

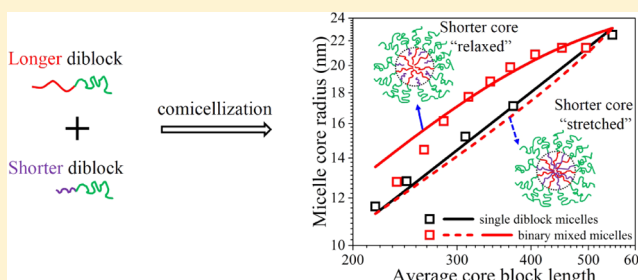
Micellization of Binary Diblock Co-polymer Mixtures in an Ionic Liquid

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S Supporting Information

ABSTRACT: The structure of mixed diblock co-polymer micelles in the aprotic ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][TFSI], was investigated by dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and small-angle neutron scattering. The diblock co-polymers are poly(methyl methacrylate)-*block*-poly(*n*-butyl methacrylate) (PMMA-*b*-PnBMA), where PMMA is solvent selective and forms the corona of the micelles, whereas PnBMA segregates into the micelle core. In these experiments, a pair of diblocks with the same corona block length but distinct core block lengths (N_{core}) was first mixed homogeneously and then allowed to self-assemble into well-defined mixed micelles. DLS and SAXS measurements show that the hydrodynamic radius (R_h) and core radius (R_c) increase monotonically with the fraction of the longer diblock in the mixture. Interestingly, the dimensions of the binary mixed micelles are significantly larger than those formed by a single diblock with the same number average core block length ($\langle N_{\text{core}} \rangle$). Similarly, the aggregation number is also much larger for the mixed micelles. These results can be understood by recognizing that in the binary mixed micelles, the shorter core blocks are not necessarily stretched to the center of the micelle core, which will be predominantly occupied by the longer core blocks. This relief of the shorter core block stretching effectively increases the aggregation number. Free-energy calculations confirm this hypothesis and are able to predict the R_c values of the binary mixed micelles quantitatively by eliminating the elastic free energy of the shorter core blocks. These results provide new physical insight into the micellization of binary co-polymer mixtures and demonstrate that block polymer blending is a facile strategy for precise tuning of the micellar structure (e.g., core radius and corona density).



INTRODUCTION

Block co-polymers (BCPs), which can self-assemble into various nanoscale micellar structures in a selective solvent,^{1–3} offer advantages in diverse emerging technologies, including drug and gene delivery,^{4–8} nanolithography,⁹ nanoreactors,^{10,11} oil recovery,^{12–14} and synthesis of mesoporous materials.¹⁵ For many of these applications, it is desirable to control the micelle structure, such as the core dimension, the interfacial area per chain, and the corona density. For instance, the micelle core/corona interfacial structure and the corona density profile are critical factors affecting the transport of small molecules into or out of the micelles, which in turn play important roles in drug delivery and nanoreactor applications. Additionally, the size of micelles determines their blood circulation time as drug carriers. Moreover, it has been recently shown that higher solvent (i.e., water) content in the micelle corona (related to corona density) provides better micelle mobility, leading to improved interaction with cell receptors and, therefore, enhanced biological activity.¹⁶

One common way to tune the micellar structure is to vary the BCP molecular characteristics (such as core and corona block length)^{2,17–20} and solvent selectivity.¹ However, precise

structural control requires the synthesis of BCPs with exact chain lengths and compositions. A more facile and efficient way to tune the micelle structure is to blend BCPs with different molecular characteristics or functionality. In fact, this is a common strategy encountered in biological (e.g., lipids) and industrial (e.g., surfactant) systems. Several additional factors make the blending methodology attractive. First, other thermodynamic properties, such as the critical micelle concentration, critical micelle temperature (CMT), and the gelation and rheological behavior of concentrated micelle dispersions, can be manipulated by self-assembly of binary BCP mixtures.^{21–25} Second, micellization of binary BCP mixtures can lead to distinct morphologies or structures that cannot be achieved with single BCPs.^{26–31} For instance, it has been postulated that a binary mixture of two diblock co-polymers with a common core block but incompatible corona blocks might self-assemble into “patchy” micelles.³¹ It has also been shown that mixed micelles from BCPs provide superior

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physical stability and redispersion properties, which can enhance their application in drug delivery.^{7,32} Third, blends of amphiphilic molecules are commonly formulated and used in commercial practice, since it is difficult to recycle and separate mixtures of surfactants or BCPs.

Micellization of binary BCP mixtures has been extensively investigated by theory,^{33–35} simulation,^{36–38} and experiment. Measurements have been conducted in aqueous solutions (particularly Pluronics in water),^{21–23,39–41} organic solvents,^{42–46} and very recently in a protic ionic liquid (IL).⁴⁷ Among these studies, the two BCPs could differ in core block length, core block chemistry, corona block length, or corona block chemistry. Here, we highlight the previous work on self-assembly of binary BCPs of identical chemical nature and corona block length but distinct core block lengths. In general, the two co-polymers could assemble into monomodal mixed micelles (with uniform composition) or demixed ones with a bimodal distribution (the two populations could be pure and mixed micelles or both mixed ones with distinct compositions). This depends primarily on the difference between the core block lengths, the stoichiometry of the binary mixture, and the process of micellization. Specifically, the theory predicts that when the core block lengths are similar, only mixed micelles are stable, but when the difference is large, mixed micelles co-exist with pure micelles.^{33,35} This prediction was experimentally confirmed by Gaisford et al. using iodine incorporation UV spectroscopy.³⁹ The proportion of the two BCPs in the mixture also plays a role. It was reported that co-micellization becomes more favorable when the two polymer species have similar concentrations.^{35,37,42} In contrast, when the relative fraction of the shorter chains in the mixture is high, the excess short chains form pure micelles, leading to the co-existence of two types of micelles.^{42,48} On the other hand, in practice, the formation of either mixed or demixed micelles is also dictated by the sample processing history, presumably as a consequence of nonergodicity.^{26,42,43} For instance, Jain et al. found that although the premixing protocol (i.e., mix the two co-polymers homogeneously before micellization) yields mixed micelles, postmixing of the individual BCP dispersions produces morphologies representing a superposition of the two pure BCP solutions (i.e., unmixed micelles).²⁶ Honda et al. studied the micellization of binary BCP mixtures with different CMTs after single-step or double-step temperature jumps (T -jumps) from the unimer region. It was reported that in a single-step T -jump, where both co-polymers form micelles, co-micellization takes place. In a double-step T -jump, first from a unimer region to an intermediate temperature at which only one co-polymer forms micelles and subsequently to a region where both co-polymers form micelles, two populations of micelles were observed.⁴² Due to these thermodynamic and kinetic factors, both mixed and unmixed micelles have been reported in the literature. For example, a bimodal distribution of micelles was confirmed by microdifferential scanning calorimetry, transmission electron microscopy (TEM), and dissipative particle dynamics simulations.^{22,37,43,46} In contrast, in many other studies, the two BCPs were found to fully hybridize into mixed micelles.^{25,26,36,38,40,41,49} In general, the structural parameters of the mixed micelles (e.g., hydrodynamic radius, core radius, and aggregation number) are intermediate between those formed with individual BCP chains. However, due to the limited resolution of the experiments and the small difference between the two BCPs used, the exact relation between the micelle dimensions and

