

1 Hybridization of a Bimodal Distribution of Copolymer Micelles

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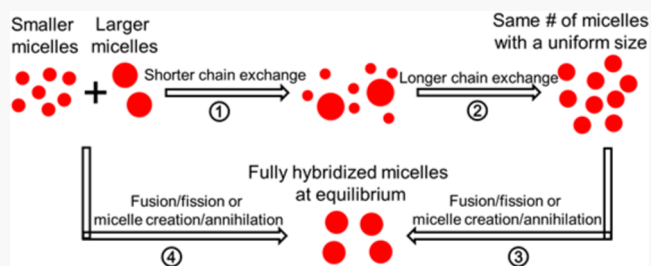


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ABSTRACT: The hybridization of two diblock copolymer micelles in mixtures of ionic liquids, 1-ethyl and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM] and [BMIM][TFSI], or EMIM and BMIM in short), was studied by time-resolved dynamic light scattering (DLS) and small-angle X-ray and neutron scattering (SAXS/SANS). Two poly(methyl methacrylate)-*block*-poly(*n*-butyl methacrylate) (PMMA-*b*-PnBMA) copolymers, where PnBMA and PMMA are the core- and corona-forming blocks, respectively, were employed. The two diblocks have the same corona block molecular weight (25 000 g/mol) but core block lengths differing by a factor of 2.2 (24 000 and 53 000 g/mol). Both polymers assemble into spherical micelles in mixed ionic liquid solvents containing 0–30 wt % BMIM, albeit with different sizes. The solvent selectivity decreases with increasing BMIM content. Time-resolved SANS quantified the unimer exchange time for each copolymer as a function of solvent composition. In the most selective solvent (100% EMIM), the longer chains exchanged $\sim 10^4$ times more slowly than the shorter ones; this difference was reduced to a factor of ca. 50 in 30% BMIM. The two micelle solutions in a given solvent were then mixed in equal proportions, and the structural evolution of the blended micelles was monitored over several months. From previous work, we know that at equilibrium the two copolymers should form a uniform population of mixed (“hybridized”) micelles, with size intermediate between the precursor micelles (albeit closer to the larger ones). In the more selective solvents, both light and neutron scattering show that the apparent weight-average molecular weight (M_w) of the micelles initially increases with time, while SAXS shows an increase in the average micelle core size. These observations reflect a net transfer of shorter chains from smaller to larger micelles, as the shorter-chain exchange is much more facile but, in a certain sense, takes the system further away from equilibrium. The long-time evolution monitored by DLS shows that the process of micellar hybridization depends greatly on solvent selectivity. In 100% EMIM, M_w continues increasing even after several months, indicating that equilibrium is not reached within the experimental time scale. For less selective solvents, the micelle size eventually begins to decrease and approaches the equilibrium size, indicating that a unimer exchange of both molecular weights is operative. In the least selective solvent, 30% BMIM and both M_w and the average hydrodynamic size of the micelles start to decrease immediately and ultimately approach the values of the equilibrium micelles. However, this process must involve other relaxation mechanisms, e.g., micelle fusion/fragmentation or micelle creation/annihilation, as the total number of micelles also needs to be adjusted. Overall, this work exposes the possibility of different routes to equilibrium for a given system and thereby underscores the complexity of equilibration in block copolymer micelles.



32 ■ INTRODUCTION

33 Self-assembly of block copolymers into various micellar
34 nanostructures in a selective solvent has great potential to
35 enable a host of diverse applications.^{1–7} To facilitate these
36 applications, a fundamental understanding of the thermody-
37 namic and dynamic characteristics of block copolymer micelles
38 is important. Over the past few decades, the equilibrium
39 structure of polymeric micelles has been well studied by both
40 theory and experiment.^{8–14} More recently, the kinetics of
41 block copolymer micellization and the subsequent equilibra-
42 tion mechanisms have also been extensively investigated.^{15–26}
43 It is generally accepted that micelle equilibration relies on
44 some combination of three processes: molecular exchange,
45 micelle creation/annihilation, and micelle fusion/fragmenta-
46 tion.¹⁸ When the system is close to equilibrium, molecular
47 exchange is dominant, while when the system is far away from

the thermodynamically stable state, the other two processes are 48
more effective. In the past decade, progress has been made in 49
understanding the unimer exchange process near equilibrium, 50
especially by time-resolved small-angle neutron scattering (TR- 51
SANS). It has been found that the kinetics of chain exchange 52
depends on many molecular characteristics, including core 53
block length and dispersity,^{20,27} corona block length,^{28,29} 54
solvent selectivity,^{30,31} micellar size and morphology,^{32,33} and 55
micelle concentration.³⁴ However, in practice, the formulation 56

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57 of block copolymer micelles often leads to a nonequibrated
58 state, which might gradually relax toward equilibrium. The
59 equilibration process is generally complicated, involving
60 multiple mechanisms, which remains to be clearly resolved.
61 Several studies have been designed to understand the
62 nonequilibrium relaxation processes of block copolymer
63 micelles. In some cases, sudden thermodynamic changes
64 (e.g., temperature or solvent selectivity) were introduced into
65 an equilibrated system and the following structural evolution in
66 the micelles was examined.^{35–39} In others, various micelle
67 preparation protocols (e.g., direct dissolution or cosolvent
68 removal) yield kinetically trapped micellar morphologies,
69 which were then annealed and monitored. For instance, for
70 polybutadiene-*block*-poly(ethylene oxide) (PB-*b*-PEO) in
71 imidazolium-based ionic liquids, the initially formed poly-
72 disperse and large micellar aggregates relax into smaller and
73 narrowly distributed spherical micelles upon annealing at high
74 temperatures, predominantly via fragmentation.^{21,22,40,41} Addi-
75 tionally, Kelley et al. have reported that, upon removal of
76 cosolvent, PB-*b*-PEO micelles in water slowly grow through a
77 distinct bimodal distribution separated by multiple fusion
78 events.⁴² Note that in both these systems, no unimer exchange
79 was observed.^{42,43}

80 A third class of experiment follows the relaxation of mixtures
81 of micelles, i.e., micelle hybridization, which is the primary
82 focus of this report. A first hybridization experiment was
83 performed by Cantu and co-workers,⁴⁴ who measured the light
84 scattering intensity upon mixing two different micelles and
85 found that the equilibration time could be related to the critical
86 micelle concentration (CMC) of the individual micelles.
87 Furthermore, it was concluded that the formation time of
88 mixed micelles correlates with the unimer exchange rates.
89 Subsequently, Tian et al. studied micelle hybridization by
90 sedimentation velocity and found that the rate of hybridization
91 depends on the copolymer architecture and the thermody-
92 namic properties of the solvent mixture.⁴⁵ In particular, it was
93 reported that hybridization did not occur if the solvent is very
94 poor for the core-forming block. More recently, Cai and
95 coauthors studied the hybridization of coil-rod-like copolymer
96 micelles by a combination of static and dynamic light
97 scattering and found that, upon mixing, larger hybrid micelles
98 were formed at the expense of each kind of the “pure”
99 micelles.⁴⁶ It was argued that the driving force for hybrid-
100 ization comes from the entropy gain and the space-filling as the
101 core block is rodlike. Despite these interesting studies, there
102 are still many open questions about micelle hybridization that
103 have not been fully addressed: (i) what are the relative roles of
104 chain exchange or other processes (e.g., fusion/fragmentation
105 and formation of new micelles/disintegration of existing
106 micelles) in micelle hybridization? (ii) what are the possible
107 hybridization pathways? and (iii) how does the solvent
108 selectivity affect the micelle hybridization?

