Phase Behavior of Colloid-Polymer Depletion Mixtures with Unary or Binary Depletants

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Supplemental Information 1 (SI1): Supplemental Figures

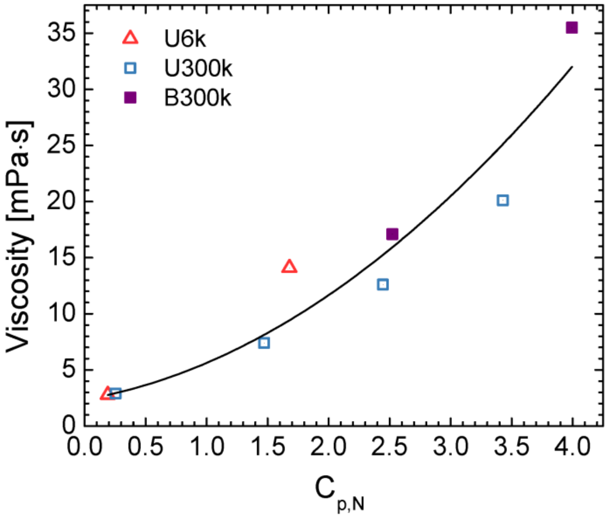

Figure S1: Viscosity of polystyrene solutions in mixture of decahydronaphthalene and cylohexyl bromide. The quadratic fit to the curve, $\eta = 2.36 + 1.88C_{p,N} + 1.39C_{p,N}^2$, resulted in $R^2 = 0.96$ with a y-intercept of 2.36 mPa·s, which was the viscosity of the pure solvent.

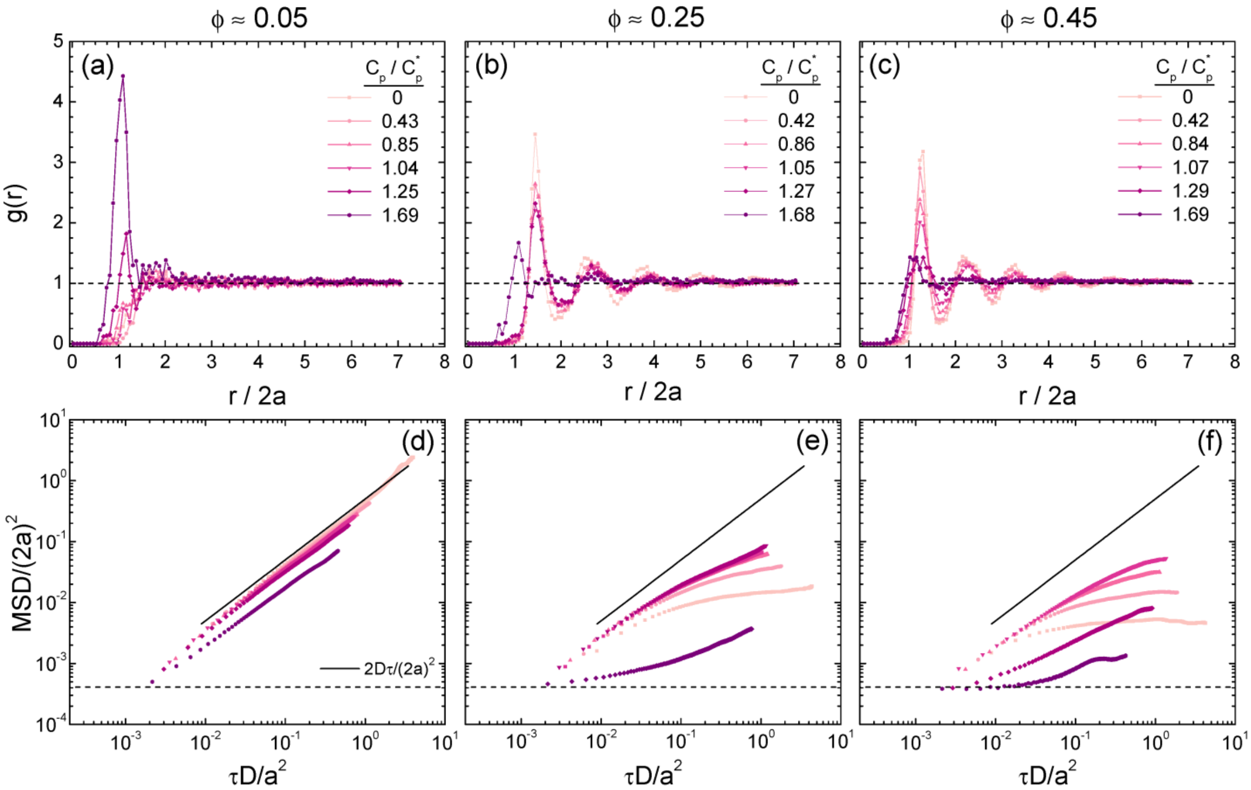

Figure S2: (a-c) Radial distribution function $g(r)$ as a function of normalized distance from the center of particle r / 2a. (d-f) Normalized mean squared displacement MSD/(2a)^2 as a function of non-dimensional delay time $\tau D/a^2$ for PMMA suspensions with various concentrations of 6.40 kDa PS (C_p/C_p^*). The particle volume fractions are (a,d) $\phi \approx 0.05$, (b,e) $\phi \approx 0.25$, or (c,f) $\phi \approx 0.45$. The dashed lines in (a-c) indicate the limiting value of $g(r)$ at large r ($g(r)$ = 1); the dashed lines in (d-f) indicate the resolution of the tracking algorithm $\varepsilon^2/(2a)^2$.

