Associative and Segregative Liquid-Liquid Phase Separation in Macromolecular Solutions

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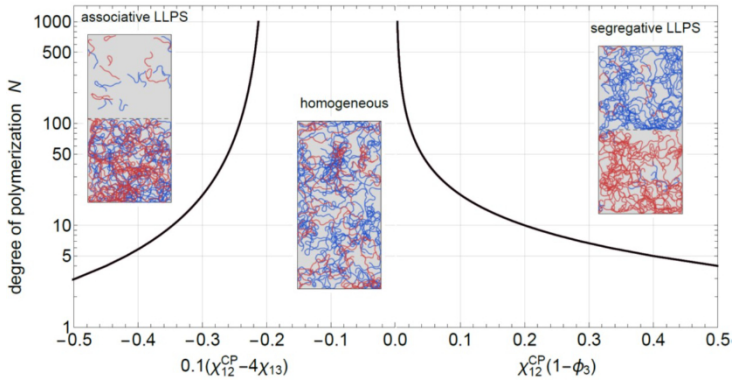
We investigated liquid-liquid phase separation (LLPS) and interfacial properties of two LLPS modes: associative (ALLPS) and segregative (SLLPS). Analytical expressions for the critical point (CP) and binodal boundaries are derived and show excellent agreement with self-consistent field (SCF) lattice computations.
Distinct thermodynamic features differentiate ALLPS from SLLPS: (1) in ALLPS, polymers co-concentrate within a single dense phase coexisting with a solvent-rich phase, whereas in SLLPS each polymer forms a separate phase; (2) the attractive interaction per monomer in ALLPS is strongly dependent on solvent quality, but solvent independent in SLLPS; and (3) ALLPS binodals exhibit near-universal behavior, largely independent of solvent content.
SCF results further show that interfacial tension increases and interfacial width decreases with distance from the CP. We provide scaling relations for both quantities. Compared with SLLPS, ALLPS displays higher interfacial tension and a thinner interface, reflecting distinct molecular organization at the liquid-liquid boundary.

Keywords:
Liquid–liquid phase separation; Associative phase separation; Segregative phase separation; Polymer mixtures; Interfacial tension; Interfacial width



LLPS phase diagram: associative, homogeneous, and segregative regimes for symmetric polymers.