

Supporting Information

for

Exchange Kinetics for a Single Block Copolymer in Micelles of Two Different Sizes

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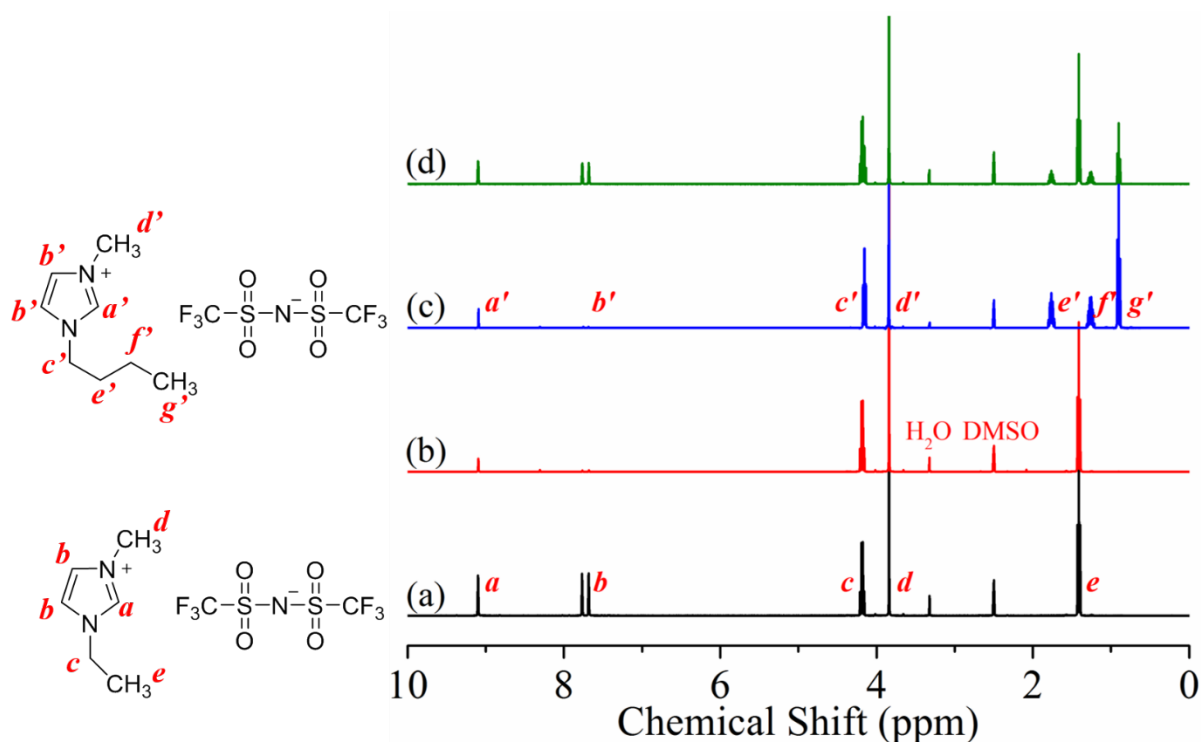


Figure S1. ¹H NMR spectra of (a) [EMIM][TFSI], (b) d[EMIM][TFSI], (c) d[BMIM][TFSI] and (d) the contrast-matching solvent mixture in deuterated dimethyl sulfoxide (*d*₆-DMSO). Note that the integration ratios of the NMR peaks in (d) are consistent with the compositions of the mixture, confirming the ideal mixing process.

Table S1. Structural Characteristics of 1 wt % Deuterated Diblock Copolymer Micelles in 30 wt % [BMIM] ionic liquid

	R_h (nm)	$\mu_2/\bar{\Gamma}^2$	R_c (nm)	σ_R (nm)	L_{corona} (nm)
CS	27.7	0.04	15.4	1.5	12.3
TF	32.9	0.05	19.5	2.5	13.4

Table S2. Scattering Length Densities and Volume Fractions for the 30% [BMIM][TFSI] Contrast-Matching Solvent Mixture

ionic liquid	Scattering length density (10^{10} cm^{-2})	volume fraction ^a
[EMIM][TFSI]	2.41	0.39
<i>d</i> [EMIM][TFSI]	3.07	0.30
<i>d</i> [BMIM][TFSI]	2.67	0.31

^aThe mixture of the ionic liquids based on these volume fractions has a scattering length density of $2.69 \times 10^{10} \text{ cm}^{-2}$, equal to that of the 50/50 *h*-/*d*-PnBMA. These values were confirmed by the NMR analysis of the solvent mixture.