the average core block length ($\langle N_{\text{core}} \rangle$) has not been established. Additionally, although in some cases, one clearly sees systematic deviations of the structural or dynamic characteristics of the mixed micelles from those expected for pure micelles with an equal $\langle N_{\text{core}} \rangle$,^{26,36,41,48,50} a good understanding of these observations is missing. Moreover, how the micelle core radius depends on the proportion of the two BCPs has not been directly probed.

To address these interesting questions, we report the micellization of binary mixtures of poly(methyl methacrylate)-*block*-poly(*n*-butyl methacrylate) (PMMA-*b*-PnBMA) diblock co-polymers in 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonfyl)imide, [EMIM][TFSI]. As shown in our previous studies,^{51,52} PMMA is the solvent-selective block and forms the micelle corona, whereas PnBMA, displaying a lower critical solution temperature (LCST) in [EMIM][TFSI], forms the micelle core. The two diblocks have the same corona block length (N_{corona}) but different core block lengths (N_{core}). Each pair of diblocks studied here co-assemble into mixed micelles at all proportions. The structure of the formed mixed micelles is characterized by a combination of dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and small-angle neutron scattering (SANS). Due to the relative monodispersity and good scattering contrast, the micelle core radius can be precisely determined by SAXS or SANS. The measurements were performed at 55 °C, which is ~130–180 °C above the LCST of PnBMA in [EMIM][TFSI].⁵³ Additionally, the experimental temperature is much higher than the glass transition temperature (T_g) of the solvophobic PnBMA block ($T_g \approx 20$ °C),⁵⁴ thus the kinetically trapped states associated with a glassy, frozen micelle core can be circumvented.⁵⁵ The results are interpreted in detail using an extension of the classical micelle free-energy balance.^{3,56,57}

EXPERIMENTAL SECTION

Synthesis and Characterization. Sequential radical addition–fragmentation chain-transfer polymerization was used to synthesize a series of diblock co-polymers of PMMA-*b*-PnBMA, with the details provided in a previous report.⁵² Briefly, the PMMA block was first prepared and following that the PnBMA block was grown from the PMMA macrochain transfer agent. The number-averaged molecular weight (M_n) of the PMMA block and the dispersity ($\mathcal{D}$) of the diblocks were obtained from size exclusion chromatography (SEC) with a multiangle laser light scattering detector (Wyatt DAWN). The M_n of the PnBMA block was determined by ¹H nuclear magnetic resonance spectroscopy (¹H NMR, Varian Inova 500). The molecular characteristics of the diblocks are presented in Table 1. The IL

Table 1. Molecular Parameters of Diblock Co-polymers

PMMA- <i>b</i> -PnBMA	$M_{n,\text{PMMA}}^c$ (kg/mol)	$M_{n,\text{PnBMA}}^c$ (kg/mol)	N_{PMMA}^d	N_{PnBMA}^d	$\mathcal{D}^e$
(25–24) ^a	25	24	250	169	1.05
(25–31) ^b	25	31	250	218	1.05
(25–35) ^b	25	35	250	246	1.05
(25–44) ^b	25	44	250	310	1.07
(25–50) ^a	25	50	250	352	1.08
(25–53) ^b	25	53	250	373	1.07
(25–78) ^b	25	78	250	549	1.11

^aThe SEC traces of these two diblocks are shown in Figure S1. ^bAs reported previously.⁵² ^c $M_{n,\text{PMMA}}$ and $M_{n,\text{PnBMA}}$ are number-averaged molecular weights of the individual blocks. ^d N_{PMMA} and N_{PnBMA} are the degrees of polymerization of the two blocks. ^eDispersity of the diblock co-polymer.

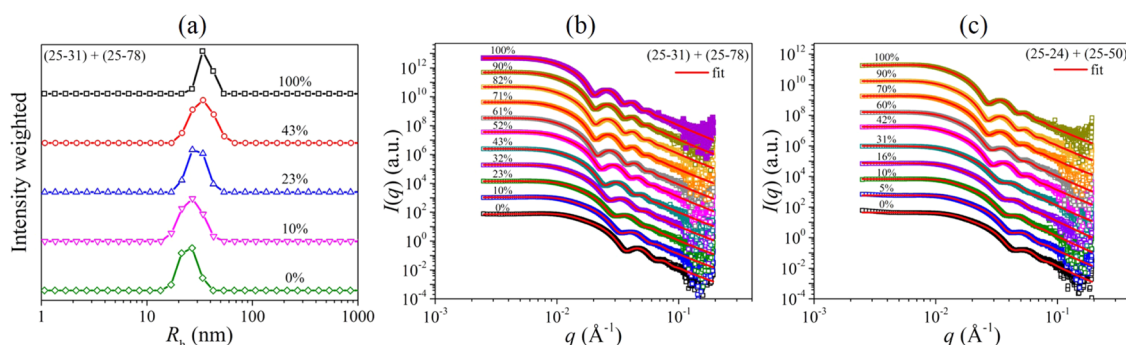


Figure 1. (a) Representative hydrodynamic radius distributions at $\theta = 90^\circ$ for 0.5 wt % mixed micelle solutions of (25-31) + (25-78) in [EMIM][TFSI]. The weight fractions of the longer diblock (25-78) in the co-polymer mixture are indicated inside the graph. SAXS intensity $I(q)$ vs scattering vector q for 1 wt % binary mixed micelles of (b) ((25-31) + (25-78)) and (c) ((25-24) + (25-50)) in [EMIM][TFSI]. The weight fractions of the longer diblock in the co-polymer mixture are indicated inside the graph. The symbols represent the experimental data, and the red lines are best fits to the Pedersen model with the Percus–Yevick structure factor. The scattering traces were vertically shifted by factors of 10 for clarity.

[EMIM][TFSI] was synthesized by the ion-exchange reaction of [EMIM]Br and Li[TFSI] at 70°C for 24 h. To enhance the contrast in the neutron scattering experiment, partially deuterated [EMIM]-[TFSI] was also prepared via the isotopic exchange of the three hydrogens on the imidazole ring with deuterated water at 100°C for 3 days. All other chemicals were obtained from Sigma-Aldrich.

