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Thermodynamics and Dynamics of Hetero-Associative Polymer Solutions and Gels

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Polymer associations due to the formation of reversible bonds between different groups (heterotypic A-B type) are qualitatively different from pairwise associations of the same groups (homotypic A-A type). The degree of conversion for A-B associations is lower than for A-A associations and depends on the stoichiometry of the associating groups. We predict re-entrant sol-gel-sol transitions for solutions of heterotypic A-B associating polymers as functions of stoichiometry. Both A-B gelation and phase separation are suppressed relative to A-A solutions, with phase diagrams for both dependent on solvent quality. Chemical incompatibility between A and B polymers results in competition between A-B association-induced attractive phase separation and incompatibility-driven repulsive phase separation. An example of A-B associating solutions is a coacervate of oppositely charged polyelectrolytes. Weak associations between oppositely charged polyelectrolytes (less than thermal energy kT per charge) with asymmetry of the polyanion and polycation line charge densities form double-semidilute solutions. Dynamics of higher charged polymers in these asymmetric coacervates are slower due to dynamic coupling between polyanions and polycations, including reptation of higher charged polyelectrolytes along the confining tubes of lower charged polyelectrolytes. Strong associations with binding energy higher than thermal energy kT form reversible gels, and, in the case of asymmetry of charge line density, these networks have bottlebrush or star-brush symmetry and unusual properties.

References:

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