

Role of Distance from Equilibrium in the Fragmentation Kinetics of Block Copolymer Micelles

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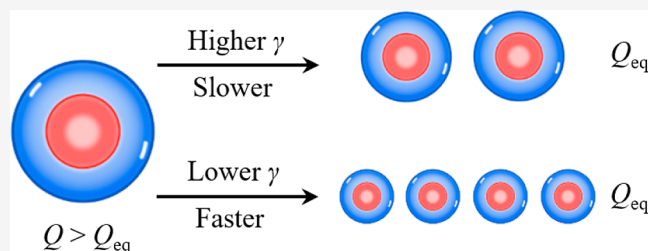
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ABSTRACT: The fragmentation kinetics of 1,2-polybutadiene-*b*-poly(ethylene oxide) ($M_n = 17.2$ kDa and $f_{\text{PEO}} = 0.38$) block copolymer micelles have been examined with an emphasis on elucidating the role of driving force for micellar fragmentation, represented by the aggregation number ratio Q/Q_{eq} . Large micelles with size $Q > Q_{\text{eq}}$ were formed in an ionic liquid $[\text{C}_2\text{mim}][\text{TFSI}]$ by the direct dissolution method. A broad range of Q/Q_{eq} was then obtained by altering the solvent quality after micelle formation by addition of a second solvent, selected from a series of imidazolium-based ionic liquids $[\text{C}_x\text{mim}][\text{TFSI}]$ with $x = 2, 4, 6, 8, 10$, and 12.

In order to quantify the change in solvent quality by dilution, the interfacial tension γ between the different ionic liquids and 1,2-polybutadiene homopolymer was determined using the pendant drop method. Micelles in a solution diluted with a second ionic liquid with $x \geq 2$ were equilibrated by high-temperature annealing at 170 °C, during which in situ dynamic light-scattering measurements were made to follow the decay of average micelle size with time. Micelles were further characterized using small-angle X-ray scattering and cryogenic transmission electron microscopy to obtain micelle core size distributions. Q_{eq} and γ were found to exhibit a power-law correlation, $Q_{\text{eq}} \sim \gamma^{6/5}$, in accordance with the scaling prediction for star-like micelles. The reduction in γ on dilution with a lower γ solvent ($x > 2$) results in a smaller equilibrium micelle size, enabling access to a higher Q/Q_{eq} in the range from 1.1 to 5. The rate of fragmentation was found to increase significantly with an increase in Q/Q_{eq} , thus the greater thermodynamic driving force leads to a systematic acceleration of fragmentation kinetics. The detailed mechanism by which micelles with $Q \gg Q_{\text{eq}}$ achieve Q_{eq} remains to be elucidated; the data suggest that it is not a sequential process but concerted.



INTRODUCTION

Block copolymers (BCPs) self-assemble into a variety of nanostructures in bulk as well as in solutions with selective solvents.^{1–6} Precise control of the polymer block fraction, chain architecture, temperature, concentration, and solvent selectivity results in a myriad of interesting nanostructures,^{7–9} particularly spherical, cylindrical, or planar micellar particles.^{10–13} Of particular interest for the present study is core–shell spherical BCP micelles, which find a diverse range of applications in biology, biomedicine, and various industrial processes such as viscosity modification and nanotemplating.^{14–19} While the equilibrium morphology of micellar structures is well-documented, understanding of the dynamics and mechanisms responsible for the formation and equilibration of the micellar structures is still incomplete.²⁰ A comprehensive picture of the kinetics of micellar relaxation processes is important to realize the full potential of BCP micelles. Concurrently, ionic liquids (ILs) have received increased attention due to their fascinating physico-chemical properties.²¹ ILs can be attractive solvent media for micelle formation because of their superior thermal and chemical stabilities, extremely low vapor pressure, and tunable cohesive energy density.²²

Typically, as-prepared BCP micelles are out of equilibrium and can exhibit a broad size distribution that depends upon the preparation method. Through processes of relaxation, the as-prepared micelles attain a nearly monodisperse equilibrium size. The relaxation can be followed as a function of time by subjecting as-prepared micelles to jumps in temperature, pressure, flow conditions, or solvent quality. Fragmentation, fusion, and single-chain exchange are the key mechanisms responsible for equilibration of BCP micelles. Significant progress has been made toward developing an understanding of the equilibration process of surfactant micelles, both theoretically and experimentally.^{23–25} Micellar equilibration can be monitored by temperature-jump, pressure-jump, and stopped flow methods. Experimental techniques such as light absorption, fluorescence, small-angle neutron scattering (SANS), and small-angle X-ray scattering (SAXS) have been