109 To provide some insight into these questions, we study the
110 hybridization of two different micelles formed by poly(methyl
111 methacrylate)-*block*-poly(*n*-butyl methacrylate) (PMMA-*b*-
112 PnBMA, “MB”) diblock copolymers in mixtures of the ionic
113 liquids (ILs) 1-ethyl-3-methylimidazolium and 1-butyl-3-
114 methylimidazolium bis(trifluoromethylsulfonyl)imide,
115 [EMIM][TFSI] and [BMIM][TFSI], respectively. Previous
116 work has shown that PMMA is soluble in both ILs and forms
117 the micelle corona, while PnBMA is insoluble in both solvents
118 (with a lower critical solution temperature, LCST) and is thus
119 segregated in the micellar core.⁴⁷ Note that BMIM is a less

selective solvent than EMIM. The two diblocks have the same
corona chain length (N_{corona}), while the core block length
(N_{core}) differs by a factor of 2.2. We have previously
established that for this pair of copolymers the equilibrium
state is a uniform population of mixed (hybrid) micelles at any
mixing ratio.⁴⁸ We first prepare pure micelles of each individual
copolymer and then blend them together to examine the time
evolution of micelle hybridization by a combination of
dynamic light scattering (DLS) and small-angle X-ray and
neutron scattering (SAXS/SANS). We also investigate the role
of solvent selectivity (by varying the composition of the IL
mixture) on micelle hybridization. Based on these results, we
discuss the role of chain exchange and other processes on
micelle hybridization and propose possible hybridization
pathways. All of the experiments were conducted at 55 °C
unless otherwise noted, which is much higher than the glass-
transition temperature (T_g) of PnBMA ($T_g \approx 20$ °C);⁴⁹ thus,
frozen dynamics due to glassy cores is not an issue.^{50,51}

EXPERIMENTAL SECTION

Synthesis and Characterization. Hydrogenated and partially
deuterated (h- and d-) versions of the two diblock copolymers,
PMMA-*b*-PnBMA, were synthesized by sequential radical addition-
fragmentation chain-transfer (RAFT) polymerization. The partially
deuterated *n*-butyl methacrylate (d_9 -nBMA) monomer was prepared
by the reaction of methacryloyl chloride and d_{10} -*n*-butanol. The
synthetic details can be found in previous reports.^{30,52} The molecular
weights of the individual blocks and the dispersity of the diblocks
were thoroughly characterized by a combination of size exclusion
chromatography (SEC) with a multiangle light scattering detector
(MALS, Wyatt DAWN) and ¹H nuclear magnetic resonance
spectroscopy (¹H NMR, Varian Inova 500). The characterization
details were also described previously.⁵² Table 1 shows the physical
characteristics of the diblocks.

Table 1. Characteristics of Diblock Copolymers^a

polymer	$M_{n,\text{PMMA}}^b$ (kg/mol)	$M_{n,\text{PnBMA}}^b$ (kg/mol)	N_{PMMA}^c	N_{PnBMA}^c	$\mathcal{D}^d$
MB(25–24)	25	24	250	169	1.05
MB(25–25) <i>d</i>	25	25	250	166	1.05
MB(25–53)	25	53	250	373	1.08
MB(25–54) <i>d</i>	25	54	250	354	1.09

^aAs reported previously.³⁰ ^b $M_{n,\text{PMMA}}$ and $M_{n,\text{PnBMA}}$ are the number-averaged molecular weights of the PMMA and PnBMA blocks, respectively. ^c N_{PMMA} and N_{PnBMA} are the degrees of polymerization of the two blocks. ^d $\mathcal{D}$ is the dispersity of the diblock copolymer measured by SEC-MALS.

Ion-exchange reactions were performed to prepare the ionic liquids. Specifically, [EMIM][TFSI] was obtained from the reaction of [EMIM]Br and Li[TFSI], while [BMIM][TFSI] was synthesized by the reaction of [BMIM]Cl and Li[TFSI]. To realize the contrast-matching condition in the neutron scattering experiments, partially deuterated versions of the two ILs were also prepared via isotopic exchange of the three hydrogens on the imidazole ring with deuterated water at 100 °C for 72 h.⁵³ The degree of deuteration was quantified by ¹H NMR spectroscopy. All other chemicals were purchased from Sigma-Aldrich and used as received.

Sample Preparation. The cosolvent method was used to prepare the individual micellar solutions (larger micelles from MB(25–53) and smaller ones from MB(25–24)) with a copolymer concentration of 0.5 or 1 wt %. Briefly, the dried copolymer and an appropriate

Table 2. Characterization of Individual Micelles in Different Solvents

solvent	micelle	R_h (nm)	μ_2/Γ^{2a}	R_c (nm)	σ_R (nm)	L_{corona} (nm) ^b	N_{agg} ^c
0% BMIM	MB(25–24)	23.2	0.06	10.2	1.1	13.0	108
	MB(25–25) ^d	23.2	0.04	10.0	1.3	13.2	103
	MB(25–53)	29.3	0.03	16.9	1.5	12.4	221
	MB(25–54) ^d	28.0	0.04	16.7	1.6	11.3	225
10% BMIM	MB(25–24)	n.d. ^d	n.d. ^d	n.d. ^d	n.d. ^d	n.d. ^d	n.d. ^d
	MB(25–53)	28.7	0.03	16.8	1.6	11.9	217
20% BMIM	MB(25–24)	24.5	0.11	9.7	1.2	14.8	92
	MB(25–53)	29.2	0.04	16.7	1.6	12.5	213
30% BMIM	MB(25–24)	24.8	0.12	9.3	1.3	15.5	81
	MB(25–53)	28.4	0.03	15.7	1.4	12.7	177

^aAveraged over five scattering angles. ^b L_{corona} is the corona thickness, estimated as $R_h - R_c$. ^c N_{agg} is calculated as $4\pi R_c^3 \phi / (3\nu_{\text{PnBMA}})$, where the polymer volume fraction in the core is $\phi \approx 0.9$, which was measured in a previous report in 0% BMIM.⁴⁸ The N_{agg} values in other solvents should be viewed with caution as ϕ could be smaller than 0.9. ν_{PnBMA} is the volume per core block. ^dNot determined.

amount of IL were dissolved in good solvent dichloromethane (DCM). Following that, DCM was slowly evaporated via a nitrogen purge until constant solution weight was achieved. The obtained micellar dispersions were further dried at 50 °C for 12 h under vacuum (<100 mTorr). Complete removal of the cosolvent was confirmed by ¹H NMR spectroscopy. The individually prepared larger and smaller micellar solutions were thoroughly mixed in either equal weight (SAXS, DLS) or equal core block volume (SANS) proportions for subsequent time-resolved scattering experiments, as described below. The mixed micellar solutions made by this protocol are referred to as “postmixed”. In contrast, samples with the same overall compositions were also prepared by the “premixed” protocol, i.e., by first molecularly mixing the two diblocks with ILs together in DCM and then slowly removing DCM to form hybridized micelles. The two different protocols were adopted here to examine the thermodynamic state of the postmixed samples upon long-time thermal annealing; the premixed micelles are assumed to be close to the equilibrium state.

