In Silico Design Enables the Rapid Production of Surface-Active Colloidal Amphiphiles

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Simulations with Block Copolymer Alone

First, we studied the behavior of amphiphilic BCPs alone in the system. Figure S1 shows the number of micelles in the system for different values of the length of the hydrophilic block of the BCPs, $f_{\text{phil}}$, as a function of BCP concentration, $C_{\text{BCP}}$. For BCPs with small values of $f_{\text{phil}}$, 0.09 and 0.39, the BCPs aggregated into a single micelle, since the hydrophilic blocks were too short to stabilize small aggregates. In contrast, for $f_{\text{phil}} = 0.70$, several micelles were present in the system, indicating the strength of the steric barrier provided by the hydrophilic blocks. For the largest value of $f_{\text{phil}} = 0.91$, no micelles were formed for the entire range of $C_{\text{BCP}}$; the self-assembly behavior of these BCPs was dominated by the hydrophilic blocks, which remained dispersed in the final solvent-antisolvent mixture. We also calculated the number fraction of BCPs aggregated into micelles, $\Phi_{\text{phil}}^0$. For $f_{\text{phil}} = 0.09, 0.39,$ and 0.70, all BCPs were incorporated in a micelle, resulting in $\Phi_{\text{phil}}^0 = 1$. In contrast, for $f_{\text{phil}} = 0.91$, BCPs were dispersed as free chains in solution and $\Phi_{\text{phil}}^0 = 0$, confirming the conclusion made from Figure S1.

![Figure S1](image.png)

**Figure S1.** Number of micelles, $N_{\text{micelle}}$, in the system as a function of BCP concentration, $C_{\text{BCP}}$, at various BCP compositions, $f_{\text{phil}}$, as indicated.
Block Copolymer Adsorption on Colloid Surfaces

The number fraction of BCPs adsorbed on the surface of a colloid, $\Phi_{\text{phil}}$, was calculated for systems with different BCP compositions from $f_{\text{phil}} = 0.09$ to 0.91. For BCPs with $f_{\text{phil}}$ values of 0.09, 0.26, 0.39, and 0.70, all BCP chains adsorbed on the colloid surface resulting in $\Phi_{\text{phil}} = 1$. For the most hydrophilic BCP with $f_{\text{phil}} = 0.91$, as the block copolymer content, $C_{\text{BCP}}$, increased, more of the BCP chains remained dissolved in the solvent and did not adsorb on the colloid surface, resulting in $\Phi_{\text{phil}} < 1$, as shown in Figure S2.

Figure S2. Number fraction of BCPs on the colloid surface, $\Phi_{\text{phil}}$, for BCP composition with $f_{\text{phil}} = 0.91$. For all other values of $f_{\text{phil}}$, $\Phi_{\text{phil}} = 1$. 
Properties of the Hydrophilic Block of BCP (PEG) on the Colloid Surface

Brush Density:

The brush density of the hydrophilic block of the BCPs, $\sigma$, was calculated using

$$\sigma = \frac{n}{4\pi R_{\text{core}}^2}$$  \hspace{1cm} (S1)

where $n$ is the number of BCP chains adsorbed on the colloid surface, $R_{\text{core}}$ is the radius of the colloid core consisting only of hydrophobic beads (the hydrophobic part of the BCPs and the homopolymers). Figure S3 shows the brush density of the hydrophilic block for various $f_{\text{phil}}$ and $C_{\text{BCP}}$. For $f_{\text{phil}} = 0.09$, 0.26, and 0.39, the brush density, $\sigma$, increased with increasing number of BCP chains ($C_{\text{BCP}}$) in the system. This trend indicates that all the BCPs in the system adsorbed on the colloid surface. The values of $\sigma$ grew slightly as $f_{\text{phil}}$ increased at a fixed $C_{\text{BCP}}$ because the total polymeric mass was held constant in the system and the amount of hydrophobic beads, i.e. $R_{\text{core}}$, was larger for the system with shorter hydrophilic blocks (small $f_{\text{phil}}$). A rather different result was obtained for $f_{\text{phil}} = 0.91$, where the brush density grew only slightly with $C_{\text{BCP}}$, since the fraction of BCPs adsorbed on the colloid surface was decreasing (see Figure S2).