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employed extensively to study micellar relaxation.^{26–29} It should be emphasized that the kinetics of BCP micelle relaxation take place over substantially longer timescales (typically ranging from minutes to days) than surfactant micelles (microseconds to milliseconds).^{30–32} For BCP micelles, notable progress has been made in studying single-chain exchange between two micelles when close to equilibrium.^{33–42} However, the equilibration dynamics of micelles with sizes far from equilibrium remain largely unexplored.²⁰

Micelles of various sizes can be prepared from a single BCP using different methods of formation, allowing investigation of the relaxation of micelles with sizes on either side of equilibrium.⁴³ For example, Meli et al. prepared large micelles of 1,2-polybutadiene-*b*-poly(ethylene oxide) (BO) in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][TFSI]) using a direct dissolution method.⁴⁴ The authors examined the relaxation of these kinetically trapped micelles during prolonged annealing at elevated temperatures by in situ dynamic light scattering (DLS) measurements. The time decay of the normalized average hydrodynamic radius was found to be well-described by an Avrami-type compressed exponential function with an exponent $n \approx 2$ and a characteristic relaxation time of a few hours.⁴⁵ More recently, Early and Lodge studied the effect of solvent quality on the relaxation of kinetically trapped similar BO micelles in different imidazolium-based ILs.⁴⁶ The relaxation kinetics were found to be independent of solvent quality and concentration, suggesting that the micellar relaxation is dominated by fragmentation, a first-order process. For the same system, time-resolved SANS experiments revealed the absence of significant chain exchange over this time scale even at 200 °C, confirming fragmentation to be the dominant mechanism. Recently, time-resolved liquid-phase transmission electron microscopy (TEM) imaging provided direct evidence of fragmentation.⁴⁷ The micelle morphology transitions sequentially from a large spherical micelle to a prolate spheroid to a “peanut-shaped” particle, which pinches off leading to the creation of daughter micelles. These findings were complemented with SAXS measurements of average micellar core size. Analogous time-resolved SANS, SAXS, and TEM techniques have been employed previously to examine the kinetics of other morphological transitions in micelles.^{48–50}

Previously, kinetic parameters for fusion and fragmentation processes for PEO-*b*-PPO-*b*-PEO in water have been estimated using a fluorescence decay method.^{51,52} In addition to experiments, theoretical studies also provide useful insight into the evolution of micelle structure during fragmentation/relaxation. The characteristic fragmentation time τ is conjectured to depend on several parameters such as the size of core- and corona-forming blocks (N_{core} and N_{corona}), the interfacial tension γ between the core-forming block and solvent, the ratio of initial to final micelle aggregation number (Q/Q_{eq}), and temperature.³² Prior experimental studies have attempted to resolve the dependence of τ on these parameters, yet several questions remain unresolved. In particular, for large micelles, the role of micelle size ratio, Q/Q_{eq} , indicating the departure of the as-prepared micelle size from equilibrium, needs to be examined closely. The ratio Q/Q_{eq} is a measure of the driving force for micellar fragmentation, which could therefore strongly influence the kinetics. The experimental methodology adopted in most prior studies did not allow systematic variation of Q/Q_{eq} over a broad range; rather, it was

nearly fixed, typically ca. 1.5 to 2.^{45,46} For BO copolymers far from equilibrium, the fragmentation time was reported to depend strongly on the polymer chain size ($\tau \sim N^{\text{L}8}$), but in this case, $Q/Q_{\text{eq}} \approx 2$ for each N .⁵³ A recent study introduced an experimental methodology that enables variation of Q/Q_{eq} over a broader range, ca. 1.5–6.⁵⁴ The protocol involves changing the solvent quality after micelle preparation. As-prepared micelles in [C₂mim][TFSI] were diluted with [C₁₀mim][TFSI] to different degrees of dilution at room temperature, preserving the initial size. Upon subsequent heating, micelles undergo fragmentation in a mixed solvent with lower γ between the micelle core and solvent, which reduced Q_{eq} and thereby increased Q/Q_{eq} .

