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STAR-BRANCHED POLYELECTROLYTES AS SOFT, pH- AND THERMORESPONSIVE COLLOIDS

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Star-branched macromolecules composed of many branches (arms) which exhibit pH or/and thermo-sensitive properties exemplify multi-responsive soft polymeric nano-colloids capable to change their size/shape as a function of specific variation in environmental conditions. We present a theoretical study of conformations and conformational transitions in star-branched polyelectrolytes (PEs) in dilute aqueous solutions by combining analytical mean field approach, numerical Scheutjens-Fleer self-consistent field (SF-SCF) method and molecular dynamics (MD) simulations. The generalized Poisson-Boltzmann (PB) approach is exploited for analysis of conformations of branches and distribution of counterions in salt-free solution of strongly ionized PE stars. We prove that localization of major fraction of counterions in the star corona reduces electrostatic potential and leads to fairly uniform distribution of remaining free counterions outside the star corona.

We demonstrate that an interplay of long-range repulsive and short-range attractive (arising under poor solvent conditions, e.g. above LCST) intra-molecular forces with branched topology leads to novel features in collapse transition and phase separation in solution of PE stars. It is demonstrated, that in the case of weak, i.e., pH sensitive PE stars, coupling between conformation and ionization states strongly influences the character of the transition. An analytical mean-field theory predicts different scenario of collapse transition which is either progressive, or involvs intra-molecular microphase segregation depending on pH and ionic strength in the solution. The predictions of analytical theory are compared to results of MD simulations which indicate possibilities of formation of pearl-necklace structures in course of collapse. Our results are compared to recent experiments on star-like thermo- and pH sensitive PE as well as on spherical PE brushes.