

Chain Flexibility in Asymmetric Polyelectrolyte Complexation

A. Shakya, M. Girard, J. T. King and M. Olvera de la Cruz* *Macromol.* 53, 1258-1269 (2020)

Coarse-grained molecular dynamics simulations revealed the role of chain flexibility in the complexation of short negatively charged polyelectrolytes with long positively charged polyelectrolytes. At low ionic strengths, spontaneous segregation of chains into a condensed (polymer-rich) phase and a supernatant (polymer-depleted) phase is observed. When both the polyanion and polycation are flexible (flexible–flexible complex), denser complexes with a higher degree of structural correlation form, with fewer free chains released into the supernatant, compared to the case when the polyanion is rigid (rigid–flexible complex), in agreement with the LLPS experiments. Salt ions highly partitioned into the condensed phase for flexible–flexible complexes. The results provide molecular-level insights into LLPS of asymmetric polyelectrolyte complexation.