The present study adopts a similar methodology to study the role of Q/Q_{eq} on fragmentation kinetics. The fact that equilibrium micelle size is greatly influenced by γ between the solvent and the core-forming block is used to achieve a variation in Q/Q_{eq} . In the previous study, γ of the solvent medium was varied by varying the amount of the second solvent being added. Here, however, the solvent quality is altered by addition of a second IL chosen from a homologous series with different-length alkyl group (x) on the imidazolium cation [C_{*x*}mim][TFSI]; the polymer concentration remains fixed. Since γ controls Q/Q_{eq} , measurements of γ between a 1,2-polybutadiene (PB) homopolymer and eight different imidazolium-based ILs were made using a pendant drop method. The micelles were characterized by in situ DLS during relaxation following a T -jump to 170 °C. Micelles were further characterized using SAXS and cryo-TEM to estimate the core size and its distribution.

EXPERIMENTAL SECTION

Materials and Characterization. A diblock copolymer, BO, was synthesized previously by anionic polymerization.⁵³ The diblock copolymer is referred to as BO(9–8) with the numbers in parentheses indicating the number-average molecular weight of each block in kDa. Size-exclusion chromatography (SEC) with multiangle light-scattering detection (Wyatt Instruments DAWN) and proton nuclear magnetic resonance spectroscopy (¹H NMR) was performed to determine the polymer number-average molecular weight (M_n), dispersity ($\mathcal{D}$), and f_{PEO} . For BO(9–8), $M_{n,\text{PB}} = 9.4$ kDa, $M_{n,\text{PEO}} = 7.8$ kDa, $f_{\text{PEO}} = 0.38$, and $\mathcal{D} = 1.14$. A 1,2-PB homopolymers were synthesized previously, with $M_n = 4.8$ kDa and $\mathcal{D} = 1.06$.⁵³ The following series of ILs was purchased from IoLiTec: 1-methyl-, 1-ethyl-, 1-butyl-, 1-pentyl-, 1-hexyl-, 1-octyl-, 1-decyl-, and 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide 99%, denoted as [C_{*x*}mim][TFSI], with $x = 1, 2, 4, 5, 6, 8, 10$, and 12, respectively. The ILs used in the study are molten salts at room temperature. The IL cations and anions consist of bulky, charged small molecules. The chemical structure of IL [C_{*x*}mim][TFSI] is presented in Figure 1. The diblock copolymer and all ILs were characterized by ¹H NMR. The ¹H NMR spectrum for the polymer was collected in deuterated chloroform, and spectra for the ILs were obtained in deuterated dimethyl sulfoxide using a Bruker AVANCE HD 500 spectrometer. The Supporting Information contains the SEC chromatograms and NMR spectra for polymers and ILs.

Dynamic Light Scattering. DLS measurements were carried out on micellar samples at room temperature using a multiangle DLS instrument with a Brookhaven BI-200SM goniometer coupled with a Brookhaven BI-9000AT correlator and 637 nm laser source. The in situ DLS experiments at 170 °C were carried out on home-built equipment consisting of a Brookhaven BI-DS photomultiplier mounted onto an adjustable goniometer, equipped with a 488 nm Lexel Ar⁺ laser and a Brookhaven BI-9000 correlator. Sample temperature was kept within ± 0.5 °C using a silicon oil bath. The samples, made dust-free using 0.45 μm polytetrafluoroethylene filters, 190

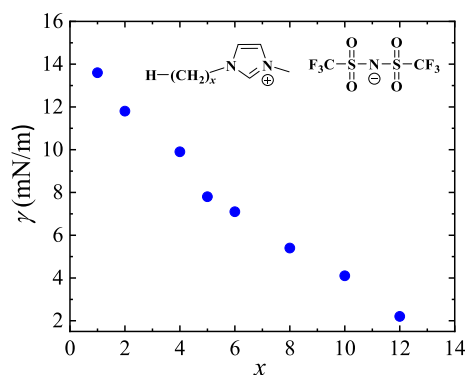


Figure 1. Interfacial tension between 1,2-polybutadiene (PB, $M_n = 4.8$ kDa) and a series of imidazolium-based ILs $[C_x\text{mim}][\text{TFSI}]$ at 70 °C. Chemical structure of 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl imide)-based ILs ($[C_x\text{mim}][\text{TFSI}]$, where $x = 1, 2, 4, 5, 6, 8, 10$, and 12).

characterizes a particular value of γ . Figure 1 demonstrates the dependence of γ on the length of the alkyl chain on the imidazolium ring, x . As x increases from 1 to 12, γ between PB and the IL decreases monotonically from 13.6 to 2.2 mN/m. Thus, an IL with a higher x becomes comparatively more favorable toward the PB polymer block and the solvent becomes less selective. The key implication of lowering γ is a reduction in equilibrium micelle size Q_{eq} .