![Figure S3. Hydrophilic brush density as a function of the BCP composition, $f_{\text{phil}}$, and BCP content, $C_{\text{BCP}}$, as indicated.](image)

Hydrophilic Block Conformation:

An analysis of the eigenvectors describing the hydrophilic block of the BCP was performed to gain insights on the conformation of the polymer chain on the colloid surface. First, we computed the radius of gyration tensor of each BCP on the colloid surface, considering only hydrophilic beads. We then identified the eigenvalues and the corresponding eigenvectors of each hydrophilic block. In our convention, the first eigenvalue corresponds to the smallest dimension of a hydrophilic block, while the third eigenvalue corresponds to the largest one. Then, we calculated the probability density distributions.
of the average angle, \( P(|\cos \theta_i|) \), between each eigenvector, \( \mathbf{e}_i \), \( i = 1, 2, 3 \), and the vector connecting the center of mass (CM) of the colloid to the first bead of the hydrophilic block, \( \mathbf{r} \) (see Figure S4). (The eigenvector \( \mathbf{e}_i \) is denoted as director \( \mathbf{n} \) in the main manuscript.) For these calculations, the vectors were obtained from snapshots of the final equilibrium morphology.

![Figure S4](image)

**Figure S4.** Probability density distributions of the average angle, \( P(|\cos \theta_i|) \) for \( i = 1, 2, 3 \), between the eigenvectors of a hydrophilic block, \( \mathbf{e}_i \), and the adsorption point of the block, \( \mathbf{r} \). Results are shown for BCPs with \( f_{\text{phil}} = 0.70 \) and \( C_{\text{BCP}} = 10\% \).

The distribution of the average angles, \( P(|\cos \theta_i|) \), for \( f_{\text{phil}} = 0.70 \) is shown in Figure S5, for a Janus colloid with \( C_{\text{BCP}} = 10\% \), but similar behavior was also observed for core-shell colloids prepared with \( C_{\text{BCP}} = 40\% \). The eigenvector \( \mathbf{e}_1 \) was parallel or anti-parallel to the vector \( \mathbf{r} \) and the highest values of \( P(|\cos \theta_i|) \) were at \( |\cos \theta_1| = 1 \). The distribution, \( P(|\cos \theta_3|) \), for the angle between the eigenvector \( \mathbf{e}_3 \) and \( \mathbf{r} \) had a maximum at \( |\cos \theta_3| = 0 \), indicating that the hydrophilic block was oriented orthogonal to the colloid surface.

**Number density distribution of hydrophilic beads:**

The number density of hydrophilic block, \( \rho_C \), was calculated with respect to the radial distance from the surface of a colloid for \( f_{\text{phil}} = 0.70 \) for selected \( C_{\text{BCP}} \) studied (see Figure S4). The magnitude of the number density increased with increasing the concentration of BCP in the system, since more BCPs adsorbed at the surface of the colloids. However, as \( C_{\text{BCP}} \) increased, the position of the peak slightly shifted to larger distances farther away from the colloid surface, which indicates more stretched conformations of the hydrophilic block.
Figure S5. Number density of beads in the hydrophilic block, $\rho_C$, with respect to the radial distance from the surface of a colloid, $r - R_{\text{core}}$.

Temporal evolution of the potential energy for $C_{\text{BCP}} = 10\%$ and $C_{\text{BCP}} = 50\%$:

Figure S6. Potential energy per particle, $E/N$, as a function of simulation time step for systems with $f_{\text{phil}} = 0.39$ at $C_{\text{BCP}} = 10$ and 50%, as indicated. The inset shows the same data as the main plot, but with a logarithmic scale for the x-axis (time step).
Experimental Studies to Probe BCP Adsorption on the PS/PI Colloid Surface

