

Microgel and coacervate formation in polyelectrolyte/multivalent ion mixtures

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When polyelectrolytes and oppositely-charged multivalent ions are mixed in aqueous solutions, they can self-assemble into an array of soft materials and complex fluids, ranging from micro- and nanoparticles, to coacervates, to macroscopic gels. Here, we describe the formation and useful/interesting properties of two such materials: (1) submicron particles formed via ionotropic gelation of the cationic polysaccharide chitosan with triphosphosphate (TPP); and (2) coacervates prepared from mixtures of the synthetic polycation poly(allylamine hydrochloride) (PAH) with either TPP or pyrophosphate (PPi). For chitosan/TPP particles (which are widely explored as potential drug carriers) we show how, by inhibiting chitosan/TPP binding, monovalent salt (NaCl) can be used to: (1) drastically slow down the rapid ionotropic gelation process to facilitate the experimental analysis of how these particles form; (2) enhance the stability of these particles to aggregation; and (3) achieve improved control over particle size.

Unlike the gel-like chitosan/TPP ionic networks, which are both soft (with 10^3 - 10^4 Pa storage moduli) and water-rich, mixtures of PAH with TPP and PPi form high-modulus, putty-like coacervates with storage moduli above 10^5 Pa and much lower (26 - 40 wt%) water contents. These moduli and water contents evidently reflect the high ionic crosslink densities enabled by the densely-charged and flexible PAH chains, and strong PAH/PPi and PAH/TPP binding (which also imparts these coacervates with long relaxation times). Besides their bulk properties, we show that the coacervates adhere to diverse substrates (both hydrophilic and hydrophobic) and, when used as wet adhesives, deliver short-term tensile adhesion strengths above 10^5 Pa. Further, the dense crosslinking within PAH/PPi and PAH/TPP coacervates makes them strong barriers to solute diffusion and (regardless of the solute-coacervate binding strength) enables them to release small water-soluble molecules over multiple months. These findings suggest that PAH/PPi and PAH/TPP coacervates can provide a simple route to both underwater adhesion and long-term controlled release.