Sample Preparation. A master micellar solution was prepared by direct dissolution of BO(9–8) in $[C_2\text{mim}][\text{TFSI}]$, “IL1”, with a polymer concentration of 1 wt %. The sample was stirred vigorously at 70 °C for 24–48 h. The solution of as-prepared micelles in $[C_2\text{mim}][\text{TFSI}]$ was then diluted by the addition of a second IL, “IL2”, from the $[C_x\text{mim}][\text{TFSI}]$ series ($x \geq 2$), reducing the polymer concentration to 0.1 wt %. The dilution was carried out in a careful manner so that the existing micelles remain unchanged in both mean size and distribution. Due to the lower γ for IL2, dilution results in an overall reduction in γ of the solvent mixture surrounding the micelles, amounting to a γ -jump for the as-prepared micelles. After the γ -jump, micelles were heated to 170 °C, followed by annealing, the process being commonly referred to as T -jump, during which micelles attain an equilibrium state, primarily (or even exclusively) through fragmentation.

RESULTS AND DISCUSSION

Fragmentation Kinetics in a Single IL. First, fragmentation kinetics were studied for the as-prepared micelles in IL1 ($[C_2\text{mim}][\text{TFSI}]$). A master solution of 1 wt % BO(9–8) in $[C_2\text{mim}][\text{TFSI}]$ was prepared. The initial hydrodynamic radius was found to be relatively large ($\langle R_h \rangle_i \approx 70$ nm) and disperse ($D_i \approx 1.27$). The sample was subjected to a T -jump, followed by annealing at 170 °C to approach the equilibrium state, during which the time-dependent average micelle size $\langle R_h(t) \rangle$ was measured using in situ DLS. The normalized average hydrodynamic radius of the micelles varying with time, $R(t)$, is expressed using the compressed exponential function

$$R(t) = \frac{\langle R_h(t) \rangle - \langle R_h(\infty) \rangle}{\langle R_h(0) \rangle - \langle R_h(\infty) \rangle} = \exp[-(t/\tau)^n] \quad (1)$$

Here, $\langle R_h(0) \rangle = \langle R_h \rangle_i$ and $\langle R_h(\infty) \rangle = \langle R_h \rangle_f$ represent average hydrodynamic radii of the micelles before and after fragmentation, respectively, τ denotes the characteristic fragmentation time, and n is the exponent. The time dependence of $R(t)$ is presented in Figure S3a. The experimental data were fit to eq 1 to obtain the kinetic parameters τ and n . As-prepared micelles in $[C_2\text{mim}][\text{TFSI}]$ are found to relax with $\tau = 260$ min and $n \approx 1.7$, in agreement with previous studies.^{45,46} The initial micelles equilibrate to generate smaller and relatively narrowly dispersed micelles with $\langle R_h \rangle_f \approx 29$ nm and $D_f \approx 1.02$, as presented in Figure S3b.

Fragmentation Kinetics in Mixed ILs. The master solution of 1 wt % as-prepared micelles of BO(9–8) in $[C_2\text{mim}][\text{TFSI}]$ was diluted by adding IL2 such that the polymer concentration dropped to 0.1 wt %. Dilution is achieved in a controlled manner such that the size distribution of the as-prepared micelles remains unchanged. Altering the solvent quality by the addition of a lower γ solvent, referred to as γ -jump, was followed by a T -jump to induce fragmentation. As with IL1 alone, micelles approach equilibrium during high-temperature annealing, and $R(t)$ was monitored by in situ DLS. Figure 2 displays the average micelle size as a function of time, $R(t)$, for the six different pairs of ILs. As IL2 goes from $[C_2\text{mim}][\text{TFSI}]$ to $[C_{12}\text{mim}][\text{TFSI}]$, the decay curves progressively shift to the left, indicating faster kinetics. For 300

were directly placed into clean oven-dried glass tubes with an ID of 5.1 mm. The sample glass tubes were subsequently flame-sealed under vacuum to avoid moisture contact and prevent polymer degradation. Light scattering was performed at multiple angles ranging from 60 to 120°, unless otherwise noted. The calculation of the apparent average hydrodynamic radius, $\langle R_h \rangle$, of the micelles from DLS intensity measurement is described in the Supporting Information. The size dispersity, D , is obtained from the reduced second cumulant.

