

## **Dense solutions of polyelectrolytes and interpolyelectrolyte complexes**

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The intrinsic stiffness of polyelectrolytes plays an essential role in the structure of their dense solutions and the ones of interpolyelectrolyte complexes.

First, we will report SAXS and SANS experiments performed on dense aqueous solutions of highly charged polyelectrolytes that reveal the existence of an Onsager transition preceded by a new regime, both depending on the intrinsic stiffness of the macroions as well as the ionic strength of the solutions. Four macroions with increasing non-electrostatic persistence length will be considered: poly(styrene sulfonate) (PSS); poly( $\alpha$ -methyl styrene sulfonate) (P $\alpha$ MSS); poly(diallyl-dimethyl ammonium) (PDADMA); hyaluronan (HA).

Second, we will report SAXS and SANS experiments performed on aqueous solutions of model interpolyelectrolyte complexes. The complexation between polycations and polyanions in the semidilute and concentrated regimes can then be described as a gelation process. This analogy is reliable for both couples PSS-PDADMA as well as HA-PDADMA and can be considered as universal. There is however a difference between these two complexes, which is associated with the primary self-assembling process. PSS and PDADMA interact through monomer units forming point junctions randomly dispersed in the semidilute or concentrated solution, while HA and PDADMA interact through long sequences of macroions. This results from the difference in the polyanion intrinsic stiffness.