Sample Preparation. All mixed micellar solutions in the IL were prepared with a polymer concentration of 0.5 or 1 wt % using a co-solvent. Mixtures of the two diblock co-polymers with a known proportion together with an appropriate amount of IL were first dissolved in dichloromethane (DCM). The co-solvent was slowly removed via nitrogen purge until no change in the solution weight was observed, during which the block co-polymer micelles were formed. Following that the resulting micellar solution was kept at 50°C for 12 h under vacuum (<100 mTorr) to completely remove any residual co-solvent. To examine the effect of the sample preparation protocol, some samples with a similar co-polymer ratio and concentration were made by the following process. First, separate micellar solutions were prepared for the two diblocks following the co-solvent method described above. Subsequently, the two micellar solutions were mixed in a predetermined ratio in the co-solvent. The mixed micelles were finally formed via removal of the co-solvent. Similar results were obtained from both protocols, as discussed below.

Dynamic Light Scattering (DLS). A multiangle light scattering instrument (Brookhaven BI-200SM, with a laser wavelength of 637 nm) was used to conduct the DLS measurements. In a typical experiment, the micelle solution (concentration 0.5 or 1 wt %) was filtered with a $0.45\ \mu\text{m}$ PTFE filter into a glass tube, which was then connected to a vacuum line to remove any air bubbles, and finally sealed with parafilm. All of the DLS experiments were performed at 55°C , and all of the micelle solutions were thermally equilibrated at this temperature for at least 10 min before data acquisition. Intensity autocorrelation functions, $g^{(2)}(t)$, were collected at multiple angles from 50 to 130° , with 20° intervals, for 10 min each. Each correlation function was first analyzed by inverse Laplace transform using the regularized positive exponential sum (REPES) method to obtain the hydrodynamic radius distribution.⁵⁸ Note that in all of the micelle solutions studied, there is only a single population of micelles with a relatively narrow distribution. Thus, the $g^{(2)}(t)$ could also be analyzed by the second-order cumulant method. From this analysis, the average decay rate ($\bar{\Gamma}$) was extracted, from which the diffusion coefficient (D_m) was obtained from a linear fit of $\bar{\Gamma}$ vs q^2 . Here, q is the scattering vector, given by $q = (4\pi n/\lambda)\sin(\theta/2)$, n is the refractive index of the IL at 55°C , λ is the vacuum wavelength of the laser, and θ is the scattering angle. Additionally, the size dispersity ($\mu_2/\bar{\Gamma}^2$) of the micelles was assessed from the normalized second cumulant. Finally, the Stokes–Einstein relation was used to calculate the average hydrodynamic radius (R_h) of the micelles, given as $R_h = k_B T / (6\pi\eta D_m)$, where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the IL at 55°C .

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Small-Angle X-ray Scattering (SAXS). The SAXS data were collected on the 5-ID-D beamline (Dupont-Northwestern-Dow Collaborative Access Team) at the Advanced Photon Source, Argonne National Laboratory. The wavelength was $0.73\ \text{\AA}$ and the sample-to-detector distance for the small-angle scattering configuration was $8.50\ \text{m}$, which provided a q range of ~ 0.0025 – $0.19\ \text{\AA}^{-1}$. For the measurements, the micelle solutions were transferred into quartz capillary tubes ($\sim 1.5\ \text{mm}$ in diameter) and then sealed with epoxy. All of the experiments were conducted at 55°C . A Rayonix CCD area detector was used to collect the two-dimensional (2D) scattering data, with a typical acquisition time of 0.5 or 1 s. The 2D isotropic scattering data were then converted into one-dimensional (1D) traces ($I(q)$ vs q) via an azimuthal average. The scattering of the IL in the capillary tube was also collected as the background. The Pedersen model for block co-polymer micelles with the Percus–Yevick hard sphere structure factor was used to analyze the scattering profiles.^{59–61}

Small-Angle Neutron Scattering (SANS). The SANS measurements were conducted on the NG7 30 m SANS beamline at the Center for Neutron Research of the National Institute of Standards and Technology (NIST). The wavelength of the neutron beam was $6.0\ \text{\AA}$, with a spread ($\Delta\lambda/\lambda$) of 0.115. Three configurations (with sample-to-detector distances of 1, 4, and 13 m) were combined to provide a q range of ~ 0.0039 – $0.56\ \text{\AA}^{-1}$. In typical runs, the micelle solutions were transferred into 1 mm banjo cells and then placed on the beamline for data collection. All measurements were performed at 55°C . The 2D scattering data at each configuration were separately reduced and converted to 1D profiles using the Igor Pro package developed by NIST.⁶² The obtained 1D data at all configurations were then merged and analyzed by the same scattering model as in SAXS.

RESULTS AND DISCUSSION

Figure 1a shows the intensity-weighted hydrodynamic radius distributions at $\theta = 90^\circ$ for 0.5 wt % mixed micelles of (25-31) + (25-78) with varying proportions in [EMIM][TFSI] at 55°C , obtained from the REPES analysis. There is a single, narrowly distributed population in micelles formed with either a single diblock or a binary mixture of two diblocks, indicating the formation of mixed micelles.^{21,40,42} As the fraction of the longer diblock increases, the peak hydrodynamic radius of the mixed micelles grows monotonically. For instance, it increases from 23.8 to $32.6\ \text{nm}$ when the weight fraction of (25-78) is raised from 0 to 43%. Additionally, the intensity correlation function $g_1^2(t)$ (Figure S2) of each micelle solution can be well

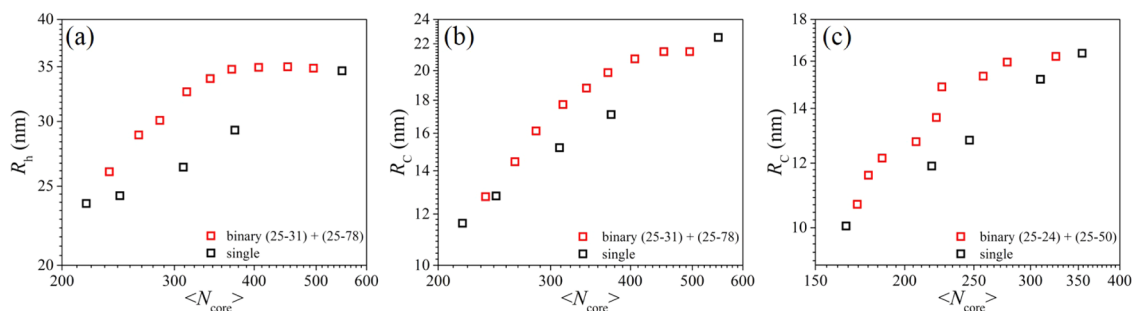


Figure 2. (a) Hydrodynamic radius R_h vs the average core block length $\langle N_{\text{core}} \rangle$ for 0.5 wt % micelle solutions in [EMIM][TFSI]. (b, c) Micelle core radius R_c vs $\langle N_{\text{core}} \rangle$ for 1 wt % micelle solutions in [EMIM][TFSI]. The black squares correspond to micelles formed with a single diblock copolymer, whereas the red ones represent mixed micelles of (b) (25–31) + (25–78) and (c) (25–24) + (25–50).

