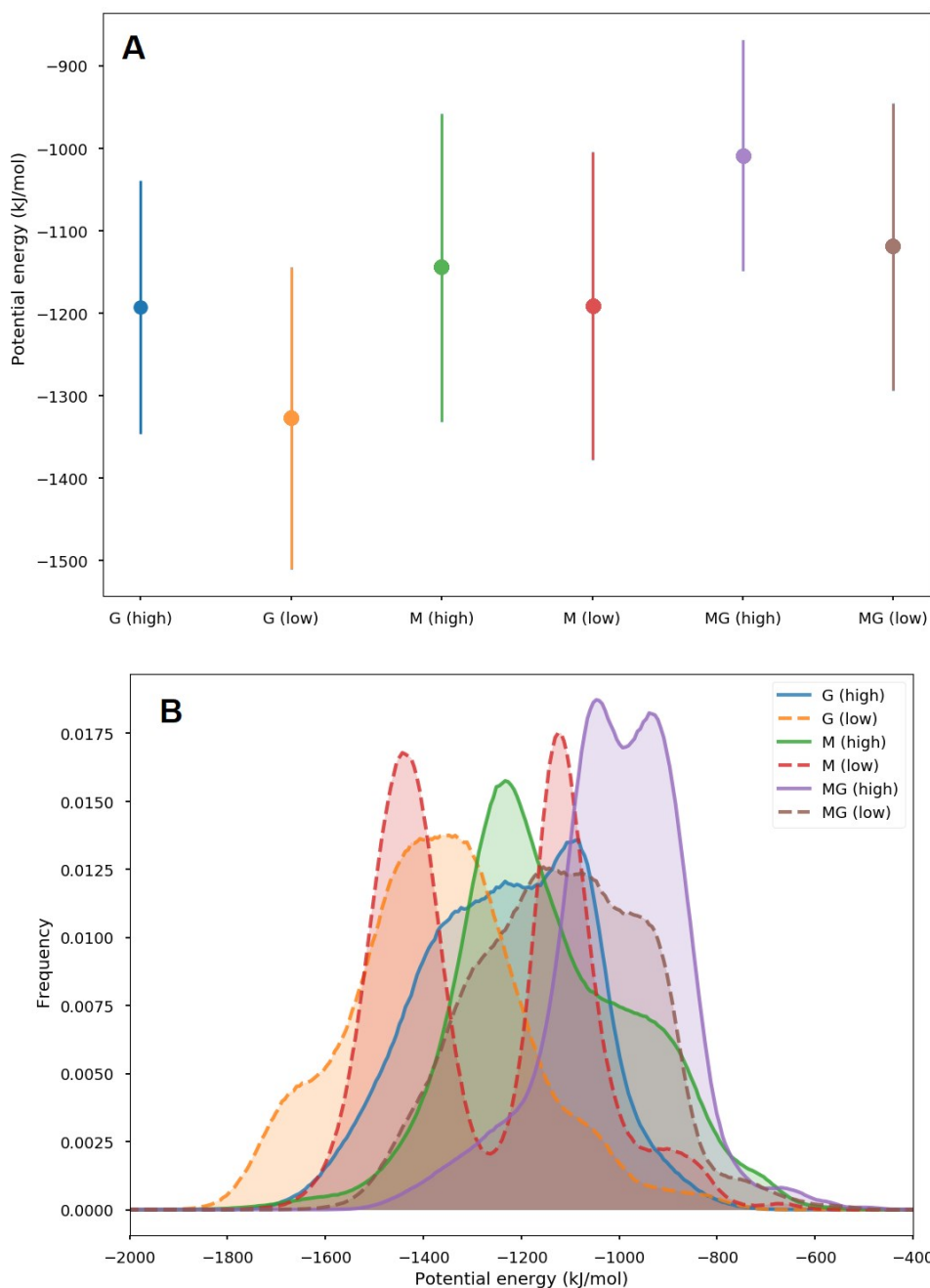


Figure S6: Average (A) and histograms (B) of the interaction energies between alginate oligomers (DP = 12) and a chitosan oligomer (DP = 8), obtained in MD simulations lasting 100 ns. The average interaction energy is lowest for the G oligomer with a low concentration of salt and largest for the MG-oligomer with a high concentration of salt.

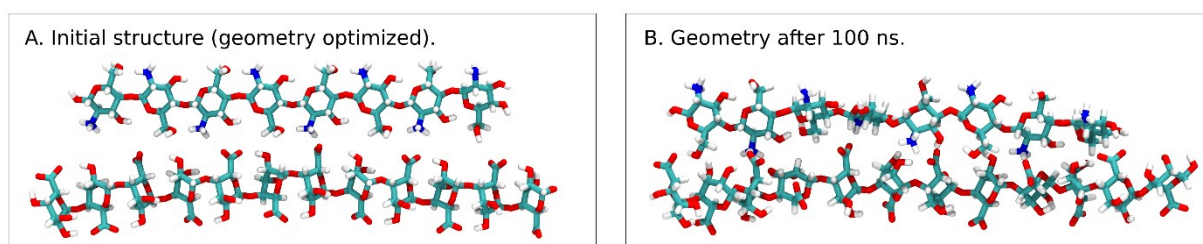


Figure S7: Simulation snapshots of the alginate G-oligomer and a chitosan oligomer (DP = 8) for a low concentration of salt (salt ions are not shown). (Left) The initial geometry optimized structure. (Right) The structure after a MD simulation lasting 100 ns. In this case, distortions of the molecular structures allow for a closer approach of charged groups in the molecules.

