

# PHASE BEHAVIOR OF COLLOID-POLYMER MIXTURES WITH UNARY OR BINARY DEPLETANTS

Jacinta Conrad, Chemical and Biomolecular Engineering, University of Houston  
 jconrad@uh.edu  
 Nayoung Park, Chemical and Biomolecular Engineering, University of Houston

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Submicron particles suspended in solutions containing surfactants, polymers, micelles, or other species are widely used in materials shaping and forming processes, including three-dimensional printing and nanocomposite processing, and in technical applications as paints, coatings, inks, and drilling muds. These applications require control over suspension rheology and microstructure, which are affected by interactions between the different constituents. Practically, constituents of high dispersity in size or molecular weight are inexpensive and hence widely used; fundamentally, the effects of size dispersity on suspension properties remain poorly understood when the particles exhibit attractive as well as repulsive interparticle interactions. As simple models of practical suspensions we formulate mixtures of submicron poly(methyl methacrylate) (PMMA) particles suspended in solutions of non adsorbing polystyrene polymers, which generate a controlled entropic depletion attraction between the particles. Here, I will discuss studies in which we investigate the effect of polymer dispersity on the phase behavior, microstructure, and rheology of colloid-polymer mixtures. We added unary or binary mixtures of polystyrene as the depletant to suspensions of charged PMMA particles. The structure and dynamics of the particles were compared over three sets of samples with various mixtures of two different polystyrenes whose size varied by an order of magnitude. The structure and dynamics were nearly independent of depletant dispersity if the polymer concentration was represented as a sum of normalized concentrations of each species. Near the transition region between a fluid of clusters and an interconnected gel at intermediate volume fractions, partitioning of polymers in a binary mixture into colloid-rich and polymer-rich phase leads to a slightly different gelation pathway. Hence this work suggests that polymers of high dispersity, which are more affordable than uniformly distributed polymers, can be used for applications requiring certain final structures if all polymers in the distribution are small compared to the particles and if the desired phase behavior is far from non-equilibrium boundaries. It also suggests the ability to tune the final polymer concentration by mixing polymers of different sizes to control particle phase behavior in solution.

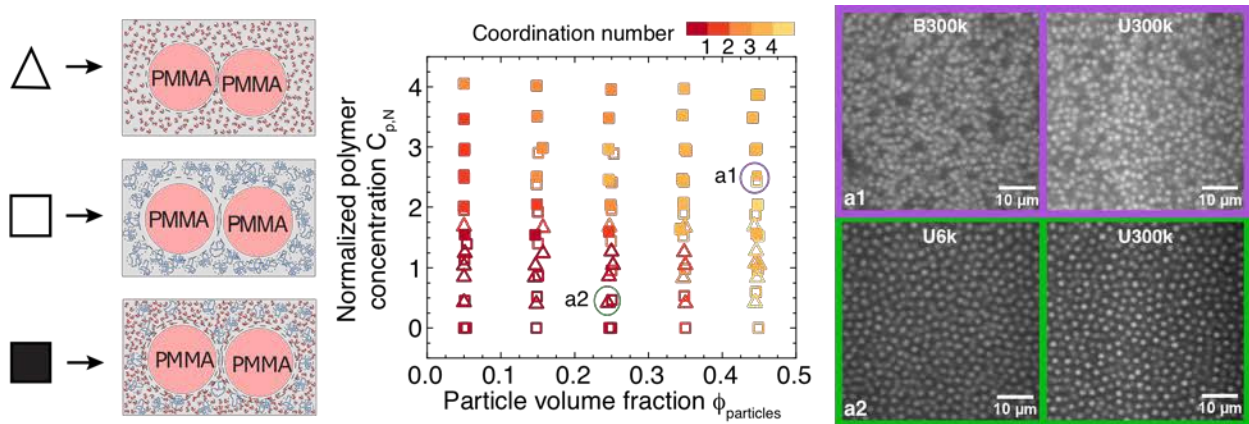


Figure 1 – The phase behavior of colloid-polymer mixtures containing unary (open symbols) and binary (closed symbols) depletants can be superimposed on a single phase diagram as a function of the particle volume fraction ( $\phi$ , x-axis) and a normalized polymer concentration ( $C_{p,N}$ , y-axis). Confocal micrographs (right) acquired a height of 30  $\mu\text{m}$  above the bottom of the sample chamber confirm that samples with similar ( $\phi$ ,  $C_{p,N}$ ) exhibit nearly identical structure (as quantitatively characterized via coordination number and density fluctuations); similarly, analysis of time series of confocal micrographs confirms that these samples exhibit nearly identical dynamics (as characterized via particle mean-square displacements).