Table S3. Fitting Parameters from the Pedersen Model

	R_c (nm)	σ_R (nm)	N_{agg}	R_{hs}^a (nm)	L'_{corona}^b (nm)	a_1^c	s (nm) ^c
CS	15.3	1.4	180	30.5	15.2	0.67	6.2
TF	19.7	2.2	392	34.7	15.0	0.68	6.1

^a the hard sphere radius

^b the corona thickness, calculated as $R_{\text{hs}} - R_c$

^c the two fitting parameters in the corona density profile, which was described by a linear combination of two partial cubic *b* spline functions. *s* gives the width of the profiles (the corona thickness is $\sim 2s$). The details about the corona density profile calculations can be found in the literature.¹

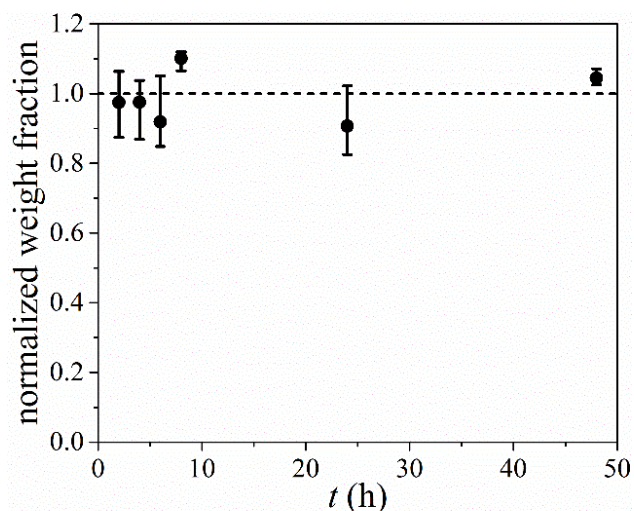


Figure S2. Normalized weight fraction of PMMA-*b*-PnBMA in 30% [BMIM] as a function of dissolution time at 80 °C. The polymer concentration at time t was measured by ^1H NMR in deuterated acetone based on the integration ratio between the $-\text{OCH}_3$ peak ($\delta = 3.63$ ppm) of PMMA and the imidazole hydrogen ($\delta = 9.06$ ppm) of the ionic liquid. This measured concentration was then normalized by the nominal value from the sample preparation, i.e. ~ 1 wt%.

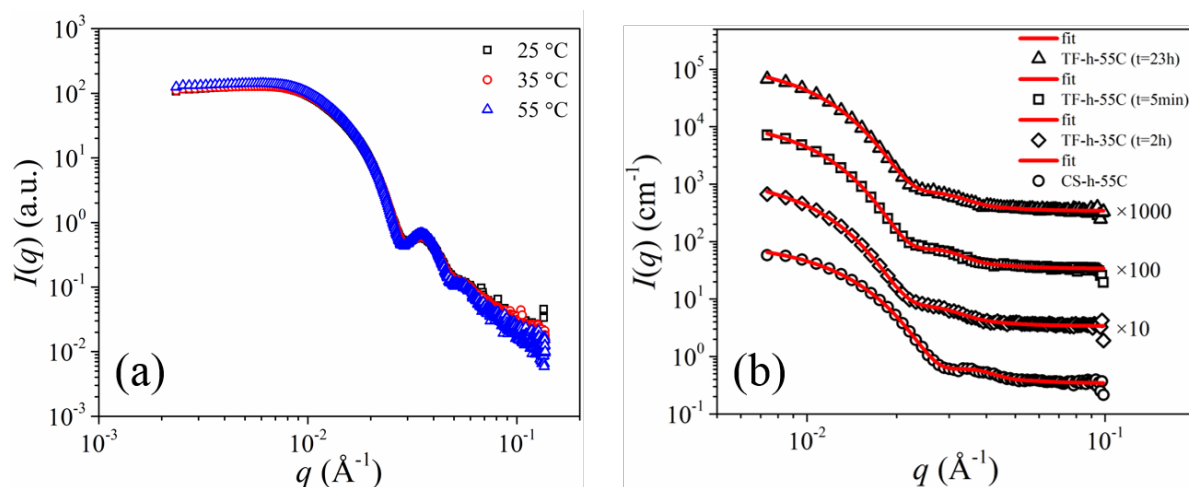


Figure S3. (a) SAXS scattering intensity $I(q)$ vs. q for 1 wt % CS micelles in 30% [BMIM] at various temperatures, 25, 35 and 55 °C. (b) SANS scattering intensity $I(q)$ vs. q for 1 wt % CS or TF protonated micelles in 30% [BMIM] at 55 °C or 35 °C, as indicated. The symbols are the experimental data and the red solid lines represent best fits to the Pederson model. The profiles were vertically shifted for clarity.