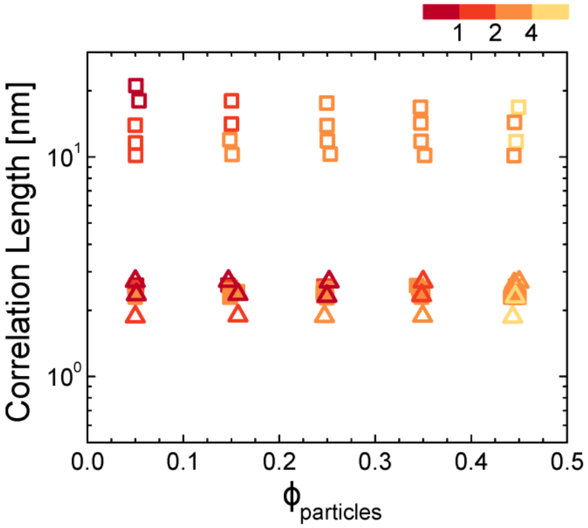

Figure S3: Color plot of the coordination number as a function of correlation length ξ and particle volume fraction ϕ for PMMA suspensions with unary (open) and binary (closed) mixtures of PS added at concentrations above the overlap concentration. Poor agreement with the values of the coordination number for samples with unary and binary depletants indicates that this metric cannot describe the phase behavior across all sample compositions. Samples U6k, U300k, and B300k are shown. *Symbol key*: △ U6k, □ U300k, ■ B300k.

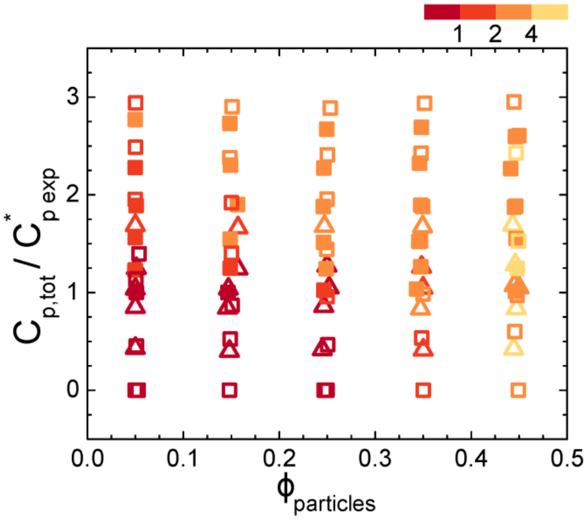

Figure S4: Color plot of the coordination number as a function of polymer concentration normalized by an average overlap concentration and particle volume fraction ϕ for suspensions of PMMA particles with unary (open) and binary (closed) mixtures of PS added as depletant. Poor agreement of the values of the coordination number for samples with unary and binary depletants indicates that this metric cannot describe the phase behavior across all sample compositions. Samples U6k, U300k and B300k are shown. *Symbol key*: △ U6k, □ U300k, ■ B300k.

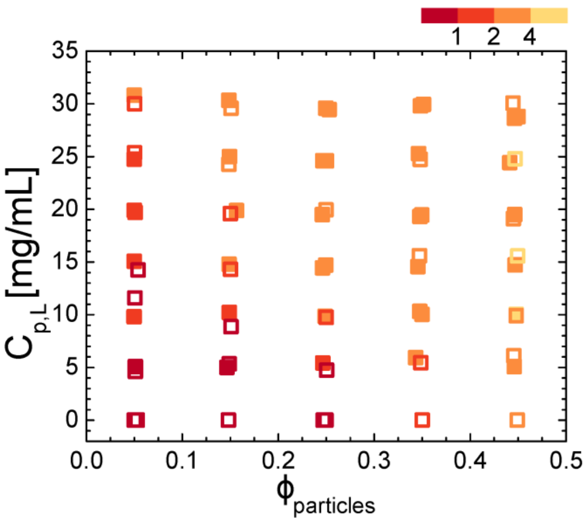

Figure S5: Color plot of the coordination number as a function of larger polymer concentration and particle volume fraction ϕ for suspensions of PMMA particles with unary (open) and binary (closed) mixtures of PS. Poor agreement of the values of the coordination number for samples with unary and binary depletants indicates that this metric cannot describe the phase behavior across all sample compositions. Samples U300k and B300k are shown. *Symbol key*: □ U300k, ■ B300k.