Dynamic Light Scattering (DLS). DLS experiments were performed on a Brookhaven BI-200SM instrument, with a laser wavelength of 637 nm. Prior to the measurement, the micelle solution was filtered with a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter into a glass tube. It was then degassed under vacuum and flame-sealed or sealed with parafilm. All light scattering experiments were performed at 55 °C after at least 10 min of thermal equilibration. To obtain the hydrodynamic radius (R_h) of the micelles, the normalized intensity autocorrelation function, $g^{(2)}(t)$, was acquired at five different angles (from 50 to 130°) for 10 min at each angle. The second-order cumulant method was used to describe $g^{(2)}(t)$, from which the average decay rate (Γ) and hydrodynamic size dispersity (μ_2/Γ^2) of the micelles can be obtained.⁵⁴ Note that the definition of size dispersity for micelles is different from that for polymer chains. We use different definitions in current work, as they are conventionally used and accepted in the polymer community. Following that, a linear fit of Γ vs q^2 gives the average diffusion coefficient (D_m). Here $q = (4\pi n/\lambda) \sin(\theta/2)$ is the scattering vector, where n is the IL refractive index, λ is the laser wavelength in vacuum, and θ is the scattering angle. From D_m , R_h can be calculated from the Stokes–Einstein relation, i.e., $R_h = k_B T / (6\pi\eta D_m)$, where k_B is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. On the other hand, for the time-resolved light scattering experiments, the two micelle solutions (0.5 wt % copolymer) were combined in a 1:1 weight ratio and well mixed by magnetic stirring at room temperature. The resulting mixed solution was then quickly filtered into the glass tube, which was degassed and flame-sealed as described above. The delay time, i.e., that between solution mixing and the first measurement, was about 30 min, including the 10 min thermal equilibration at 55 °C. The measurement was performed at an angle of 90° for 10 min at each time point, during which the scattering intensity $I(t)$ and hydrodynamic radius R_h were monitored. Note that there is typically a notable random fluctuation in $I(t)$, attributable to the ionic liquid solvents. However, the average $I(t)$ is quite

reproducible (with a 1% deviation). Additionally, the scattering intensity of an ionic liquid sample was also measured at each time point. This was then used to normalize the scattering intensity of the micellar mixture solutions to account for any potential change in the laser intensity over time. Between the long-time measurements, the solution was isothermally annealed in an oil bath at 55 °C. Due to the nonvolatility of ionic liquids, the change in polymer concentration during long thermal annealing can be neglected (also the glass tube was flame-sealed).

Small-Angle X-ray Scattering (SAXS). The SAXS experiments were performed on the 5-ID-D beamline (Dupont-Northwestern-Dow Collaborative Access Team) at the Argonne National Laboratory (Advanced Photon Source). The accessible scattering vector q range was ~ 0.0025 – $0.19 \text{ \AA}^{-1}$, using a wavelength λ of 0.73 Å and a sample-to-detector distance of 8.50 m. For these measurements, 1 wt % micelle solutions were transferred into 1.5 mm diameter quartz capillary tubes (Charles Supper Company). The capillary tubes were then sealed with epoxy. The measurement temperature was 55 °C. Isotropic two-dimensional (2D) scattering data were acquired by a Rayonix CCD area detector for 0.5 or 1 s, which was then converted into the one-dimensional (1D) traces, i.e., scattering intensity $I(q)$ vs q . The scattering data were then background-corrected using the corresponding solvent in the capillary tube and analyzed by the Pedersen model for block copolymer micelles with the Percus–Yevick hard-sphere structure factor.^{55–57}

Small-Angle Neutron Scattering (SANS). The SANS experiments were performed on the GP-SANS CG-2 instrument at the High Flux Isotope Reactor (HFIR) facility at Oak Ridge National Laboratory (ORNL). The neutron wavelength of the neutron beam was 4.75 Å (with a spread of $\Delta\lambda/\lambda = 0.13$) and the sample-to-detector distance was 10 m, which provided a q range of ~ 0.007 – $0.1 \text{ \AA}^{-1}$. To measure the chain exchange kinetics of individual micelles, as described previously,^{30,33} two populations of micelles (protonated and deuterated, 1 wt %) were prepared in a contrast-matching solvent mixture, the scattering length density of which equals the average of the protonated and deuterated core blocks. Note that the PMMA corona chains in both micelles are protonated. Afterward, different amounts of the two micelle solutions (corresponding to equal core block volumes) were thoroughly mixed at specified temperatures (25, 35, and 55 °C), quickly transferred into 1 mm banjo cells, and placed on the beamline for data acquisition. Due to the redistribution of the h- and d- chains among different populations of micelles, the scattering intensity $I(q, t)$ will decrease with time and ultimately approach that of the fully hybridized, premixed sample, $I(q, \infty)$. Here the premixed sample was prepared by blending the same amounts of h- and d-chains in a good solvent (DCM), which was then removed by nitrogen purge. Thus, micelles prepared by this route should have an equal volume of h- and d-core blocks on average in each micelle.

To quantify the rate of chain exchange, we adopt the normalized relaxation function, defined as¹⁹

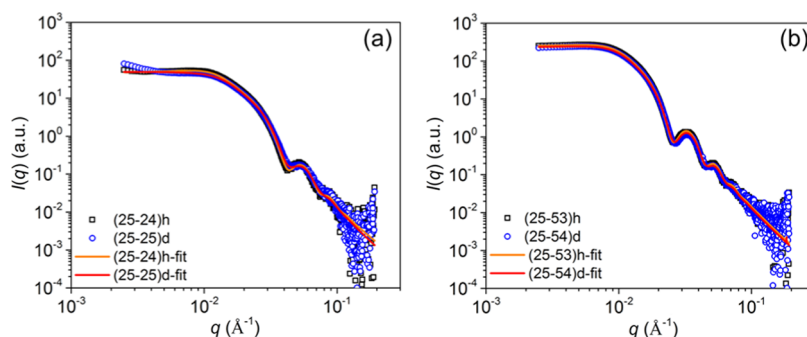


Figure 1. SAXS intensity $I(q)$ vs scattering vector q for 1 wt % micelle solutions in [EMIM][TFSI]. Panel (a) represents MB(25–24) and MB(25–25)*d* and panel (b) represents MB(25–53) and MB(25–54)*d*. The symbols represent the experimental data and the lines correspond to best fits to the Pedersen model.

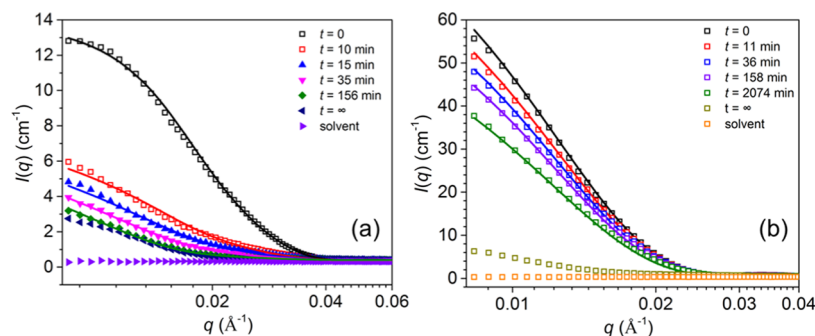


Figure 2. Representative TR-SANS profiles $I(q)$ vs q for 1 wt % postmixed micellar solutions of (a) MB(25–24) and MB(25–25)*d* and (b) MB(25–53) and MB(25–54)*d* in contrast-matching [EMIM][TFSI] at 55 °C and varying times. Note that “ $t = \infty$ ” represents the premixed sample. The symbols represent the experimental data and the lines correspond to the calculation, as detailed in the text.

$$R(t) = \sqrt{\frac{I(q, t) - I(q, \infty)}{I(q, 0) - I(q, \infty)}} \quad (1)$$

268

269 Here, $I(q, 0)$ is the scattering intensity at time $t = 0$, which was
 270 estimated by the average scattering intensity of the corresponding h-
 271 and d-micelles, as chain exchange occurs at room conditions.
 272 Similarly, the chain exchange of the hybrid micelles was measured
 273 by mixing equal core block volumes of protonated larger and
 274 deuterated smaller micelles. Additionally, the scattering intensity of
 275 mixtures of protonated larger and smaller micelles in the deuterated
 276 solvent was also measured as a function of time. In all of these time-
 277 resolved runs, the 2D scattering data were recorded in 5 min intervals
 278 for 2–3 h, which was then reduced and converted into 1D profiles
 279 using a custom-made program at ORNL.