Small-Angle X-ray Scattering. SAXS measurements were performed on micellar solutions before and after fragmentation at 201 room temperature. SAXS measurements were carried out at the Advanced Photon Source, Argonne National Laboratory, on the Sector 5-ID-D beamline. The samples were filled into borosilicate capillaries (diameter 1.5 mm), which were subsequently sealed with epoxy under an argon atmosphere inside a glovebox. 2D SAXS intensity data were collected using a Rayonix MX170-HS CCD area detector with a sample-to-detector distance of 8.5 m. The sample exposure time to X-rays ($\lambda = 0.729$ Å) was kept at 0.5 s. By integrating the isotropic 2D scattering data, 1D scattering curves I vs wavevector q were constructed. The background scattering emanating from the solvent and glass capillary was subtracted.⁵⁵ The background-corrected intensity profiles were fit with a core-shell micelle model; the Percus–Yevick structure factor was used to fit data for the as-prepared micelles.^{56,57}

Cryogenic Transmission Electron Microscopy. Cryo-TEM imaging was conducted on micelles in both pre- and postfragmentation states. TEM grids with lacey formvar coatings stabilized by carbon were procured from Ted Pella, Inc. Approximately, 0.25 μL of the sample was drop-casted directly on the TEM grid. The excess solution was removed using filter paper. The sample grid was then manually dropped in liquid nitrogen at around -190 °C prior to imaging. The imaging was performed on FEI Tecnai G2 F30 field-emission gun TEM, operated at 300 kV accelerating voltage. A Gatan 626 cryo-holder was maintained at -175 °C while imaging. A Gatan UltraScan 4000 4k $\times$ 4k CCD camera was used to record digital images. Image analysis was performed using ImageJ software.

Interfacial Tension Measurement. The interfacial tension γ between a series of ILs and the core-forming polymer block PB was determined using pendant drop tensiometry on a Kruss DSA-30S drop shape analyzer as previously described⁵⁴ using standard procedures.^{58,59} A droplet of IL was suspended in a reservoir of PB homopolymer at 70 °C. Measurements were taken for multiple droplets for a given IL, and for each droplet, multiple frames or measurements were collected. Figure S1 demonstrates the resulting γ values between the PB homopolymer and eight different ILs, i.e., $[C_x\text{mim}][\text{TFSI}]$ with $x = 1, 2, 4, 5, 6, 8, 10$, and 12. Step numbers denote the individual measurements taken from multiple droplets. The γ values are listed in Table S1, and the corresponding pendant drop profiles are presented in Figure S2. Each droplet shape

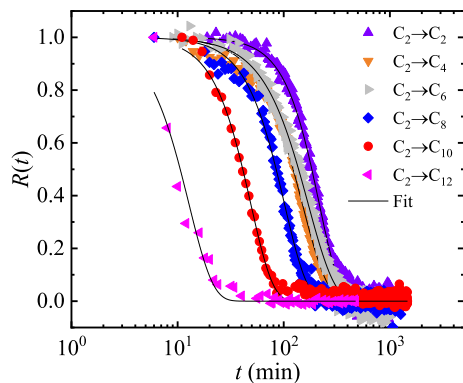


Figure 2. Time decay of the normalized average hydrodynamic radius $R(t)$ of the BC micelles in different pairs of mixed ILs at 170 °C. The solid lines represent best fits to eq 1. The polymer concentration was fixed at 0.1 wt %.

all IL2s, the experimental data fit the Avrami expression (eq 1) well. The resulting two kinetic parameters, τ and n , are summarized in Table 1. The initial size of the micelles is essentially independent of dilution (except for $[C_{12}mim][TFSI]$, which possibly initiates some fragmentation at room temperature). The as-prepared micelles with size around 70 nm attain near-equilibrium sizes that depend on the choice of IL2: $\langle R_h \rangle_f$ gradually decreases from 29 to 22 nm as the IL2 is changed from $[C_2mim][TFSI]$ to $[C_{12}mim][TFSI]$. After relaxation, the micelle size distribution becomes quite narrow, with $D_f \leq 1.03$ for all IL2s. The corresponding regularized positive exponential sum (REPES) analysis is presented in Figure S4. Interestingly, the characteristic fragmentation time, τ , is found to decrease significantly upon dilution with a progressively lower γ solvent: as x increases from 2 to 12, τ decreases from 216 to 10 min. Whereas τ decreases, the exponent $n \approx 2$ irrespective of IL2.