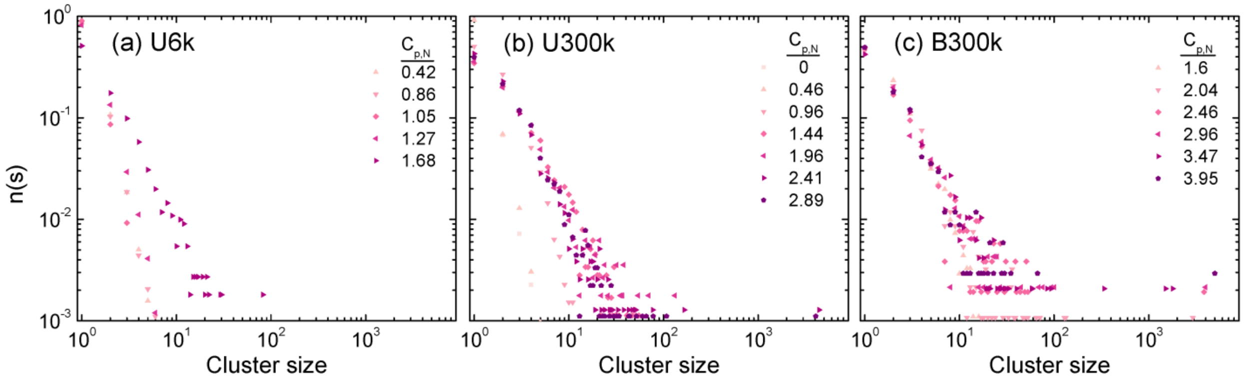

Figure S6: Fraction of clusters $n(s)$ of size s as a function of s for the three sets of samples at $\phi = 0.25$.

Supplemental Information 2 (SI2): Estimates of pairwise interactions between particles:

To estimate the electrostatic interactions between the PMMA particles, we measured the radial distribution function $g(r)$ of a low-volume-fraction sample at $\phi \approx 0.01$ with approximately 1.5 mM TBAC, but without added PS. Sixty z-stacks were captured and analyzed as described in the Materials and Methods section in the main text. The $g(r)$ data at this low volume fraction was translated to the pairwise interaction potential between the particles via $\lim_{\phi \to 0} g(r) =$

$\exp[-u(r)/k_BT]$.[1, 2] The screened Coulomb potential $\frac{\mathrm{u(r)}}{k_BT} = \frac{a^2}{\lambda_B}\left(\frac{e\zeta}{k_BT}\right)^2 \frac{\exp(-\kappa(r-2a))}{r}$ [3, 4] was fit to the $u(r)$ data, and the resulting fit was translated back to $g(r)$ for comparison with the experimental data (Figure S7). The fit gave estimates for zeta potential (ζ) of -4.4 mV and for Debye length (κ^{-1}) of 480 nm. Using the estimated $u(r)$ from $g(r)$, we also calculated an effective hard sphere diameter: $d = 2a + \int_{2a}^{\sigma}[1 - \exp(-u(r)/k_BT)]\mathrm{d}r$,[3, 5, 6] where d is the effective hard sphere diameter, a is the particle radius, and σ is the radial distance at which $u(r) = 0$. We numerically integrated the $u(r)$ data using the trapezoidal rule to calculate the effective diameter: $d = 2300$ nm. This diameter was 16% larger than the diameter measured using DLS.

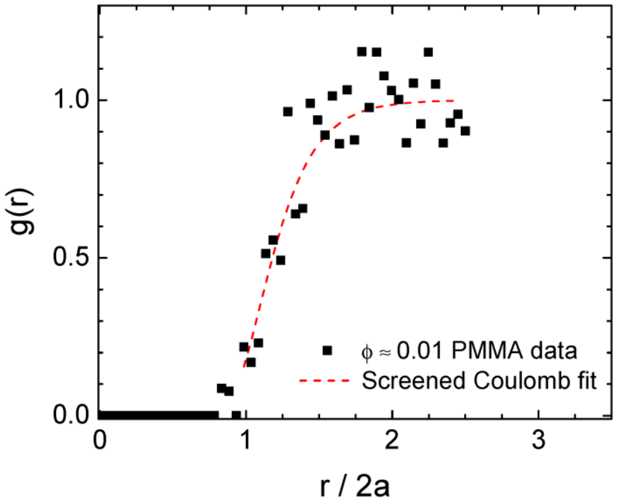

Figure S7: The radial distribution function $g(r)$ of a $\phi \approx 0.01$ PMMA suspension without added PS as a function of normalized radial distance (r / $2a$). The symbols are the data, and the dashed line is the screened Coulomb equation fitted to the data.

SI References:

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2. C. P. Royall, W. C. K. Poon and E. R. Weeks, *Soft Matter*, 2012, **9**, 17-27.
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