280 ■ RESULTS

281 We first characterize the structure of individual protonated/
 282 deuterated (h-/d-) larger and smaller micelles via a
 283 combination of DLS, SAXS, and SANS, with the results
 284 presented in Table 2. Unless otherwise noted, the data were
 285 acquired with the hydrogenated version of the micelles and all
 286 of the measurements were performed at 55 °C. Note that it has
 287 been previously shown that the structure of these micelles
 288 barely changes with temperature under these experimental
 289 conditions.^{33,52} DLS shows a single, narrowly distributed
 290 population of micelles formed by either the shorter, MB(25–
 291 24), or the longer, MB(25–53), diblocks (Figure S1). The
 292 average hydrodynamic radius and size dispersity in EMIM are
 293 23.2 nm and 0.06 for the smaller and 29.3 nm and 0.03 for the
 294 larger micelles, respectively. Figure 1 shows the SAXS profiles
 295 of 1 wt % protonated/deuterated micelles in EMIM. Analysis
 296 based on the Pedersen model with a hard-sphere structure

factor yields structural parameters including the average
 micelle core size (R_c) and dispersity; R_c was 10.2 and 16.9
 nm for the smaller and larger micelles, respectively, with
 standard deviations of 1.1 and 1.5 nm. Very similar values were
 obtained for the corresponding deuterated versions (Table 2).
 The micelle structure was also characterized by SANS, which
 provides similar core sizes and dispersity between the
 protonated and deuterated micelles for each copolymer.
 However, as shown in Figure S2, the scattering profiles
 between the h- and d-micelles are visually distinct, due to the
 different scattering length densities of the h- and d-cores of the
 micelles (more details are provided in the Supporting
 Information). On the basis of these results, other structural
 parameters can be estimated. For instance, the difference
 between R_h and R_c was taken as the average corona thickness.
 The mean aggregation number can also be estimated under the
 reasonable assumption that there is ~10% solvent (or ~90%
 polymer) in the micelle core.⁴⁸ All of the structural
 characteristics of the individual micelles in different solvents
 are shown in Table 2.

We next examine the chain exchange kinetics of the two
 individual micelles. Figure 2 shows the evolution of the
 scattering intensity with time at 55 °C for both micelles in
 EMIM. In each case, the scattering intensity monotonically
 drops with time, reflecting the redistribution of h- and d-chains
 via the unimer exchange process. Clearly, the chain exchange
 rate of the smaller micelles is much greater than the larger
 ones, as evidenced by the larger decrease in intensity after a
 given time. Integration of the scattering intensity (over the q
 range of 0.008–0.04 Å^{−1} for MB(25–24) and 0.008–0.03 Å^{−1}
 for MB(25–53)) and following eq 1, the relaxation function

328 $R(t)$ can be calculated and is presented in Figure S3. To
 329 facilitate comparison, the $R(t)$ curves at different temperatures
 330 were then time–temperature-superposed at a reference
 331 temperature of 35 °C (Figure 4a). The superposed $R(t)$ can
 332 be well described by the model proposed by Choi et al.,²⁰ in
 333 which two fitting parameters were obtained: $\alpha\chi$ and the
 334 dispersity of the core block (N_w/N_n), where α is a scale factor
 335 and χ is the Flory–Huggins parameter between the core block
 336 and the solvent. For the smaller micelles MB(25–24), $\alpha\chi =$
 337 0.030 and $N_w/N_n = 1.10$, while for larger micelles MB(25–53),
 338 $\alpha\chi = 0.035$ and $N_w/N_n = 1.15$. Following the model of Choi et
 339 al., the characteristic relaxation time for chain exchange is given
 340 by $\tau \sim N_{\text{core}}^2 \exp(\alpha\chi N_{\text{core}})$. Thus, the unimer exchange for the
 341 smaller micelles is about 4 orders of magnitude faster than that
 342 of the larger ones, primarily due to the difference in the core
 343 block length. This is consistent with earlier reports that the
 344 molecular exchange in diblock copolymer micelles is hyper-
 345 sensitive to the core block length.^{20,27,30}
 346 Next, the hydrogenated larger and deuterated smaller
 347 micelles were mixed, with the scattering intensity of the
 348 micellar mixture monitored as a function of time (Figure 3).

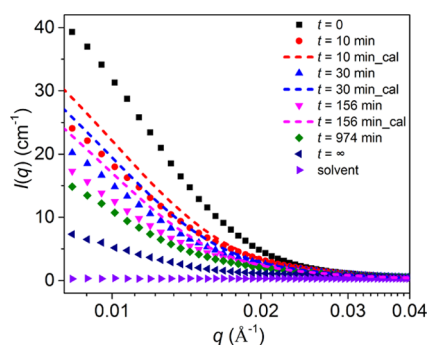


Figure 3. Representative TR-SANS profiles $I(q)$ vs q for 1 wt % postmixed micellar solutions of MB(25–53) and MB(25–25)d in contrast-matching [EMIM][TFSI] at 55 °C and varying times. Note that $t = \infty$ represents the premixed sample. The symbols represent the experimental data and the dashed lines correspond to the calculation, as described in the text.

349 Again, the scattering intensity progressively decreases with
 350 time. This clearly indicates that there is “crosstalk”, or
 351 exchange, between the two populations of micelles; if there
 352 were only chain exchange among the same population of
 353 micelles, the scattering intensity would remain constant.

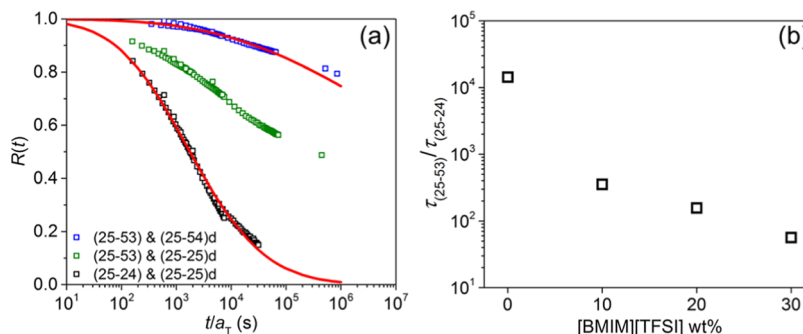


Figure 4. (a) Time–temperature-superposed $R(t)$ vs t/a_T for 1 wt % postmixed micellar solutions in contrast-matching [EMIM][TFSI]. The reference temperature is 35 °C. The symbols represent the experimental data and the red lines correspond to the best fits to the model proposed by Choi et al.²⁰ (b) Ratio of the chain exchange time of MB(25–53) and MB(25–24) ($\tau_{\text{MB}(25-53)}/\tau_{\text{MB}(25-24)}$) vs the weight fraction of [BMIM][TFSI] in the solvent mixture.