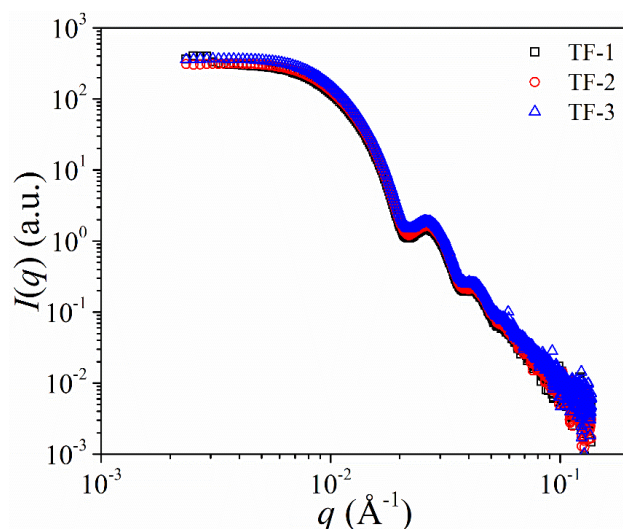


Figure S4. SAXS scattering intensity $I(q)$ vs. q for three replicate experiments of 1 wt % TF micelles in 30% [BMIM] at 55 °C, as indicated. The three curves represent three different samples, in which the position of the first q minimum occurs at nearly the same q value, indicating the micelle core size is almost the same. Note that the slight difference in the intensities presumably come from the different thickness of the capillaries.

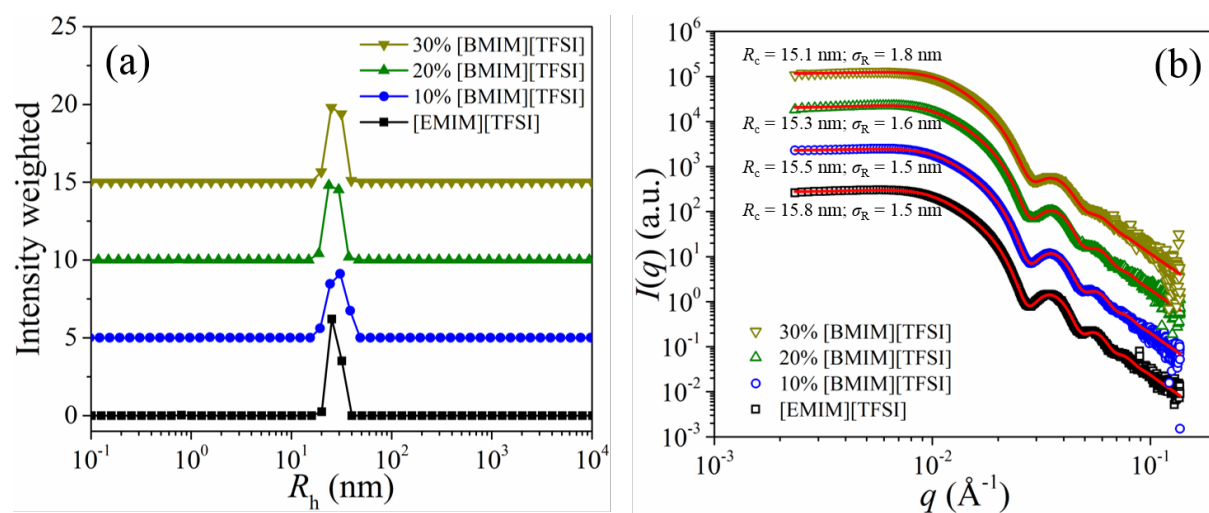


Figure S5. (a) Intensity weighted hydrodynamic size distributions and (b) SAXS scattering intensity $I(q)$ vs. q for 1 wt % CS micelles in ionic liquids of varying compositions at 25 °C, as indicated. The solid lines in (b) represent the best fits to the Pederson model with a hard sphere structure factor. In this plot the core size (R_c) and dispersity (σ_R) for each sample are also shown. Note that both R_h and R_c do not change significantly with the solvent composition, although R_c slightly decreases and σ_R becomes larger with the increase in the volume fraction of [BMIM][TFSI].