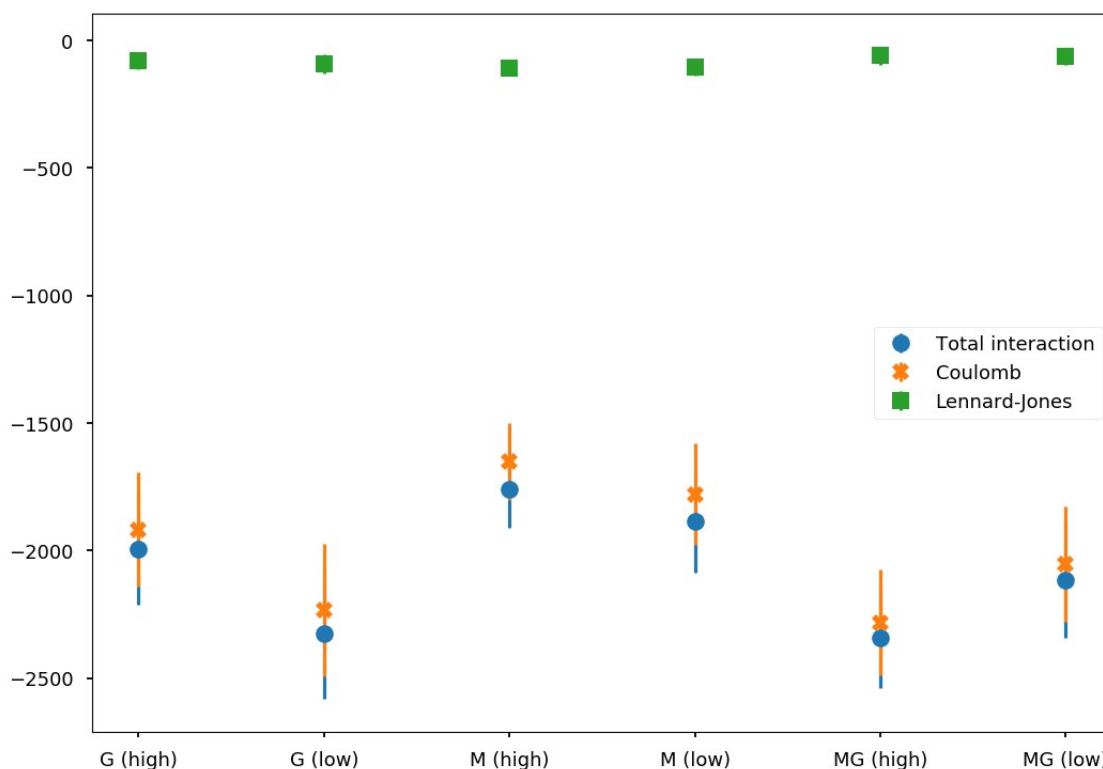
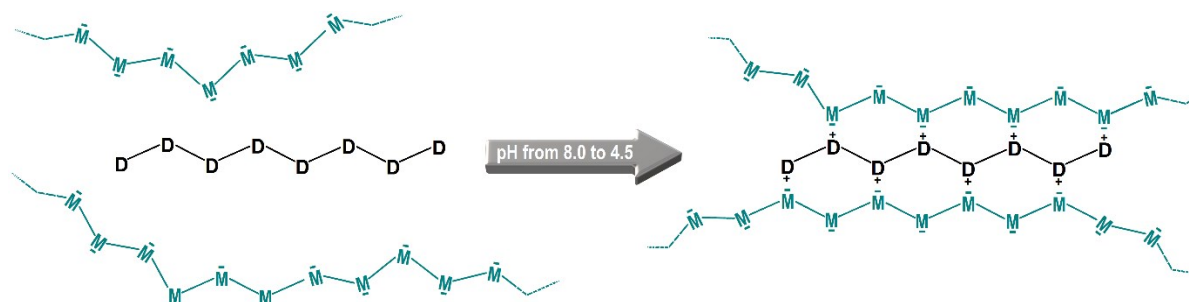


Figure S8: Average interaction energy between alginate (DP = 12) and chitosan (DP = 8) oligomers for 2:1 alginate:chitosan mixtures and high and low ion (Na^+/Cl^-) concentrations.



Scheme S1: Schematic illustration of the interaction between a chitosan oligomer (black) and poly-M alginate (green) at different pHs. Monosaccharide units: glucosamine (D), mannuronate (M). At $\text{pH} \leq 8$ the amino groups of chitosan are mostly uncharged, while the carboxyl groups of alginate are mostly charged. At $\text{pH} 4.0\text{--}5.0$ both chitosan and alginate are predominantly charged, leading to ionic crosslinking of the two components and a zippier-like chain alignment due to the similar charge distance in both compounds.