Bare PS/PI Janus particles are stabilized by a net negative surface charge that electrostatically repels the colloids and prevents them from coagulation.\(^1\)-\(^3\) The addition of salt to the colloidal suspension screens the surface charges and reduces the electrostatic repulsion between colloids, causing them to coagulate at sufficiently high salt concentrations – critical coagulation concentration (CCC).\(^4\) Particle size was measured by dynamic light scattering (DLS) technique at salt concentrations varied between 0.0002 M and 2 M KCl and a constant colloid concentration of 0.17 mg/mL. Figure S7a-c shows the average diameter of PS/PI colloids, normalized by their initial size as a function of KCl concentration and \(C_{BCP}\) for three different \(f_{phil}\). PS/PI Janus colloids with 1% BCP became unstable at a salt concentration between 0.002 M and 0.02 M regardless of \(f_{phil}\). However, increasing \(C_{BCP}\) to 5% was enough to keep the colloids stable when the PEG brush was the long at \(f_{phil} = 0.74\). This indicates a transition from the electrostatic colloidal stabilization mechanism to the steric mechanism. At intermediate BCP contents (10% to 30%), where a Janus structure is expected (see Figure 3 in the manuscript), a gradually increasing trend in the particle size was observed as the salt concentration increased. This trend, which was not observed for homogenous PS colloids with BCP (Figure S7d), can be potentially attributed to the clustering of Janus colloids with their PI domains with the PEG-covered PS domains facing the aqueous environment – see the schematics in Figure S7e. In such clusters, PI may also fuse resulting in one large colloid. The increase in the particle diameter was between 1.5 and 3 times the original diameter, which corresponds to a clustering of two to three Janus colloids. This behavior also implies that the BCP covered only the PS domain of PS/PI Janus colloids making the Janus colloids amphiphilic. Colloidal stability at 40% BCP contents and high salt concentrations suggests that the amphiphilic BCP formed a PEG corona around the colloids (a core-shell structure as shown in Figure 3 in the manuscript) that sterically repels them against aggregation – see the schematics in Figure S7f. This agrees with the stability of the homogenous PS colloids covered with large loads of PS-\(b\)-PEG BCP as a function of salt concentration (Figure S7d).
Figure S7. The average diameter of PS/PI colloids normalized by their initial size as a function of KCl concentration and $C_{BCP}$ for $f_{phil} = 0.27$, $f_{phil} = 0.55$, and $f_{phil} = 0.74$ shown in (a), (b), and (c), respectively. (d) The average diameter of PS colloids covered with PS-b-PEG normalized by their initial size as a function of KCl concentration and $C_{BCP}$ for $f_{phil} = 0.74$. (e) and (f) Stability/aggregation of Janus colloids and core-shell, respectively, in the bulk upon the addition of salt.
Pickering Emulsions Stability

The stability of Pickering emulsions generated by amphiphilic Janus colloids may originate from a two-step mechanism: (i) Due to a small $\zeta$-potential (Figure 4b in the manuscript), amphiphilic Janus colloids overcome the small energy barrier against adsorption and assemble at the oil-water interface; (ii) When a dense layer of adsorbed particles forms at the oil-water interface, the oil drops become protected against coalescence (steric stabilization). Formation of a dense layer of colloids is only possible when adsorbed particles at the oil-water interface experience a small energy barrier between themselves at a short separating distance. Therefore, this particle dense layer can only form when PS/PI colloids are amphiphilized with hydrophilic BCP, which significantly reduces the negative surface charge – see Figure 4b in the manuscript. In the case of purely hydrophobic PS/PI Janus colloids, however, the formation of a dense layer of particles could be kinetically limited due to the larger absolute $\zeta$-potential, imposing energy barriers between colloids and against colloidal adsorption at the oil-water interface. These energy barriers slow down the rate of particle adsorption and further prevent particles to form a dense layer at the oil drops. Since the emulsification method carried over in this study was the same for all the cases, we may assume that the equilibrium drop size of the dispersed phase is essentially the same in all tests. With the knowledge of particle size, particle mass concentration, particle density, and oil volume fraction, the size of oil drops can be estimated from a mass balance for particles adsorbed at the oil drops. Accordingly, a mean value of $\sim 173$ $\mu$m is found for the diameter of oil drops that are completely covered by the colloids (a 91% coverage). This oil drop size can be obtained when Pickering emulsions are stabilized by $\sim 100$ nm amphiphilized PS/PI Janus colloids comprising the most hydrophilic BCP ($f_{\text{phil}} = 0.74$). Nonetheless, when 660 nm non-amphiphilic PS/PI Janus colloids are used to stabilize $\sim 173$ $\mu$m oil drops, an interfacial coverage of $<15\%$ may be expected. At this low coverage, the only plausible mechanism of Pickering emulsion stability is the particle bridging between two oil drops which is not subject to the emulsions in this study.

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