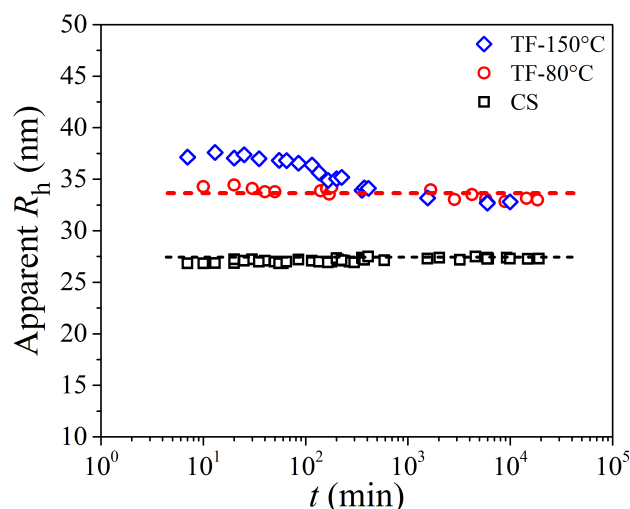


Figure S6. Apparent hydrodynamic size (R_h) vs time for 1 wt % CS (black) and TF (red and blue) micelles in 30% [BMIM] ionic liquid at 55 °C. The two TF micelles were prepared by dissolving the copolymer at 80 and 150 °C for 2 h, respectively. The dashed horizontal lines are drawn as guides to the eye. Note that the sizes of the micelles prepared by the TF method converge at long annealing times (up to nearly two weeks), which is still distinct from that of the CS micelles.

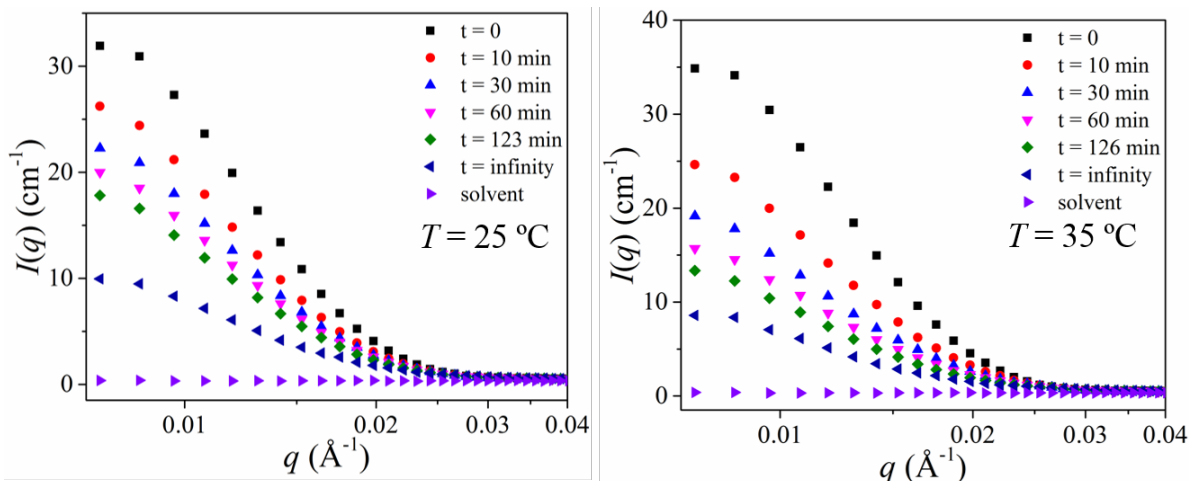


Figure S7. Representative TR-SANS profiles $I(q)$ vs. q for 1 wt % postmixed CS micellar solutions in 30% [BMIM] at varying temperatures and times, as indicated. Note that “ $t = \text{infinity}$ ” corresponds to the scattering of the premixed sample, which primarily comes from the scattering of the PMMA corona chains.

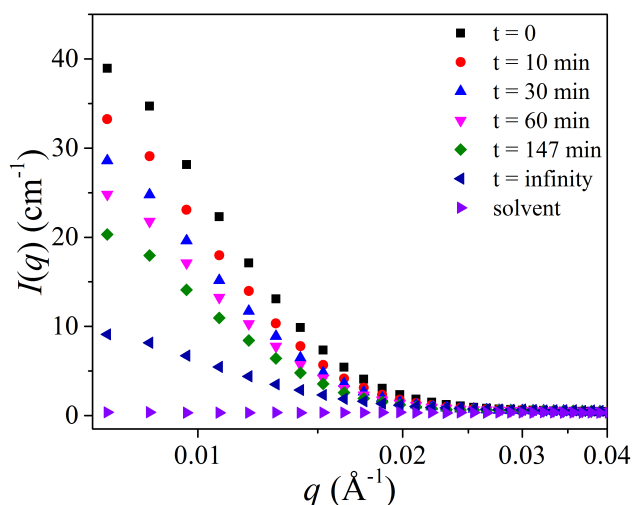


Figure S8. Representative TR-SANS profiles $I(q)$ vs. q for 1 wt % postmixed TF micellar solutions in 30% [BMIM] at 35 °C and varying times, as indicated.