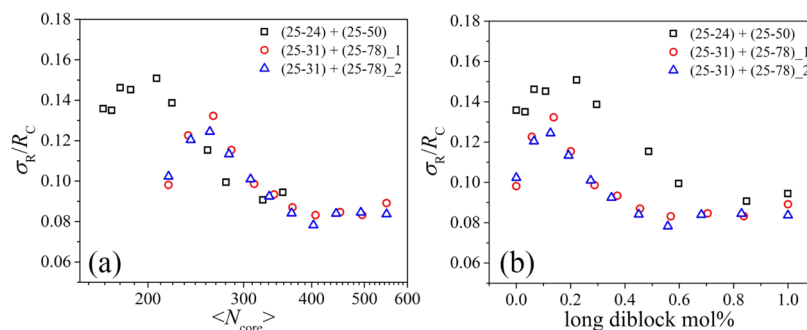


Figure 3. (a) Coefficient of variation σ_R/R_c vs $\langle N_{\text{core}} \rangle$ for 1 wt % binary diblock co-polymer micelles in [EMIM][TFSI]. The “(25–31) + (25–78) _1” and “(25–31) + (25–78) _2” were prepared following two different protocols, as described in the Experimental Section. (b) The same data in (a) plotted vs the mole fraction of the longer diblock.

described by the second-order cumulant expansion, with the obtained decay rate $\bar{\Gamma}$ plotted as a function of q^2 in the inset of Figure S2. Clearly, as shown there, $g_1^2(t)$ decays at later times with the increase in the weight fraction of (25–78) in the copolymer mixture, indicating a larger micelle size, consistent with Figure 1a. The linear fits of $\bar{\Gamma}$ vs q^2 yield the diffusion coefficient of the micelles and from there R_h can be obtained. The mean R_h is shown in Figure 2a as a function of the average core block length $\langle N_{\text{core}} \rangle$, defined by

$$\langle N_{\text{core}} \rangle = \bar{x}_L N_{\text{core,L}} + (1 - \bar{x}_L) N_{\text{core,S}} \quad (1)$$

$$\bar{x}_L = \frac{\omega_L / M_{n,L}}{\omega_L / M_{n,L} + (1 - \omega_L) / M_{n,S}} \quad (2)$$

where $\bar{x}_L$ is the mole fraction of the longer diblock in the copolymer mixture, $N_{\text{core,L}}$ and $N_{\text{core,S}}$ are the core block lengths of the longer and shorter diblock, respectively, ω_L is the weight fraction of the longer diblock in the mixture, $M_{n,L}$ and $M_{n,S}$ are the molecular weights of the longer and shorter diblocks, respectively, which are equal to 103 and 56 kg/mol for the diblock pair of (25–78) and (25–31). As shown in Figure 2a, the average R_h of the binary mixed micelles increases monotonically with $\langle N_{\text{core}} \rangle$. Moreover, the dispersity of the hydrodynamic radius ($\mu_2/\bar{\Gamma}^2$) is smaller than 0.1 for all of the micelles (Figure S3), confirming that the two diblocks formed mixed micelles with a single population.⁴² Figure 2a also shows R_h for single component micelles, with different core block lengths. As expected, with the increase of the core block length, the micelle size becomes larger. Interestingly, for a given $\langle N_{\text{core}} \rangle$, the R_h of the mixed micelles is significantly larger than for the pure micelles. For example, at $\langle N_{\text{core}} \rangle \approx 370$, $R_h = 29.3$ and 34.7 nm, respectively, for the pure and mixed diblock co-

polymer micelles. Similar results were obtained for another pair of diblocks, (25–24) + (25–50) (Figure S4). The underlying mechanism for these intriguing findings will be discussed later.

We next compare the core dimensions of the mixed micelles to pure micelles. Figure 1b,c shows scattering profiles of mixed micelles of (25–31) + (25–78) and (25–24) + (25–50), respectively, in [EMIM][TFSI] at 1 wt %. For each trace, the scattering intensity oscillates in the high q regime and levels off at lower values of q , characteristic of spherical micelles without any larger-scale aggregates in the solution. As the scattering contrast results primarily from the core,⁶³ the micelle core radius R_c can be inferred from the position of the first q minimum ($q_{1,\text{min}}$). As shown in Figure 1b,c, in both pairs of diblocks, as the weight fraction of the longer diblock increases, $q_{1,\text{min}}$ systematically shifts to lower q values, indicating larger core sizes. The scattering data can be well described by the Pedersen model combined with the Percus–Yevick structure factor, from which R_c can also be determined; the results are plotted against $\langle N_{\text{core}} \rangle$ in Figure 2b,c. Note that the values of R_c extracted from the fittings and that from the characteristic equation for the minima in q (i.e., $q_{1,\text{min}} R_c = 4.49$) agree very well (Figure S5). Additionally, to check the reproducibility of the measurements and to evaluate the effect of sample preparation, we prepared another set of mixed micelle solutions of (25–31) + (25–78) by first preforming two pure diblock co-polymer micelles, then blending the two micelles in DCM and finally forming the mixed micelles via removal of DCM. This protocol also yields well-defined spherical micelles (Figure S6). Moreover, the core dimensions of the mixed micelles prepared by the two different methods are nearly the same (Figure S5b), supporting the robustness of the sample preparation and measurements.