Similar treatment of the data as that for individual micelles
 yields $R(t)$ for the micellar mixture. Figure 4a shows that $R(t)$
 decreases continuously with time and falls in between that of
 the larger and smaller micelles, which is intuitively reasonable.
 Similar results were obtained in another solvent, i.e., 20%
 BMIM (Figure S4). We have to note that, for calculation of
 $R(t)$ for the micellar mixture, $I(q, \infty)$ is assumed to be that of
 the premixed micelles, which could be a good first
 approximation but might not be exact, as discussed later in
 the text. Thus, some caution needs to be taken in interpreting
 the $R(t)$ data of the micellar mixture. Additionally, the SANS
 experiments were performed up to ~ 16 h, which only accesses
 the relatively short-time hybridization. The long-time process
 will be examined by time-resolved light scattering comple-
 mented by SAXS.

Figure 5 shows the time dependence of the average
 hydrodynamic radius R_h (Figure 5a) and the normalized
 scattering intensity (Figure 5b) of 0.5 wt % postmixed micellar
 mixtures of MB(25–24) and MB(25–53) in varying solvents
 at 55 °C. Note that the experimental time here is up to 53–
 223 days, depending on the solvent. As shown in Figure 5, in
 EMIM (i.e., 0% BMIM), both R_h and the scattering intensity
 increase with annealing time. Consistent results were found
 from SANS (Figure S5). At 10% BMIM, the average micelle
 size and scattering intensity first increase with time and then
 apparently level off. At both 15 and 20% BMIM, the intensity
 shows a clear maximum with time; R_h vs t is also consistent
 with this behavior, albeit with greater scatter. By 30% BMIM,
 there is barely any change in either R_h and $I(t)$ during the early
 stage of hybridization, and then both decrease at longer times,
 ultimately approaching the values of the premixed sample.
 Concurrently, the size dispersity of the micellar mixtures was
 also monitored during these time-resolved experiments, as
 shown in Figure S6. There is no systematic change in size
 dispersity with time, presumably due to the fact that the R_h of
 the two micelles are not that different ($<25\%$) and there is a
 significant overlap in the size distributions (Figure S1).
 Overall, the micellar mixture can reach the thermodynamically
 stable state only in the least selective solvent (i.e., 30%
 BMIM), as indicated by the fact that in this case similar
 micellar structures were obtained via preparation from two
 different routes (postmixed vs premixed). In contrast, in the
 other solvents, even after annealing for several months, the R_h
 and $I(t)$ of the postmixed micellar mixtures are still
 substantially larger than that obtained from the premixing

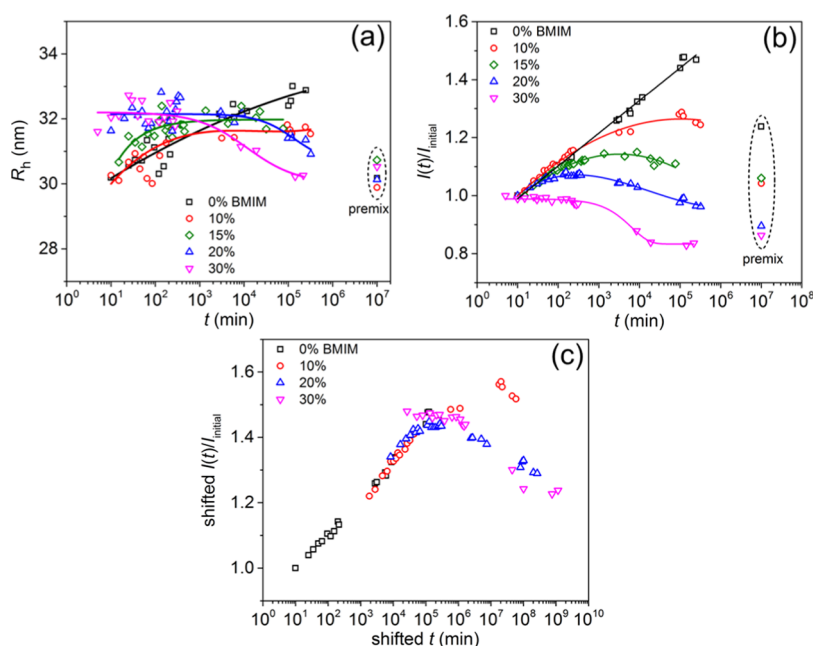


Figure 5. (a) Hydrodynamic radius (R_h) and (b) normalized background-corrected scattering intensity ($I(t)/I_{\text{initial}}$) vs the mixing time t for 0.5 wt % postmixed micellar solutions of MB(25–24) and MB(25–53) in varying solvents at a scattering angle of 90° and a temperature of 55°C . Note that the data points at “ $t = 10^7$ min” correspond to the premixed samples with identical content. The symbols are the experimental data and the solid lines are drawn as guides to the eye. (c) Shifted normalized scattering intensity ($I(t)/I_{\text{initial}}$ based on data in (b)) vs the shifted mixing time t . Note that the time shift factors are based on the different chain exchange times of the larger micelles in varying solvents. Additionally, the normalized intensities were arbitrarily vertically shifted to construct the master curve. The vertical shift factors are 1, 1.22, 1.34, and 1.48, respectively, for 0, 10, 20, and 30% [BMIM][TFSI]. Finally, the reference for all of the data shifts is the “0% BMIM”.

protocol (Figure 5b). In Figure 5c, we present a “master curve” for the mixed micelle equilibration process, by shifting the intensity versus time curves both vertically and horizontally. This is an empirical and nonrigorous procedure, but it reveals important aspects of the process. In particular, an early-time growth in the average micelle size and scattered intensity is apparent, followed by a long-time decay toward the equilibrium state. The early-time increase is interesting, in that it appears to represent a trajectory in phase space that begins by moving further away from equilibrium, prior to reversing course. The horizontal shift is based on the unimer exchange time of the longer chains and correlates with variation in solvent selectivity; the less selective the solvent, the more rapid the equilibration, and a certain selectivity is necessary to access the regime of the early-time increase. The selectivity is manifest in the separation of the time scales for unimer exchange for shorter and longer chains (Figure 4b), as will be discussed further below.

Figure 6a–e presents the SAXS traces in the five solvents, respectively. Each panel includes data for the premixed sample, the postmixed sample at $t = 0$, and a postmixed sample after long-time annealing at 55°C (from 53 to 223 days). Note that the annealed postmixed solutions correspond to the last data points in Figure 5a,b; the premixed and postmixed solutions have identical compositions but different sample histories. As shown in Figure 6a,d,e, upon annealing for a long time, the $I(q)$ traces of the postmixed solutions display significant changes in the intermediate q range, which contains information about the average micelle core size and dispersity (form factor scattering). Specifically, minima (or slight depressions) in the scattering curves in this q range shift to lower q , indicating an apparent increase in the average micelle core size of the micellar mixtures. This observation is

consistent with the in situ SANS data (Figure S7). Additionally, a distinct dip in each curve appears in each solvent after annealing. Comparing the scattering data of the premixed (red symbols) and postmixed solutions after long-time annealing (black symbols), significant differences still persist in the intermediate q range in all solvents except 30% BMIM. Interestingly, the intensity gap between the two solutions seems to be progressively smaller as the solvent becomes less selective toward the core block (i.e., the fraction of BMIM increases). In particular, in 30% BMIM, the two scattering curves nearly overlap, indicating almost the same micellar structure between premixed and postmixed samples, suggestive of full equilibration. This is consistent with the results from light scattering (Figure 5). To quantify structural disparities between the premixed and annealed postmixed solutions, the scattering data were fit to the Pedersen model (for postmixed solutions, a sum of two polydisperse block copolymer micelles was adopted), and the fits are also shown in Figure 6 (green lines). The obtained R_c and σ_R values for each fit are summarized in Table S1. A few salient points are noted here. First, the core size of the premixed solutions lies between the larger and smaller populations of the postmixed solutions after annealing. Second, in 0, 10, and 15% BMIM, the larger micelles in the postmixed samples are even larger than in the pure individual larger micelles. For instance, in 0% BMIM, R_c of MB(25–53) and the larger population in the postmixed micellar mixture are 16.9 and 18.8 nm, respectively. On the other hand, in 20 and 30% BMIM, the two sizes are very similar (16.7 vs 16.6 nm in 20% BMIM and 15.7 vs 15.4 nm in 30% BMIM). Additionally, the sizes of the pure individual smaller micelles and the smaller population in the postmixed micellar mixture are comparable (e.g., 10.2 vs 10.3 nm and 9.3