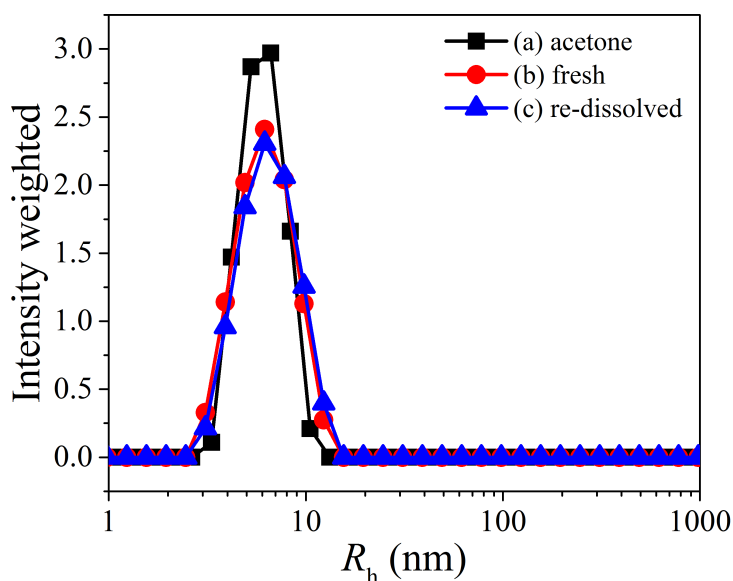


Figure S9. Representative hydrodynamic radius distributions for 0.3 wt % (25-53) diblock copolymer chains in (a) acetone, (b) and (c) a mixture of 30% [BMIM] and dichloromethane (with a weight ratio of 3:7). The solution (b) was obtained by directly dissolving the polymer chains in the solvent mixture, without any thermal treatments while (c) was obtained by re-dissolving the already-formed and annealed micelles in dichloromethane. The size distributions are all quite comparable, indicating the micelles can be readily dissolved into single chains after sample preparation and thermal annealing, ruling out any significant chemical cross-linking during solution processing.

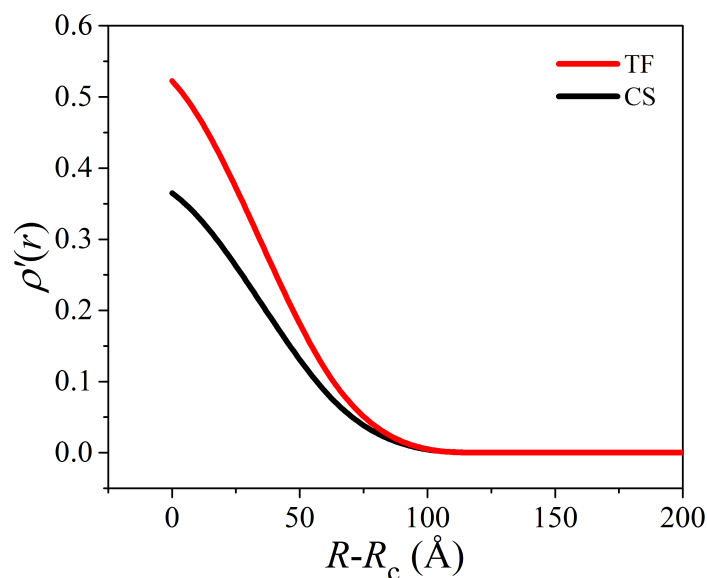


Figure S10. The normalized radial density profile $\rho'(r)$ for the corona as a function of the distance from the core/corona interface, R is the radial distance from the center of the micelle core, R_c is the core radius. The density profiles were normalized according to the protocol in the literature.²

References

- (1) Pedersen, J. S.; Gerstenberg, M. C. The structure of P85 Pluronic block copolymer micelles determined by small-angle neutron scattering. *Colloids Surf., A* **2003**, *213*, 175-187.
- (2) Bang, J.; Viswanathan, K.; Lodge, T. P.; Park, M. J.; Char, K. Temperature-dependent micellar structures in poly(styrene-*b*-isoprene) diblock copolymer solutions near the critical micelle temperature. *J. Chem. Phys.* **2004**, *121*, 11489-11500.