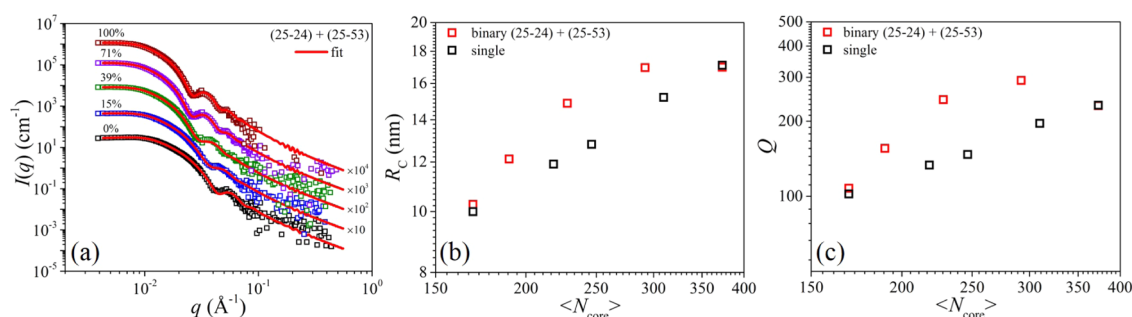


Figure 4. (a) SANS intensity $I(q)$ vs scattering vector q for 1 wt % binary diblock co-polymer ((25-24) + (25-53)) micelles in partially deuterated [EMIM][TFSI]. The weight fractions of (25-53) in the co-polymer mixture are indicated. The symbols represent the experimental data, and the red lines are best fits to the Pedersen model with the Percus–Yevick structure factor. The scattering traces were vertically shifted for clarity. (b) R_c vs $\langle N_{core} \rangle$ and (c) the micelle aggregation number Q vs $\langle N_{core} \rangle$ for 1 wt % micelle solutions in partially deuterated [EMIM][TFSI]. The black squares represent experimental data of single diblock co-polymer micelles adapted from a previous report,⁵² whereas the red ones correspond to the binary mixed micelles. For the single diblock micelles, Q was estimated from the SAXS R_c values assuming that there is ~10 vol % solvent in the micelle core.

Figure 2b,c presents R_c vs $\langle N_{core} \rangle$ for binary mixed micelles of (25-31) + (25-78) and (25-24) + (25-50), respectively. In both cases, R_c increases monotonically with $\langle N_{core} \rangle$. This agrees well with the change in $q_{1,min}$ in Figure 1b,c as well as the trend of R_h with $\langle N_{core} \rangle$ in Figures 2a and S4. Figure 2b,c also includes R_c of pure micelles adapted from an earlier work.⁵² As reported previously, the R_c of single diblock micelles scales as $\langle N_{core} \rangle^{0.71}$; in contrast, R_c of the binary mixed micelles vs $\langle N_{core} \rangle$ does not follow a power law. Instead, R_c increases more rapidly at smaller values of $\langle N_{core} \rangle$ and nearly plateaus when $\langle N_{core} \rangle$ approaches that of the longer diblock. Consistent with the behavior of R_h , R_c of the mixed micelles is significantly larger than for pure micelles at the same $\langle N_{core} \rangle$. A similar result was found by Jain et al. for micelles with a spherical morphology.²⁶ Figure 3a shows the coefficient of variation in R_c ($CV = \sigma_R/R_c$) as a function of $\langle N_{core} \rangle$. In mixed micelles formed with both pairs of diblocks, there is an apparent maximum in σ_R/R_c which occurs roughly near 15 mol % of the longer diblock in both cases, as shown in Figure 3b. This result will be discussed subsequently.

We examine the aggregation number of the binary mixed micelles based on the SANS measurements. Figure 4a presents the neutron scattering intensity $I(q)$ vs scattering vector q for mixed micelles of (25-24) + (25-53) in partially deuterated [EMIM][TFSI]. Consistent with the SAXS data, $q_{1,min}$ clearly decreases with increasing fraction of the longer diblock, again implying an increase in R_c . The SANS traces were also well fit by the Pedersen model with a hard sphere structure factor, from which R_c and the micelle aggregation number Q can be simultaneously determined. Consistently, R_c increases with $\langle N_{core} \rangle$, and it is significantly larger for the binary mixed micelles than pure ones at the same $\langle N_{core} \rangle$ (Figure 4b). Interestingly, in Figure 4c, we see that Q first increases and then decreases with $\langle N_{core} \rangle$. This indicates that at some intermediate fraction of the longer diblock, one mixed micelle contains more co-polymer chains than that formed with only the longer diblock co-polymer. Similarly, Newby et al. observed that the hydrodynamic radius of a 50/50 binary co-polymer mixture is larger than either pure micelles, which they attributed to a higher aggregation number for the mixed micelles.⁵⁰ This is consistent with the observation in Figure 4c. Going further, similar to R_c , Q of the mixed micelles is much larger than for single diblocks (estimated from the SAXS R_c data assuming that there is ~10 vol % solvent in the micelle

core, Figure S7). To summarize, by combining three different scattering techniques, we consistently show that the micelle dimensions can be precisely tuned by blending two diblock copolymers, with the values of the micelle size systematically increasing with the fraction of the longer diblock. Importantly, the micelle size (both R_h and R_c) and the aggregation number are significantly larger for the binary mixed micelles than those formed with a single diblock co-polymer. In the following, free-energy calculations on both pure and mixed micelle systems are performed to reveal the underlying mechanism for these intriguing results.

We start from the single diblock co-polymer micellar system. We adopt the theory developed by Zhulina et al.,³ which explicitly takes all contributions (core, corona, and interface) to the free energy of the micelle into account. This allows the model to be applicable to the crossover regime between the crew-cut and starlike micelles,¹⁸ appropriate for the current system. Moreover, the numerical coefficients for all of the free-energy terms were calculated from theory.^{3,64} According to this model, the free energy per co-polymer chain (F_{chain}) within the micelle is given by

$$\begin{aligned} \frac{F_{chain}}{k_B T} = & \frac{4\pi R_c^2 \gamma}{Q a_B^2} + \frac{3\pi^2 R_c^2}{80 N_{core} b^2} + \frac{1}{2\sqrt{3}} C_H p_A^{-3/4} \\ & \frac{R_c^{3/2} \phi^{1/2}}{N_{core}^{1/2} a_B^{3/2}} \ln \left[1 + \frac{2 C_H p_A^{1/4} N_{corona} \phi^{1/2} a_A^2}{\sqrt{3} R_c^{1/2} N_{core}^{1/2} a_B^{3/2}} \right] \\ & + F_{chain,0} \end{aligned} \quad (3)$$

where $\gamma = (\gamma_{BaB}^2)/(k_B T)$ is the normalized interfacial tension at the micelle core/corona interface, γ_B is the surface free energy per unit area; $a_A = 0.52$ nm and $a_B = 0.6$ nm are the volumetric sizes of one repeat unit of the corona and core block, respectively; $b = 0.61$ nm is the statistical segment length of the core block;⁶⁵ $p_A = 1.44$ is the corona chain stiffness parameter; $\phi \approx 0.9$ is the volume fraction of the core block in the micelle core (Figure S7). Calculation of these parameters is shown in Supporting Information. $F_{chain,0}$ accounts for the free energy at a reference state and also any other Q -independent free-energy difference between the micelle and the reference states (e.g., the enthalpy of mixing for the core block). As described by Zhulina et al.,³ C_F and C_H depend on the solvent quality of the corona block; eq 3 was derived for micelles in a θ solvent or

