Supporting Information

On the transition between a heterogeneous and homogeneous corona in mixed polymeric micelles

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Small angle neutron scattering input parameters

PAA\textsubscript{42}-b-PAAm\textsubscript{417} / PAA\textsubscript{42} and P2MVP\textsubscript{42}-b-PEO\textsubscript{446} / P2MVP\textsubscript{43} mixtures were used in the SANS experiments to gradually vary the amount of EO / AAm monomers in the micellar corona, while keeping $f_+$ fixed at 0.5. Hence, for the C3Ms in this study, we may define a building block as a unit consisting of one equivalent PAA\textsubscript{x}-b-PAAm\textsubscript{y} polymer and one equivalent P2MVP\textsubscript{n}-b-PEO\textsubscript{m} polymer (with $x / n$ including the AA / 2MVP monomers of both the homopolymer and the copolymer) so that $f_+ = 0.5$. For example, for 0% PAAm in the micellar corona ($f_{EO} = 0$), a building block consists of PAA\textsubscript{42} + P2MVP\textsubscript{43}-b-PEO\textsubscript{457} ($f_+ = 0.51$). A building block is present $P_{agg} = P_{agg}^+ = P_{agg}^-$ times in one particle. An overview of the coherent scattering length densities, $\rho_N$, specific volume, $v_0$, and molecular weights, $M_w$ of the C3M building blocks is given in Table S1.

\textbf{Table S1.} Coherent neutron scattering length density in D\textsubscript{2}O, $\rho_N / 10^{10}$ cm\textsuperscript{-2}, specific volume, $v_0 /$ cm\textsuperscript{3} g\textsuperscript{-1}, molecular weight in D\textsubscript{2}O, $M_w /$ g mol\textsuperscript{-1}, and specific refractive index increment in H\textsubscript{2}O, $dn / dc /$ cm\textsuperscript{3} g\textsuperscript{-1} of the building blocks of C3Ms of PAA\textsubscript{42}(-b-PAAm\textsubscript{417}) and P2MVP\textsubscript{42}(-b-PEO\textsubscript{446}) in D\textsubscript{2}O. Input values for $\rho_N$: 6.37 (D\textsubscript{2}O), 1.88 (PAAm in H\textsubscript{2}O), 4.15 (PAAm in D\textsubscript{2}O), 0.68 (PEO), 1.81 (PAA), 1.33 (P2(M)VP), 1.55 (P2VP in H\textsubscript{2}O), 2.15 (P2VP in D\textsubscript{2}O).\textsuperscript{20-22} Input values for $dn / dc$ (mass-weighted additivity is assumed): 0.187 (PAAm), 0.136 (PEO), 0.261 (PAA), 0.27 (P2(M)VP).\textsuperscript{20-22}

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<th>$M_w$</th>
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**2D $^1$H NMR NOESY**

To demonstrate that chemically unlike protons of miscible segments give rise to observable NOE signals, we present a line plot at $\delta = 1.64 \pm 0.01$ ppm (= proton ‘13’, corresponding to PAAm) for C3Ms of PDMAEMA-$b$-PGMA and PAA-$b$-PAAm.\(^8\)

Amongst others, we clearly observe intermolecular NOE interactions with protons 9, 8, 10, and 7 (most pronounced), corresponding to the PGMA segments (Figure S1).

![Figure S1. Line plot at $\delta = 1.64 \pm 0.01$ ppm for C3Ms of PDMAEMA-$b$-PGMA and PAA-$b$-PAAm.](image)

**Light scattering**

Plots of $\Gamma$ (Figure S2a), $R_0(\theta)$ (Figure S2b), and $R(\theta,C)$ (Figure S2c) as a function of $q^2$ for C3Ms of P2MVP$_{42}$($-b$-PEO$_{446}$) and PAA$_{42}(-b$-PAAm$_{417}$) for $0 < f_{EO} < 1$ (1mM NaNO$_3$ D$_2$O, T = 25 °C). The $q^2$-dependence of $\Gamma$ in Figure S2a indicates diffusivity for all C3Ms. Deviations from linearity in the low-$q$ regime in Figure S2b and Figure S2c are caused by dust, aggregate, and/or interparticle interference contributions to the scattering. The input parameters used to obtain $P_{agg}$ and $M_{micelle}$ from the static light scattering experiments are tabulated in Table S1.

**References**

1-19. See main text
Figure S2. (a, b) Cumulant results. (a) $\Gamma$ as a function of $q^2$ and (b) $R_h^\theta$ as a function of $q^2$ for C3Ms of P2MVP$_{42}$-b-PEO$_{446}$/P2MVP$_{43}$ and PAA$_{42}$-b-PAAm$_{417}$/PAA$_{42}$ (1mM NaNO$_3$, D$_2$O, T = 25 °C) with (Δ) 100% EO ($f_x = 0.51$, $C = 7.4$ g l$^{-1}$), (◊) 76% EO ($f_x = 0.51$, $C = 9.1$ g l$^{-1}$), (□) 52% EO ($f_x = 0.51$, $C = 11.6$ g l$^{-1}$), (○) 51% EO ($f_x = 0.51$, $C = 11.4$ g l$^{-1}$), (×) 26% EO ($f_x = 0.51$, $C = 9.1$ g l$^{-1}$), and (+) 0% EO ($f_x = 0.52$, $C = 7.9$ g l$^{-1}$) in the micellar corona. The lines represent (a) a linear extrapolation of $\Gamma$ versus $q^2$ to $q^2 = 0$. Results in terms of $R_h^\theta$ are given in Table 2 in the main text. (c) Static light scattering results. $R(\theta,C)$ as a function of $q^2$ for the same mixtures. Results in terms of $P_{agg}$ and $R_g^\theta$ are given in Table 2 in the main text.