Unlocking chain exchange in highly amphiphilic block polymer micellar systems: influence of agitation

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SUPPORTING INFORMATION

**Materials.** PB-hPEO and PB-dPEO polymers were synthesized via anionic polymerization as described previously. The absolute molecular weight of the PB-OH precursor \( (M_n = 3.2 \text{ kg mol}^{-1}, \ D = 1.06, \ 1,2\text{-}PB \text{ content} = 92\pm 1\%) \) was determined using \(^1\text{H} \text{NMR spectroscopy and matrix-assisted laser desorption/ionization time of flight mass spectrometry.} \) The composition of the PB-hPEO \( (M_n = 11.1 \text{ kg mol}^{-1}, \ D = 1.08, \ w_{\text{hPEO}} = 0.71) \) and PB-dPEO \( (M_n = 11.0 \text{ kg mol}^{-1}, \ D = 1.09, \ w_{\text{dPEO}} = 0.71) \) diblock copolymers was determined by \(^1\text{H} \text{NMR spectroscopy.} \text{ The molecular weight of the diblock copolymers was calculated based on their composition and the known molecular weight of the PB-OH precursor. The dispersity of all polymers was determined by size exclusion chromatography using polystyrene standards.} \text{ H}_2\text{O was purified using an EMD Millipore Milli-Q water purification system, and D}_2\text{O was used as received (99.9\% D, Cambridge Isotopes).} \)

**Micelle solution preparation.** Polymers for the premixed PB-hPEO/PB-dPEO micelle solution were blended (50 wt% PB-hPEO) in benzene, magnetically stirred at 200 rpm overnight, and then freeze-dried to ensure complete solvent removal. Subsequently, the PB-hPEO/PB-dPEO blend was dissolved in a D\(_2\)O/H\(_2\)O mixture (64 vol% D\(_2\)O) at the desired concentration and magnetically stirred at 200 rpm for 3 days.

Individual PB-hPEO and PB-dPEO micelle solutions for the mixing experiments were prepared at the desired concentrations by dissolving each dry polymer powder separately in a D\(_2\)O/H\(_2\)O mixture (64% D\(_2\)O by volume). The resulting solution was magnetically stirred at 200 rpm for 3 days before analysis. At \( t_{\text{mix}} = 0 \text{ min,} \) equal volumes of the PB-hPEO and PB-dPEO solutions were pipetted into the mixing vial or device, and the solution was agitated by one of the methods described below.
**Vortex mixing.** Samples were vortex mixed using a Fisher Scientific analog vortex mixer (120 V, 50/60 Hz, 150 W). All samples were mixed at a rotational speed of approximately 3200 rpm (analog setting 10). The total solution volume was 1 mL in all cases, except for the 4 mL solution volume described in Figure S3. For the samples in which individual PB-hPEO and PB-dPEO micelles were mixed, equal volumes of each solution were used (e.g. 0.5 mL of PB-PEO solution and 0.5 mL PB-dPEO solution for the 1 mL samples, or 2 mL PB-hPEO and 2 mL PB-dPEO solutions for the 4 mL samples). All samples were sealed and mixed in 1 dram screw cap glass vials. To maintain approximately ambient temperature in the vials during mixing, samples were mixed in cycles consisting of at most 2 min of mixing at room temperature followed by equilibration for ~1 min before the next mixing cycle. The solution temperature fluctuated as a result of mixing and equilibration but overall did not exceed 30 °C. The reported mix time was the cumulative total of the successive mixing cycles (i.e. mix time did not include equilibration time, as no exchange occurred under quiescent conditions). Samples were analyzed using SANS after the complete mixing cycle, and each SANS curve represents an individual sample mixed from $t_{\text{mix}} = 0$ min to the desired mix time. As a result of agitation, a foam was produced above the liquid surface and was allowed to settle before transferring the solution to the SANS sample holder.

**Concentric cylinder Couette flow.** 5 mg mL$^{-1}$ micelle solutions were sheared during flow-SANS experiments at NIST$^2$ using an Anton Paar MCR 501 rheometer operating at a shear rate of 5000 s$^{-1}$. For each sample, shear was applied for 90 min, the flow was stopped, and then scattering data were collected for 5 min. The samples were sheared using a 30 mm diameter titanium cup and 29 mm diameter titanium bob, giving a 0.5 mm gap and a total scattering path
length of 1 mm. Experiments were performed at 25 °C. A solvent trap was used to prevent sample evaporation.

**Gas sparging.** 5 mg mL\(^{-1}\) micelle solutions were sparged with nitrogen gas for 60 min at room temperature. Nitrogen gas was bubbled with a constant flow rate (10 mL min\(^{-1}\)) from the bottom of a vial containing 2 mL of micelle solution using a 22-gauge stainless steel needle (ID 0.41 mm). The sparging produced a foam above the liquid surface, and the foam was allowed to settle before transferring the solution to the SANS sample holder.