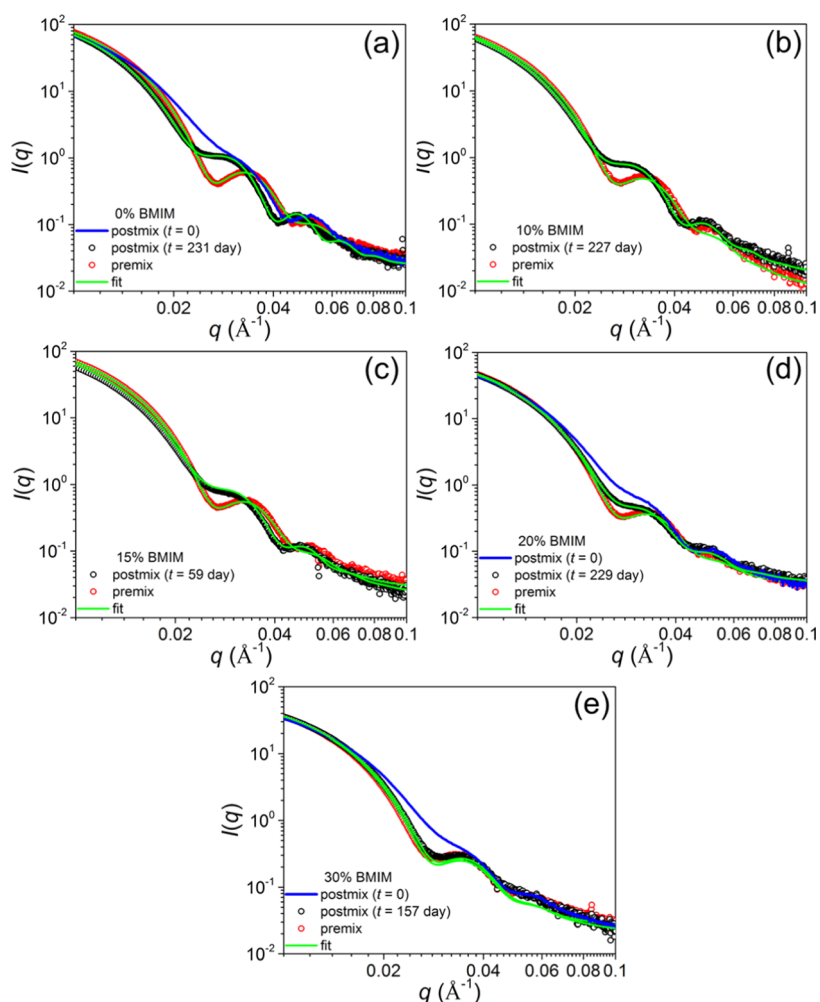


Figure 6. SAXS intensity $I(q)$ vs q for 0.5 wt % premixed and postmixed micellar solutions in (a) EMIM (0 wt % BMIM), (b) 10 wt % BMIM, (c) 15 wt % BMIM, (d) 20 wt % BMIM, and (e) 30 wt % BMIM at 55 °C. The black symbols represent the premixed samples and the red symbols correspond to postmixed solutions upon annealing at 55 °C for varying amounts of time. The green curves represent the best fits to the Pedersen model. Note that the premixed and postmixed solutions in each graph have identical total compositions but different sample histories. The blue lines are the scattering intensities of postmixed solutions at $t = 0$, which were calculated as the average of $I(q)$ of the individual micelles. For clarity, the data are shown only for the q range of 0.01–0.1 Å⁻¹; the complete data are provided in the [Supporting Information](#).

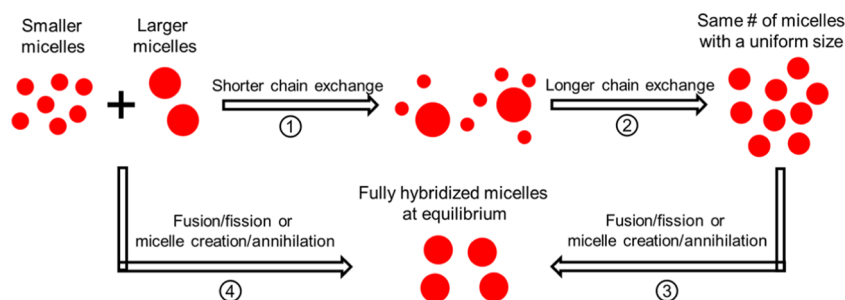


Figure 7. Schematic description of the micelle hybridization processes in different pathways. For simplicity, the red spheres represent micelles of varying sizes, roughly to the scale. The number of circles roughly corresponds to the number ratios of the smaller and larger micelles in current work. The four processes are briefly described as (1) dominated by the shorter-chain exchange, (2) the longer-chain exchange becomes facile, (3) and (4) structural reorganization via fusion/fission and micelle creation/annihilation mechanisms.

464 vs 9.8 nm in 0 and 30% BMIM, respectively). These results are
465 fully consistent with the results in [Figure 5](#).

466 ■ DISCUSSION

467 Before discussing the mechanisms of micelle hybridization, we
468 first need to determine the thermodynamically stable state of

the mixed micellar system. A good first approximation should
469 be that resulting from the premixed protocol. In this scenario,
470 our previous report has revealed that these two diblocks are
471 able to co-micellize and form a single, relatively narrowly
472 distributed population of mixed micelles, at all mixing ratios.⁴⁸
473 This is because the disparity of the core block length between
474

the two diblocks is not that large; as a result, well-mixed micelles are thermodynamically more favorable than a binary micellar mixture of different sizes. Figure 7 presents a general overview of possible mechanisms for hybridizing micellar mixtures. There are three processes involved: chain exchange, fusion/fragmentation, and formation of new micelles from unimers/disintegration of existing micelles. In the case of chain exchange, the shorter-chain exchange will be dominant at the very beginning, as the rate of exchange is very sensitive to the core block chain length. This process will make the smaller micelles become even smaller and larger ones become even larger (step 1 in Figure 7) and could explain the increase in scattering intensity in Figure 5b,c. At longer times, the longer-chain exchange becomes facile, and the transfer of longer chains to smaller micelles will make the micelle sizes more uniform, ultimately leading to hybridized micelles with uniform size (step 2 in Figure 6). Note, however, that the chain exchange itself cannot adjust the number of micelles in the system. Therefore, to fully equilibrate the system, at least one of the other two processes (fusion/fission or micelle creation/annihilation) needs to be involved (step 3 in Figure 7). This two-stage micelle relaxation mechanism, i.e., first relaxation by unimer exchange and then equilibration of the total number of micelles, has been proposed in the theoretical study of Nyrkova and Semenov,⁵⁸ which agrees well with the interpretation in current work. As noted above, previous work has shown that the equilibrium state is a uniform population of spherical micelles, each containing a mixture of long and short chains, with an intermediate size. However, because of the relief of chain stretching in a “mixed” core, the size of the hybrid micelle is much closer to that of the larger precursor.⁴⁸ The scattering intensity decrease in Figure 5c could reflect either step 2 or step 3 or a combination of both. It should be emphasized that, although steps 1–3 are drawn as occurring in series, they are independent and likely occur at the same time, i.e., in parallel, especially steps 2 and 3. As discussed further below, this will depend on the solvent selectivity. On the other hand, even if there is no chain exchange, in principle, equilibration to a fully hybridized state could still occur via the other two mechanisms (step 4 in Figure 7).^{21,22}

