

The three possible states of polyelectrolyte complex coacervates: soluble, dispersed & macroscopic phase.

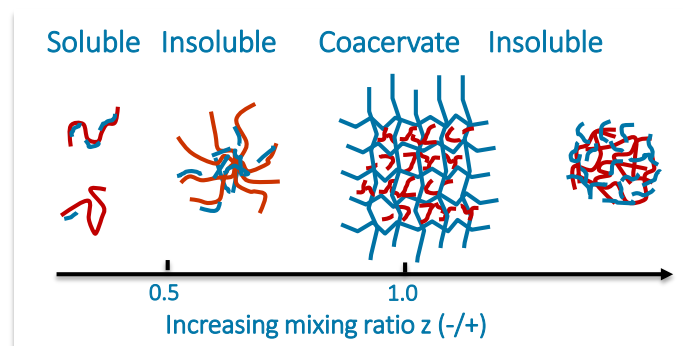
J.-P. Chapel^{a*}, X. Liu^{a,b}, M. Haddou^{a,b}, C. Pucci^{a,b}, J. Giermanska^a, Ch. Schatz^b

a. CRPP, CNRS - Univ. Bordeaux, 115 Av. A. Schweitzer 33600 Pessac.

b. LCPO, CNRS- ENSCPB - Univ. Bordeaux, 16 Av. Pey-Berland 33607 Pessac.

*chapel@crpp-bordeaux.cnrs.fr

Complex coacervation is a well-known liquid-liquid phase separation resulting from the electrostatic interaction of oppositely charged polyelectrolytes (PEs) or colloids. We put forward SANS evidences of the local structures of the three distinctive association states found in a model PANA/PDADMAC [1] coacervating system, i.e., soluble and dispersed PECs together with the coacervate phase. We show the unambiguous presence of the very controversial soluble complexes between PEs with a large chain length asymmetry. Indeed, with just few short guest chains, the long host chain holds the characteristic of a charged PE, that is, its water solubility in a thermodynamic sense. With more short chains, the hydrophobic segments start to associate and microphase separate generating dispersed PECs. The core-shell structure evolves into compact sphere as the mixing charge ratio Z approach 1. Soluble PECs are absent for more symmetric systems or in the presence of salt where only dispersed PECs are obtained. At stoichiometry ($Z=1$) complex coacervation occurs. This dense phase can be regarded as a network of random mixed polyanion chains with a mesh size much smaller than the R_g of PE chains. An additional scattering maximum is found in our system at high q arising from the relatively stiff PDADMAC cylinders (non-electrostatic persistence length ~ 3 nm), randomly distributed in the concentrated network as anticipated by the “jammed state” proposed by the Rawiso’s group. [2]



[1] Liu et al. *Soft Matter* (2016), 12, 9030 & *Adv. Col. Int. Sci.* (2017), 239, 178.

[2] Lorchat et al. *EPL*, **106** (2014) 28003.