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Multi-Scale Structure of Coacervates formed by Oppositely Charged Polyelectrolytes[1]

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We develop a scaling model of coacervates formed by oppositely charged polyelectrolytes and demonstrate that they self-organize into multi-scale structures. The intramolecular electrostatic interactions in dilute polyanion or polycation solutions are characterized by the electrostatic blobs with size D_- and D_+ respectively, that repel neighboring blobs on the same chains with electrostatic energy on the order of thermal energy kT. After mixing, electrostatic intramolecular repulsion of polyelectrolytes with higher charged density, say polyanions, keeps these polyanions in coacervates aligned into stretched arrays of electrostatic blobs of size $D_- < D_+$ on length scales smaller than inter-polyanion distance $\xi_- \approx D_-^{1/4} D_+^{3/4}$ in a θ-solvent for uncharged backbones, while their conformations are random walks on larger length scales. Weaker charged polycations adsorb on stronger charged polyanions forming a screening "coat" around them analogous in its structure to a semidilute solution of uncharged polymers with correlation length $\xi_+ \approx D_-^{-1/8} D_+^{9/8}$ and random walk confromations on all length scales. In this coat, the electrostatic attraction of polycations to polyanions is balanced by the short-range repulsion between sections of polycations. This attraction slowly decreases in strength with increasing distance from a polyanion due to screening by the polycation "coat" resulting in a slow decrease of coat concentration. The inter-polyanion correlation length ξ_- is determined by the length scale at which the polycation "coat" compensates the polyanion charge. The relative values of length scales in the coacervate are $D_- < \xi_+ < \xi_-$. The opposite charges form bound pairs and larger ionic clusters at higher strength of electrostatic interactions resulting in the formation of mixed ionic/"screening coat" coacervates and eventually at the highest electrostatic strength – in ionic networks of comb/bottlebrush-like polyanion backbones with polycation loops and bridges. These coacervate networks are super-tough, can be used for microencapsulation and drug delivery, and can also function as underwater glue.

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