To further characterize the micelles before and after relaxation, SAXS measurements were carried out to obtain the average micelle core radius $\langle R_{core} \rangle$, which provides an estimate of the mean micelle aggregation number Q . Figure 3a shows $I(q)$ profiles for 1% BO(9–8) micelles in pure $[C_2mim][TFSI]$, before and after fragmentation. The spherical form factor is clearly evident in both cases. The micelle core radius can be calculated from the first minimum in $I(q)$ as $\langle R_{core} \rangle \approx 4.493/q_{min}$. A shift to a larger value for q_{min} indicates a decrease in $\langle R_{core} \rangle$ after fragmentation. Based on $\langle R_{core} \rangle$ values obtained from SAXS for the as-prepared micelles ($\langle R_{core} \rangle = 17.4$ nm), the average aggregation number for micelles before fragmentation was determined to be $Q \approx 1350$, assuming the micellar core to be solvent-free. After fragmentation, the average aggregation number attains an equilibrium value of $Q_{eq} \approx 1275$. Thus, the initial size ratio Q/Q_{eq}

for the equilibration of as-prepared micelles in $[C_2mim][TFSI]$ is estimated to be around 1.1. This modest change suggests that many of the initial micelles do not, in fact, undergo any fragmentation in this solvent.

SAXS measurements were also carried out for the micelles equilibrated after dilution. It should be noted that for the diluted samples, the characteristics of the micelles before fragmentation are assumed to be the same as those for the as-prepared micelles in IL1, depicted in Figure 3a. Figure 3b shows the background-corrected $I(q)$ curves for the micelles after fragmentation for different IL2s. As IL2 changes from $[C_2mim][TFSI]$ to $[C_{12}mim][TFSI]$, the first minimum in $I(q)$ shifts to larger q , indicative of decreasing $\langle R_{core} \rangle$. $\langle R_{core} \rangle_f$ and σ_{core} (standard deviation of the core radius) were obtained by fitting $I(q)$ profiles with the core–shell model.⁵⁶ The decrease in $\langle R_{core} \rangle_f$ upon dilution with an IL with larger x reflects the decrease in γ of the solvent mixture. Table 2 summarizes the micelle characteristics estimated from SAXS. $\langle R_{core} \rangle_f$ decreases from 17 nm for IL2 having $x = 2$ to 10 nm when IL2 with $x = 12$; σ_{core} remains small for all IL1–IL2 pairs. Consequently, Q_{eq} decreases from 1250 to 260 as micelles undergo fragmentation in solvents with progressively lower γ values. Since Q is fixed for all the diluted samples, the ratio of aggregation numbers, Q/Q_{eq} , increases from 1.1 to 5.2 as IL2 is changed from $[C_2mim][TFSI]$ to $[C_{12}mim][TFSI]$. Thus, diluting the micellar solution with a progressively less-polar IL2 renders the as-prepared micelles further from the equilibrium size, indicating an enhancement in driving force for fragmentation. It should be noted that in the calculation of Q_{eq} , the assumption of solvent-free core may not hold for a lower γ solvent such as $[C_{12}mim][TFSI]$. However, the difference is expected to be within the uncertainty for the ratio Q/Q_{eq} .

Cryo-TEM imaging was also conducted to confirm the spherical nature of the micelles as well as to obtain the core size and its distribution. Imaging was performed on the micellar solutions before and after fragmentation. Representative micrographs for 1% BO(9–8) in $[C_2mim][TFSI]$ before and after thermal annealing at 170 °C are presented in Figure 4a,c, respectively. The bright regions are micelle cores embedded in a dark matrix representing corona and solvent. Evidently, micelles are spherical and relatively uniform in size. The structural details such as micellar core size and distribution were obtained by analyzing the micrographs. Image analysis provides a histogram for the distribution in micelle core size; about 400 micelles were taken into consideration in each case. Figure 4b,d depicts the histograms before and after fragmentation, respectively. The continuous curves represent a lognormal distribution constructed using the mean and standard deviation values for each case. The average micellar core radius $\langle R_{core} \rangle$ for the as-prepared micelles is