**SANS.** Experiments were performed on the NG-7 30 m SANS instrument at the NCNR. An incident wavelength of 6.0 Å was used with sample-to-detector distances of 1 m, 4 m, and 13.5 m to cover a \(q\)-range from 0.004 Å\(^{-1}\) < \(q\) < 0.4 Å\(^{-1}\). The scattering vector modulus, \(q\), was defined as \(q = 4\pi\lambda/\sin(\theta/2)\). SANS performed on micelle solutions inside the Couette flow device used a sample-to-detector distance of 10 m and \(q\)-range of 0.006 < \(q\) < 0.017 Å\(^{-1}\). Scattering data were collected for 5 min, and all measurements were performed at 25 °C. The data were reduced in IGOR Pro using the standard procedures provided by NIST.\(^3\)

**SANS data fitting.** The effects of vortex mixing on the micelle structure were determined by comparing the micelle structure before and after mixing (Figure S1). SANS data for the 5 mg mL\(^{-1}\) sample at \(t_{\text{mix}} = 0\) min, \(t_{\text{mix}} = 20\) min, and under premixed conditions were analyzed using a form factor model for block polymer micelles described elsewhere.\(^4\) Data for the sample at \(t_{\text{mix}} = 0\) min were fit assuming a mixture of PB-\(h\)PEO and PB-\(d\)PEO micelles, and the volume fraction of each micelle population was fixed based on the known mixing ratio. Data for the sample at \(t_{\text{mix}} = 20\) min and the premixed sample were fit assuming the scattering length density of the corona was equal to that of the solvent.
**Dynamic light scattering (DLS).** DLS experiments were performed using a Brookhaven Instruments Light Scattering System (BI-2000SM) equipped with a CNI 532 nm solid-state laser. Data were collected at a 90° scattering angle and fit with the quadratic cumulant expansion using the Brookhaven Instruments software package. All experiments were performed at 25 °C.
Figure S1. SANS data for 5 mg mL\(^{-1}\) PB-\(h\)PEO and PB-\(d\)PEO micelles before (\(t_{\text{mix}} = 0\) min) and after vortex mixing (\(t_{\text{mix}} = 20\) min). Similar maxima (\(q \sim 0.05\) Å\(^{-1}\)) and minima (\(q \sim 0.04\) Å\(^{-1}\)) indicated that micelles were approximately the same size before and after vortex mixing. The consistency in size was confirmed by modeling the data with a form factor model for block polymer micelles (red lines). Similar model fits described both the \(t_{\text{mix}} = 20\) min and premixed samples, suggesting that the chains were randomly distributed within the micelles after mixing. Key parameters from the model fits are given in Table S1.
Table S1. SANS fitting parameters.

| Sample          | Aggregation number | Core radius (nm) | Polydispersity |
|-----------------|--------------------|------------------|----------------|
| Vortexed 0 min  | 896 ± 17<sup>a</sup> | 11.2 ± 0.5       | 0.06           |
|                 | 851 ±160<sup>b</sup>| 11.4 ± 0.6       | 0.06           |
| Vortexed 20 min | 890 ± 5<sup>c</sup> | 11.5 ± 0.5       | 0.1            |
| Premixed        | 909 ± 5<sup>c</sup> | 11.6 ± 0.5       | 0.06           |

<sup>a</sup>PB-<i>h</i>PEO micelles
<sup>b</sup>PB-<i>d</i>PEO micelles
<sup>c</sup>50% PB-<i>h</i>PEO / 50% PB-<i>d</i>PEO
Figure S2. Dynamic light scattering of PB-hPEO and PB-dPEO micelles (5 mg mL\(^{-1}\)) before \((t_{\text{mix}} = 0 \text{ min})\) and after vortex mixing for \((t_{\text{mix}} = 5 - 20 \text{ min})\), samples in Figure 2a in the main text. The autocorrelation function was independent of vortex mix time, suggesting that vortex mixing did not lead to significant changes in the micelle hydrodynamic diameter or morphology.
**Table S2.** Results of quadratic cumulant fits to DLS correlation functions in Figure S2

| Sample           | $<R_H>$ (nm) | Poly |
|------------------|--------------|------|
| Vortexed 0 min   | 34           | 0.11 |
| Vortexed 5 min   | 34           | 0.10 |
| Vortexed 15 min  | 34           | 0.09 |
| Vortexed 20 min  | 32           | 0.13 |
| Premixed         | 35           | 0.08 |

*The variability in the effective hydrodynamic radius $<R_H>$ values was ~ 1-3 nm.*
Figure S3. SANS results before ($t_{\text{mix}} = 0$ min) and after rapid vortex mixing of PB-$h$PEO and PB-$d$PEO micelle mixtures prepared in 64 vol% D$_2$O with different total solution volumes (1 mL or 4 mL). Both solutions contained the same polymer concentration (5 mg mL$^{-1}$) and were vortex mixed in a 1 dram glass vial for 15 min at the same agitation rate (~ 3200 rpm). As expected, the 4 mL solution with lower air-water volume ratio (i.e. less available air-water interfacial area to total solution volume) showed less chain exchange as a fraction of the total number of chains compared to the 1 mL sample. This result demonstrated the importance of the air-water interface in the chain exchange process and was in agreement with the linear exchange kinetics that suggested a surface-limited mechanism. Error bars represent the standard deviation in the measured scattered intensity.
REFERENCES

1  Hillmyer, M. A. & Bates, F. S. *Macromolecules*, **1996**, 29, 6994-7002.
2  Eberle, A. P. R. & Porcar, L. *Current Opinion in Colloid & Interface Science*, **2012**, 17, 33-43.
3  Kline, S. *Journal of Applied Crystallography*, **2006**, 39, 895-900.
4  Pedersen, J. S. & Gerstenberg, M. C. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2003**, 213, 175-187.
5  Pedersen, J. S., Svaneborg, C., Almdal, K., Hamley, I. W. & Young, R. N. *Macromolecules*, **2003**, 36, 416-433.
6  Bang, J., Viswanathan, K., Lodge, T. P., Park, M. J. & Char, K. *Journal of Chemical Physics*, **2004**, 121, 11489-11500.
7  Kelley, E. G., Smart, T. P., Jackson, A. J., Sullivan, M. O. & Epps, T. H. *Soft Matter*, **2011**, 7, 7094-7102.