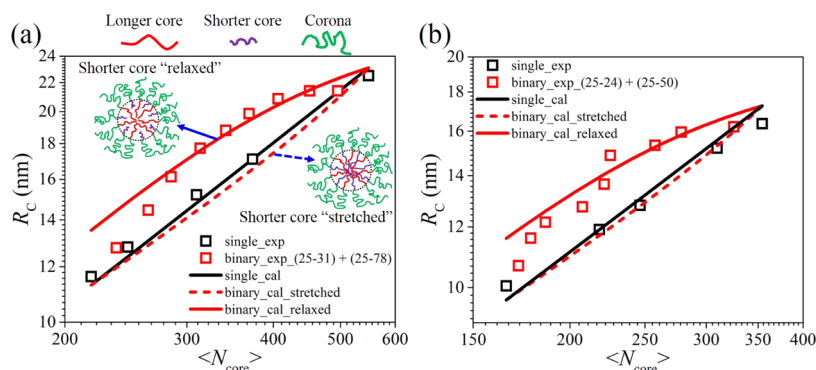


Figure 5. R_c extracted from the SAXS data vs $\langle N_{\text{core}} \rangle$ for 1 wt % micelle solutions in [EMIM][TFSI], including binary mixed micelle of (a) (25–31) + (25–78) and (b) (25–24) + (25–50). In both (a) and (b), the black squares represent R_c of single diblock micelles and the red squares are the binary mixed ones. The solid black and dashed red lines are the free-energy calculations for single and binary diblock micelles, respectively, under the assumption that all core blocks are uniformly deformed to fill the micelle core. The solid red line is the free-energy calculation for the binary mixed micelles assuming no stretching of the shorter core block. The cartoons in (a) depict the “stretched” and “relaxed” conformations of the shorter core block, where the red, purple, and green lines correspond to the longer core block, shorter core block, and the corona block, respectively.

when the corona chain conformation is not significantly modified by the excluded volume interactions. As the corona block in the current work is relatively short, eq 3 is applicable (see the justification in the Supporting Information). In fact, the exact expressions for C_F and C_H are not important for our purpose as they will be estimated by fitting to the experiments.

The first term on the right-hand side of eq 3 is the micellar interfacial energy, the second term is the entropic stretching penalty for the core block, and the third term represents the free energy of the corona block (elastic free energy and excluded volume interactions). Additionally, Q and R_c are related by

$$\frac{4}{3}\pi R_c^3 \phi = Q N_{\text{core}} a_B^3 \quad (4)$$

By minimizing the free energy in eq 3 with respect to R_c

$$\frac{d\left(\frac{F_{\text{chain}}}{k_B T}\right)}{dR_c} = 0 \quad (5)$$

the equilibrium values of R_c can be obtained. To perform the calculation in eq 5, there are still three unknown parameters (γ , C_F , and C_H), which we determine from the comparison with the experimental data of single diblock micelles. Figure S8 shows that the calculations from eq 5 agree very well with the experimental data (also shown by the solid black lines in Figure 5). From here, we obtain $\gamma = 0.096$, $C_F = 1.40$, $C_H = 0.67$ and summarize the model parameters in eq 3 in Table S1 in the Supporting Information. Note that these parameters are quite similar with those obtained in the literature^{3,18} and will be fixed in the following calculations.

We next consider the binary diblock co-polymer mixed micelle system. In this case, additional terms need to be included for the free energy of one block co-polymer chain, as given by

$$\begin{aligned} \frac{F_{\text{chain}}}{k_B T} = & \frac{4\pi R_c^2 \gamma}{Q a_B^2} + x_s \frac{3\pi^2 R_c^2}{80 N_{\text{core},S} b^2} + x_L \frac{3\pi^2 R_c^2}{80 N_{\text{core},L} b^2} \\ & + \frac{1}{2\sqrt{3}} C_F p_A^{-3/4} \frac{R_c^{3/2} \phi^{1/2}}{\langle N_{\text{core}} \rangle^{1/2} a_B^{3/2}} \\ & \ln \left[1 + \frac{2 C_H p_A^{1/4} N_{\text{corona}} \phi^{1/2} a_A^2}{\sqrt{3} R_c^{1/2} \langle N_{\text{core}} \rangle^{1/2} a_B^{3/2}} \right] + \frac{\phi_S}{N_{\text{core},S}} \ln(\phi_S) \\ & + \frac{\phi_L}{N_{\text{core},L}} \ln(\phi_L) + F_{\text{chain},0} \end{aligned} \quad (6)$$

where Q is the total aggregation number of one mixed micelle, including both shorter and longer diblocks, x_s and x_L are the mole fractions of the shorter and longer diblock co-polymer chains in one mixed micelle; $x_s + x_L = 1$. Here, it is assumed that the two diblocks are completely mixed, i.e., there is single population of micelles and the composition of the two diblocks in each micelle is the same, which can be known from the blending formulation (i.e., $x_L = \bar{x}_L$). ϕ_S and ϕ_L are the volume fractions of shorter and longer diblocks in one mixed micelle. Thus, the two terms containing volume fractions in eq 6 account for the mixing entropy of the two diblocks in the mixed micelle core. As we assume that the composition of the two diblocks is constant among the micelles, these two terms will not affect the minimization of the free energy. In eq 6, we essentially separate the core free energy into two terms, one for the longer core block and the other for the shorter core block. For the calculation of the corona free energy, the average core block length $\langle N_{\text{core}} \rangle$ was used. Additionally, in the binary mixed micelle we have

$$\frac{4}{3}\pi R_c^3 \phi = Q(x_s N_{\text{core},S} a_B^3 + x_L N_{\text{core},L} a_B^3) \quad (7)$$