The short-time structural reorganization is presumably dominated by chain exchange mechanism in the current system, particularly that of the shorter chains (step 1). The chain exchange rate of the shorter diblocks is much greater (e.g., by ~4 orders of magnitude in 0% BMIM), so there is a net flux of shorter chains to larger micelles. This accounts for the short-term increase in the size of the larger micelles (Figures 5a, 6, and S7, except in 30% BMIM) and, accordingly, a decrease in the smaller micelle size. As a result, the weight-averaged molecular weight (M_w) of the micelles in the mixture increases, leading to an increase in the scattering intensity (Figures 5b and S5; $I \sim KcM_w$, where K is the optical constant and c is the copolymer concentration). Notably, this process is reminiscent of Ostwald ripening in colloid systems. The transfer of some shorter chains to larger micelles could be thermodynamically favorable, as the interfacial energy per chain is lower in the larger micelles.

To quantify the role of chain exchange in the early stages of hybridization, we performed the following calculation based on the TR-SANS data. First, for both individual larger and smaller micelles, we estimated the “survival” fraction $f(t)$ of h- and d-chains remaining in the original h- and d-micelles after chain exchange time t , either from $R(t)$ or by fitting to the scattering

data of postmixed h- and d-micelles at time t (the solid lines in Figure 2). The relationship between $f(t)$ and $R(t)$ (derived in the Supporting Information, and note $R(t)$ here refers to an individual micelle) is

$$f(t) = \frac{R(t) + 1}{2} \quad (2)$$

Therefore, the fraction of chains that has been expelled and redistributed $f(t)_{\text{expelled}}$ is

$$f(t)_{\text{expelled}} = 2(1 - f(t)) \quad (3)$$

This can be extended to the mixture of larger and smaller micelles, assuming independent chain exchange⁵⁹ in hybridized micelles (i.e., micelles containing both longer and shorter chains) and that the expelled chains are reinserted into the larger and smaller micelles with equal probability. Also, we assume that the number of larger and smaller micelles are both constant. On this basis, the average micelle core size and core scattering length density of each population can be calculated at any time. For instance, at time t of mixing, the fraction of chains expelled from each larger and smaller micelle is $f(t)_{\text{expelled,L}}$ and $f(t)_{\text{expelled,S}}$. The net transfer of shorter core blocks to larger micelles is $(f(t)_{\text{expelled,S}} n_L)/(n_L + n_S)$, where n_L and n_S are the number densities of the larger and smaller micelles, respectively. Similarly, the net transfer of longer core blocks to smaller micelles is $(f(t)_{\text{expelled,L}} n_S)/(n_L + n_S)$. Take the larger micelle population, the volume fraction of core blocks in solution at time t is

$$\nu_{L,t} = \nu_{L,0} \left(1 - \frac{f(t)_{\text{expelled,L}} n_S}{n_L + n_S} + \frac{f(t)_{\text{expelled,S}} n_L}{n_L + n_S} \right) \quad (4)$$

where $\nu_{L,0}$ is the volume fraction of longer core blocks in solution at zero time. The core size of the larger micelles will be updated as

$$R_{L,t} = \left(R_{L,0} \frac{\nu_{L,t}}{\nu_{L,0}} \right)^{1/3} \quad (5)$$

where $R_{L,0}$ is the larger micelle core size at time 0. The volume fraction of shorter core blocks in the larger micelle core is

$$\nu_{s,L,t} = \left(\frac{f(t)_{\text{expelled,S}} n_L}{n_L + n_S} \right) / \left(1 - \frac{f(t)_{\text{expelled,L}} n_S}{n_L + n_S} + \frac{f(t)_{\text{expelled,S}} n_L}{n_L + n_S} \right) \times (1 - \varphi_{s,c}) \quad (6)$$

where $\varphi_{s,c}$ is the volume fraction of the solvent in the micellar core. Similarly, the volume fraction of longer core blocks in the larger micelle core $\nu_{l,L,t}$ can be calculated. Hence, the average scattering length density in the core of the larger micelles is

$$\rho_{\text{core,L},t} = \rho_{\text{core,d}} \nu_{s,L,t} + \rho_{\text{core,h}} \nu_{l,L,t} + \rho_s \varphi_{s,c} \quad (7)$$

where $\rho_{\text{core,d}}$, $\rho_{\text{core,h}}$, and ρ_s are the scattering length densities of the d-, h- core blocks, and the solvent, respectively. Similarly, the volume fraction, core size, and scattering length density of the smaller micelles can be calculated. With these parameters being updated, the scattering intensity of the micellar mixture after mixing time t can be calculated (the dashed lines in Figure 3). As can be seen, the measured intensities are systematically lower than the calculated ones for all three mixing times. A few factors could lead to this deviation. First,

expelled chains could be preferentially reinserted into one population over the other. For instance, the expelled shorter chains might favorably go to the larger micelles to reduce the interfacial energy; on the other hand, the expelled longer chains could enter the smaller micelles with a much higher probability, as they can help reduce the shorter core block stretching.⁴⁸ Alternatively, new micelles could form from a direct hybridization of free unimers in solution.⁴⁶ Both scenarios would accelerate the redistribution of the h- and d-chains among the larger and smaller micelles, thus leading to a more rapid drop in scattering intensity, as observed in Figure 3; the former explanation seems more probable, given the failure to fully equilibrate most of the mixtures at long times. Although the scattering intensity increases at short times upon mixing of micelles in all solvents (except 30% BMIM; Figure 5b), the rate of increase goes up with solvent selectivity. One likely cause is that $\tau_{\text{MB}(25-53)}/\tau_{\text{MB}(25-24)}$ decreases with the weight fraction of BMIM in the solvent mixture, as shown in Figure 4b. Presumably, the larger mismatch in the unimer exchange of the two populations of micelles in highly selective solvents (e.g., 0% BMIM) effectively transfers more shorter chains to larger micelles, thus resulting in a more rapid increase in the scattering intensity. On the other hand, in 30% BMIM, the scattering intensity barely changes with time in the early stage of hybridization, which could be accounted for by several reasons. First, it is likely that the initial structural change upon mixing of micelles in this solvent is too fast to capture by the light scattering experiment due to the delay in sample preparation (~ 30 min). Alternatively, as discussed above, the time scale for chain exchange differs only by a factor of ~ 50 (Figure 4b), and for the two micelles of equal total core block volume, the number of smaller micelles is ~ 4 times that of the larger ones. This makes the net transport of chains between the two populations of micelles more balanced, thus leading to less change in the scattering intensity. Additionally, other processes (formation of new micelles or fusion/fragmentation) could also be invoked at an earlier time scale in this solvent. For instance, there should be more free chains due to lower solvent selectivity, which will facilitate the assembly of new micelles from the direct hybridization of different unimers.