Similarly, by minimizing the free energy in eq 6 with respect to R_c , the core radius of the mixed micelles at equilibrium can be predicted, as shown by the dashed red lines in Figure 5. These calculations significantly underestimate the experimental values in both binary mixed micelle systems and are even smaller than the calculations of the single diblock micelles. This is because in this calculation, it is assumed that both the shorter and longer core blocks are uniformly stretched to fill the micelle

core, which favors a smaller micelle size to reduce the stretching of the shorter core block, considering the fact that the core block is significantly stretched in the micelle core in the current system ($R_c \sim N_{\text{core}}^{0.71}$).⁵² However, for spherical micelles, not all of the core blocks are necessarily stretched to fill the central space of the micelle core. This is especially true for the binary mixed micelle case, in which the longer core blocks can relatively easily reach the center of the micelle, making the shorter ones essentially relaxed. To explore this physical picture, we removed the shorter core elastic free energy in eq 6 (i.e., make the second term on the right-hand side of eq 6 equal to zero) and performed the same free-energy minimization calculation. The new predictions are represented by the solid red lines in Figure 5. As expected, when there is no elastic penalty for the shorter core blocks, larger values of R_c are obtained. Interestingly, reasonable agreement is achieved between the calculations and the experiments (except at smaller $\langle N_{\text{core}} \rangle$), justifying the physical picture proposed. This idea can be further elaborated from the distribution of the core block free ends. According to the calculation of Semenov,⁶⁴ in pure micelles, the density of core block end monomers maximizes in the central part of the core and progressively decreases in regions further away from the micelle core center. In the mixed micelles, although the end monomer density profile remains roughly the same for the longer core blocks as that in pure micelles, the free ends of the shorter core blocks should concentrate around some radial distances (presumably close to the unperturbed end-to-end dimension) from the micelle core/corona interface. This interpretation is corroborated by the Brownian dynamics simulations of Hafezi et al.,³⁸ who have found that in binary mixed micelles, the inner micelle cores are mainly occupied by the longer blocks; the shorter core blocks are more concentrated in the outer parts of the core. Finally, at smaller $\langle N_{\text{core}} \rangle$, the predicted R_c is noticeably larger than that obtained from experiments for both sets of calculations. Presumably, this is due to the fact that in this regime, most of the core blocks are the shorter ones, which are, therefore, still required to stretch to fill the entire space of the core. Therefore, based on this analysis, we propose that in the binary mixed spherical micelles, the composition of the two diblocks controls the relative degree of deformation of the shorter core block. In other words, the partial or complete release of the shorter core block stretching due to the presence of the longer ones leads to a larger aggregation number and, thus, a larger micelle dimension in the binary mixed micelles, which is significantly larger than the pure micelles at the same $\langle N_{\text{core}} \rangle$. In fact, self-consistent field theory also predicts less stretched chain conformations for mixed long and short block co-polymers in the melt.^{66–68} Additionally, it has been reported in block co-polymer melts by both experiment and theory that the domain spacing increases with increasing polydispersity at a fixed average chain length.^{69,70} This is understood based on the idea that disperse co-polymers release part of the stretching energy of the chains. All these results are conceptually in line with the interpretation presented here.

One important assumption made in the calculations is that the two diblocks are fully mixed on the molecular level, i.e., there is a single population of mixed micelles with an identical average composition of the two diblocks. Several pieces of evidence support this assumption. First, we compared the SANS scattering traces of two micelle solutions formed with diblocks of (25–24) and (25–53) in partially deuterated [EMIM][TFSI] (Figure S9). The two samples have identical

content but were prepared in two different ways. One of them was prepared following the same protocol as described above (i.e., premixing), which yielded binary mixed micelles of (25–24) + (25–53); the other one was prepared by first forming the individual micelle solutions of (25–24) and (25–53), respectively, which were then mixed in a predetermined ratio (i.e., postmixing). As shown in Figure S9, the scattering traces of these two samples are very different especially in the middle q range. Specifically, one sees a clear first q minimum in the binary mixed micelles but not in the blend of single diblock micelle solutions, which instead displays a broad bump. This result strongly implies co-micellization of the two diblocks in the premixing protocol.⁴⁷ It might be noted that the cosolvent premixing protocol adopted here for micelle preparation could facilitate the hybridization of the two diblocks during micellization. As the evaporation of the co-solvent is relatively fast, the two diblocks will assemble into micelles roughly at the same time, leading to the formation of well-mixed micelles. This is in contrast with the postmixing protocol and the temperature jump/ramp from the unimer to micelle regime, often adopted in the literature, which could form different populations of micelles, depending on the molecular exchange kinetics. Second, as mentioned earlier, there is only a single narrow size peak observed from the DLS data for the mixed micelles. In fact, the dispersity of the hydrodynamic radius μ_2/Γ^2 is always smaller than 0.1 (Figure S3, comparable to the values of the pure micelle solutions), indicating that the distribution of the mixed micelle size is relatively narrow. Similar observations were made by Honda et al.⁴² Third, as shown in Figure 3, the coefficient of variation in R_c (σ_R/R_c) from SAXS of the binary mixed micelles is comparable or even smaller than that of the single diblock micelles (except when the mole fraction of the longer diblock is smaller than 30%). This suggests very similar core size distributions between the binary mixed and pure micelles.

We have noted that the micelle core dimension is more disperse at small mole fractions of the longer diblock (i.e., <30%) and presents an apparent maximum at ~15 mol % (Figure 3). If one looks closely at the scattering profiles (Figures 1b,c, and S6) in this co-polymer composition regime, the first q minimum is relatively shallow, i.e., a broader distribution for the core radius. Several possible explanations could be suggested. First, there is frustration of shorter and longer core block packing within this composition window, yielding two populations of micelles with slightly different compositions of the two diblocks.^{35,37,39} Apparently, even this is true, the difference in the micelle dimensions between the two populations is so small that it cannot be resolved in experiments.^{37,40} On the other hand, it is likely that there is fluctuation in the composition of the two diblocks among distinct mixed micelles;³⁸ this composition fluctuation brings more variation in the core radius of smaller micelles, i.e., when $\langle N_{\text{core}} \rangle$ is smaller. To elaborate on this, the following calculations were performed. We added different mole fractions of longer diblocks to a certain number of monodisperse pure smaller micelles. Similarly, different mole fractions of the shorter diblocks were added to monodisperse pure larger micelles. Assume that the number of longer or shorter diblocks incorporated into distinct micelles follows Gaussian statistics, the distribution of the micelle core size after the incorporation of various numbers of the other diblocks can be determined. Two sets of calculations were conducted: in one, the CV in the number of the other diblocks assigned to

one micelle was fixed, whereas in the other, a constant standard deviation was assumed. The results are summarized in Figure S10. As shown there, in both cases, the CV of core radius in the smaller micelles incorporating low fractions of longer diblocks is significantly larger than that in the larger micelles upon addition of the same fraction of shorter diblocks. This is qualitatively consistent with the results in Figure 3. All these factors need to be considered to understand the variation in the R_c distribution of the binary mixed micelles with co-polymer composition. Nevertheless, it is reasonable to conclude that the two diblocks co-micellize into binary mixed micelles in a concerted fashion. The same conclusion was drawn by Jain et al., who had used a similar premixing protocol to prepare binary mixed diblock co-polymer micelles and argued that the two BCPs are uniformly distributed across all of the micelles.²⁶