Next, we discuss the hybridization mechanisms at long times, focusing on the distinct feature that the scattering intensity in Figure 5b starts to decrease with time (except in 0% BMIM). The time scale where the intensity starts to drop correlates with increasing solvent selectivity. To examine how this is related to unimer exchange, the time axis in Figure 5 was shifted by the ratio of the chain exchange time relative to that in 0% BMIM, which was taken as the reference. Two different ways of time shifting were performed, based on the differences in the chain exchange time of either smaller (Figure S8) or larger micelles (Figure 5c). Apparently, that calculated from the larger micelles can better superpose the intensity vs time curves in various solvents (Figure 5c). This reflects the fact that the scattered intensity is dominated by the larger micelles and that the chain exchange of the larger micelles is the rate-limiting step (Figure 7). However, other processes such as fusion/fragmentation or micelle annihilation/creation must be involved to fully equilibrate the micellar mixture, and they could also contribute to the intensity decrease in Figure 5b,c. Assuming that the premixed samples are good approximants of the equilibrium states, only the micellar mixture in the 30% BMIM is able to reach the equilibrium within the experimental time scale of 7 months. This indicates that, even in micellar

systems where chain exchange is facile, it is still difficult or even impossible to fully equilibrate within a reasonable time frame. For micellar mixtures in 0–20% BMIM, the structure of the postmixed micelles after long-time annealing is still significantly different from the premixed counterparts (Figures 5 and 6). Detailed analyses of the SAXS data (Figure 6) reveal that there are still two distinct populations of micelles even after long-time annealing, with the size of the larger population being greater than the pure individual larger micelles. In fact, to reach the equilibrium state, the number of micelles in the postmixed solution needs to be adjusted, again suggesting that the other two relaxation processes must be involved, as chain exchange itself cannot adjust the number of micelles (Figure 7). Table 3 summarizes the structure and number of micelles

Table 3. Characterization of Individual, Premixed, and Postmixed Micelles

solvent	micelle	R_c (nm)	N_{agg}^a	# of micelles (total block copolymer weight of 10^{-15} g) ^{b,c}
0% BMIM	MB(25–24)	10.2	108	114
	MB(25–53)	16.9	221	35
	postmix	^c	^c	114 + 35 = 149 ^d
	premix	16.3	301	66 ^e
20% BMIM	MB(25–24)	9.7	92	133
	MB(25–53)	16.7	213	36
	postmix	^c	^c	133 + 36 = 169 ^d
	premix	16.2	293	68 ^e
30% BMIM	MB(25–24)	9.3	81	151
	MB(25–53)	15.7	177	44
	postmix	^c	^c	151 + 44 = 195 ^d
	premix	15.1	238	84 ^e

^a N_{agg} , the aggregation number of micelles, was estimated as described in Table 2, assuming that the polymer volume fraction in the core is ~ 0.9 in all cases. ^bThe number of micelles for a total mass of 10^{-15} g for either shorter and longer diblocks. The number of micelles for the premix and postmix solutions corresponds to a total mass of 2×10^{-15} g. ^cNot applicable. ^dThe total number of micelles (sum of smaller and larger ones) upon mixing or at zero mixing time. ^eThe number of premixed micelles with equal masses (10^{-15} g) of shorter and longer diblocks.

for both premixed and postmixed hybrids. In all three solvents, the number of micelles in the premixed solution is much smaller than the sum of smaller and larger micelles in the postmixed solution. For example, in 30% BMIM, as shown in Table 3, the number of micelles in the premixed solution (on the basis of a total mass of each diblock of 10^{-15} g) is 84, while the sum of the number of smaller and larger micelles in the postmixed solution at zero time is 195. This indicates that the number of micelles needs to be reduced by more than half in the hybridization process. Presumably, most of the smaller micelles disintegrate by being incorporated into the existing larger micelles or forming new micelles. Similar calculations were performed in the other two solvents, 0 and 20% BMIM, with similar results.

Finally, we summarize the hybridization processes in solvents of varying selectivity. In a highly selective solvent (e.g., 0% BMIM), the unimer exchange between the two populations of micelles results in a dominant transport of

shorter chains to larger micelles, making the larger micelles become even larger and smaller ones even smaller. This process seems to continue even after annealing for more than 7 months, leading to a kinetically trapped state that cannot be fully relaxed within the experimental time scale. On the other hand, in a weakly selective solvent (e.g., 30% BMIM), the postmixed and premixed micellar mixtures are able to reach the same thermodynamic state, indicating that equilibrium is obtained. We propose the following pathways. At short times, chain exchange is the dominant mechanism (steps 1 and 2 in Figure 7), but eventually, micelle fusion/fragmentation or micelle creation/annihilation occurs. Unimer exchange makes the micelle size disparity even larger, which actually brings the system farther away from equilibrium. This might favor the process of fragmentation, which is more probable when the micelles are too large.^{18,21,22} Additionally, “unidirectional” chain exchange could make the smaller micelles less stable, such that they break apart into unimers. Also, the nucleation and growth of new micelles definitely require a continuous supply of free chains from existing micelles, which could be realized via the chain expulsion process. Therefore, although the other two mechanisms are required to fully hybridize the two micelles (steps 3 and 4 in Figure 7), chain exchange/expulsion still plays a critical role in the entire hybridization process.

SUMMARY

In this report, we have investigated the hybridization of two different sized micelles in ionic liquids of varying selectivity. We first characterized the structure and chain exchange kinetics of the two pure individual micelles. It was found that both the shorter and longer diblocks self-assemble into well-defined spherical micelles with different sizes. Additionally, due to the difference in the core block length, the rate of chain exchange is much higher in smaller micelles than in larger ones. The two micellar solutions were mixed, and the hybridization process was monitored by time-resolved SANS and light scattering, complemented by SAXS. TR-SANS data undoubtedly show that there is crosstalk between the two populations of micelles. Specifically, in a highly selective solvent, 0% BMIM, the scattering intensity continues to increase even after annealing for more than 7 months, which apparently results from the predominant transfer of shorter chains to larger micelles, due to the several orders of magnitude disparity in chain exchange rates of the two micelles. This leads to a locally stable, kinetically trapped state that cannot be equilibrated within the experimental time scale. SAXS data confirm this conclusion and show the existence of two distinct populations of micelles in the postmixed micellar mixture even after long-time annealing. On the other hand, in a much less selective solvent, 30% BMIM, two stages of micelle hybridization were proposed. First, at short times, chain exchange should be the dominant process. This actually brings the system farther away from equilibrium and thus invokes the other two relaxation mechanisms, micelle fusion/fragmentation or micelle creation/annihilation. All of these processes combined together are able to fully hybridize the two micelles. Therefore, both light and X-ray scattering show a similar structure between the premixed and postmixed micellar mixtures after long-time annealing. Our results suggest that the micelle hybridization process depends greatly on the solvent selectivity and the findings provide new insight into how a micellar system transforms from a nonequilibrated to a

thermodynamically more stable state. TR-SANS can provide detailed measurements of unimer exchange, but more experimental studies of the kinetics of fusion, fragmentation, and micelle annihilation/creation would be very useful.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.0c01419>.

DLS data, SANS data and analysis, additional time-resolved SANS and DLS data, fitting results of SAXS data on both premixed and postmixed solutions upon long-time annealing, derivation of the relationship between $R(t)$ and $f(t)$, and time-shifted light scattering data (Figures S1–S9 and Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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