Another assumption embedded in the model is that the binary mixed micelles adopt a spherical morphology, with a uniform radius in all orientations. However, recent computer simulation suggests that the mixed micelles could be ellipsoidal, with the shorter chains straddling the core and corona in the region of ellipsoidal interface that is closer to the center of the micelle.³⁷ Similar arguments were made by Liu et al. to explain the thermodynamic stability of the Frank–Kasper phases in bulk binary blends of diblock co-polymers.⁷¹ We cannot rule this possibility out in the current system, but it would be hard to discern experimentally. However, we believe that the formation of ellipsoidal micelles (assume they do exist) is another way to regulate the packing and the degree of stretching of the two core blocks, which is conceptually in line with the argument from our work. On the other hand, the formation of ellipsoidal micelles requires the partial micro-phase separation of the two diblocks within the micelles, which will decrease the mixing entropy of the system. Additionally, as the difference between the two core blocks in our system is not that large (the unperturbed radius of gyration differs by a factor of ~ 1.5), the aspect ratio of the putative ellipsoidal micelles should not be far from unity, i.e., still close to a spherical shape. This is especially true for binary mixed micelles with extreme proportions of the two diblocks. In fact, Brownian dynamics simulations found that the relative shape anisotropy is roughly the same between pure and mixed micelles, especially for cases with long core blocks,^{36,38} as studied here. Moreover, Yoo et al. performed TEM studies on binary mixed micelles and showed that they adopt a nearly spherical shape.⁴³ Note that in their system, the core block length of the two diblocks differs by a factor of ~ 2.4 , similar to the case in our study ($N_{\text{core,L}}/N_{\text{core,S}} = 2.1\text{--}2.5$).

Based on free-energy calculations, we have provided a quantitative explanation for the intriguing finding that mixed micelles have significantly larger dimensions than pure ones. It has been argued that in spherical micelles, the volume of the micelle core interior is rather small, so that only a few core blocks are necessarily deformed to fill the micelle core.⁵⁶ From this perspective, these free-energy calculations might overestimate the core block stretching penalty. However, in the original derivation of the core block elastic energy in eqs 3 and 6,⁶⁴ the free ends of the core blocks are allowed to fluctuate within the entire space of the micelle core to provide a uniform polymer density. Moreover, the assumption of uniform stretching for the core block indeed yields the correct scaling with the core block length (Figure S8).⁵⁶ Therefore, these calculations should be appropriate. On the other hand, Zhulina

et al. have argued that the core elastic free energy is small compared to the corona and interface terms even for crew-cut micelles, and thus it does not strongly affect the micellar structure. With the model parameters in Table S1, we calculated the free energy per co-polymer chain in single diblock micelles and found that, in the current system, the core, corona, and interface contribute ~ 10 , 30, and 60%, respectively, to the total free energy. This result is qualitatively consistent with that from Zhulina et al.; however, we have found that even with this relatively small core elastic energy, the micelle core dimension can still be significantly modified (Figure 5). Specifically, Figure S11 shows that the micelle core radius could differ by 20–30%, depending on the core block length, if the core free energy is not taken into account in the calculation. This further justifies the importance of core block stretching in determining the structure of spherical micelles, especially mixed ones, and these results provide new insight into the co-micellization of binary diblock co-polymer mixtures with distinct core block lengths.

One final aspect to be noted is the relative magnitude of increase in R_h and R_c of the binary mixed micelles compared to pure ones. Although both sizes are significantly larger for the binary mixed micelles, the increase is more dramatic for R_h than for R_c (Figure 2a,b). For instance, at $\langle N_{\text{core}} \rangle \approx 370$, $\Delta R_h = 5.5$ nm is much larger than $\Delta R_c = 3.3$ nm, where $\Delta R_h = R_{h,\text{mixed}} - R_{h,\text{pure}}$, and $\Delta R_c = R_{c,\text{mixed}} - R_{c,\text{pure}}$. Presumably, this is due to the thicker corona for the binary mixed micelles. As shown in Figure 4c, the aggregation number of the binary mixed micelles is substantially larger than the pure ones at the same $\langle N_{\text{core}} \rangle$, which even displays a maximum as a function of $\langle N_{\text{core}} \rangle$. Considering that the corona block length of the two diblocks is the same, a larger aggregation number will impose higher steric repulsion among the chains in the corona. As a result, the corona chains could be more stretched, leading to a larger corona thickness (Figure S12) and, therefore, a larger increase in R_h than R_c .

SUMMARY

In this report, we have examined the structure of micelles formed with binary diblock co-polymer mixtures with the same N_{corona} but different N_{core} . The micelles were prepared via a co-solvent protocol. We have found that the two diblocks can co-micellize and form a single, relatively monodisperse population of mixed micelles. DLS and SAXS measurements show that the average dimensions (both R_h and R_c) of the mixed micelles monotonically increase with the fraction of the longer diblock in the co-polymer mixture; however, R_c vs $\langle N_{\text{core}} \rangle$ for the mixed micelles does not follow a simple power law as in the case of single diblock micelles. Additionally, the aggregation number extracted from the SANS data first increases and then decreases with $\langle N_{\text{core}} \rangle$, in contrast to the monotonic increase in the case of single diblock micelles. Interestingly, the dimensions and aggregation numbers of the binary mixed micelles assume significantly larger values than that formed with single diblocks at the same $\langle N_{\text{core}} \rangle$. Free-energy analysis was performed to predict the micelle core dimensions at equilibrium. The calculation shows excellent agreement with the experimentally measured values of R_c in single diblock micelles. However, it significantly underestimates the core sizes of the binary mixed micelles when both the shorter and longer core blocks are uniformly stretched to fill the micelle core. Importantly, if the elastic free energy of the shorter core blocks is eliminated, the predicted values of R_c match well with

experiments. Combining experiments and calculations, we propose that the shorter core blocks are, to some degree, relaxed in the micelle core in the presence of the longer ones, which will predominantly occupy the central space of the micelle core. This partial or complete release of the shorter core block stretching thermodynamically favors micelles with a larger aggregation number and, thus, a larger micelle dimension. These results underscore the fact that the molecular packing of the two core blocks with distinct lengths within a spherical micelle core is a critical factor dictating the thermodynamic structure of the mixed micelles. Moreover, this work demonstrates that the micellar structure (core radius, aggregation number, corona thickness) can be facilely and precisely tuned by blending various proportions of two diblock copolymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00613.

SEC traces, additional DLS data, comparison of R_c from Pedersen model fits and the characteristic equation for the minima in q , additional SAXS profiles, estimation of the solvent volume fraction in the micelle core, calculation of free-energy model parameters, comparison of calculations and experiments for single diblock copolymer micelles, comparison of the SANS traces of two micelle solutions prepared by two different protocols, calculation of coefficient of variation in the micelle core radius upon incorporation of a second diblock (Figures S1–S12 and Table S1) (PDF)

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Notes

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