Table 1. Micelle Fragmentation Parameters from DLS

(P + IL1) → IL2	$\langle R_h \rangle_i$ nm	D_i	$\langle R_h \rangle_f$ nm	D_f	τ (min)	n
C_2	71	1.27	29	1.02	260 ± 20	1.7
$C_2 \rightarrow C_2$	70	1.20	27	1.02	216 ± 25	2.2
$C_2 \rightarrow C_4$	67	1.17	28	1.01	150 ± 10	1.8
$C_2 \rightarrow C_6$	67	1.20	26	1.02	170 ± 20	1.7
$C_2 \rightarrow C_8$	62	1.15	24	1.01	100 ± 20	2.0
$C_2 \rightarrow C_{10}$	67	1.17	23	1.02	50 ± 10	2.0
$C_2 \rightarrow C_{12}$	40	1.10	22	1.01	10 ± 5	2.1

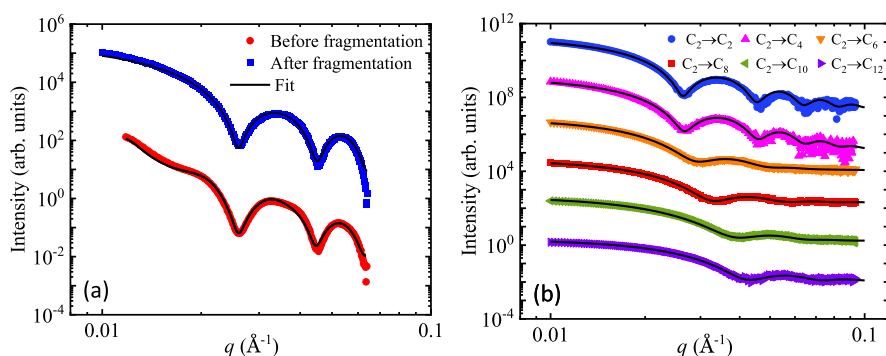


Figure 3. (a) SAXS intensity profiles for 1 wt % BO(9–8) micelles in pure [C₂mim][TFSI] at 25 °C, before and after fragmentation. (b) $I(q)$ versus q for 0.1 wt % BO(9–8) in different pairs of ILs after fragmentation at 25 °C. The curves are shifted vertically by factors of 10^2 for clarity.

Table 2. Micelle Characteristics after Fragmentation from SAXS

(P + IL1) → IL2	$\langle R_{\text{core}} \rangle_f$ (nm)	σ_{core} (nm)	Q_{eq}	Q/Q_{eq}
C ₂	17.1	0.7	1275	1.1
C ₂ → C ₂	17	0.7	1250	1.1
C ₂ → C ₄	16.8	0.8	1210	1.1
C ₂ → C ₆	15.2	1.5	900	1.5
C ₂ → C ₈	13.3	0.8	600	2.3
C ₂ → C ₁₀	11.6	1	400	3.4
C ₂ → C ₁₂	10.1	0.7	260	5.2

micrographs along with the corresponding histograms for different IL2s. The predominantly spherical shapes of the micelles are again evident. As the IL2 changes from [C₂mim] to [C₁₂mim], implying reduction in γ of the solution mixture from 11 to 3 mN/m, $\langle R_{\text{core}} \rangle_f$ decreases substantially from around 16 to 9 nm. Note also that as IL2 changes from [C₂mim] to [C₁₂mim], the change in electron density in the solvent mixture leads to weaker contrast, especially with $x \geq 8$. Micelle characteristics obtained from cryo-TEM are summarized in Table 3. As noted earlier, micelles undergoing fragmentation in a solvent medium with a lower γ result in progressively smaller micelles at equilibrium. The significant reduction in Q_{eq} leads to an enhancement in the size ratio Q/Q_{eq} , which increases from around 1.2–6; these estimates from cryo-TEM are consistent with those calculated from SAXS. Figure 6 demonstrates the dependence of Q_{eq} on γ ; Q_{eq} decreases significantly as γ is progressively reduced on dilution with IL with higher x . The driving force for larger micelles is

estimated to be 17 nm. After relaxation, the size distribution becomes slightly narrower ($\sigma_{\text{core}} = 0.8$) and $\langle R_{\text{core}} \rangle$ decreases to 16 nm. The TEM estimates for $\langle R_{\text{core}} \rangle$ are therefore in close agreement with those calculated from SAXS. Cryo-TEM imaging was also performed on the micelles equilibrated in the mixed ILs. Figure 5a–f presents the

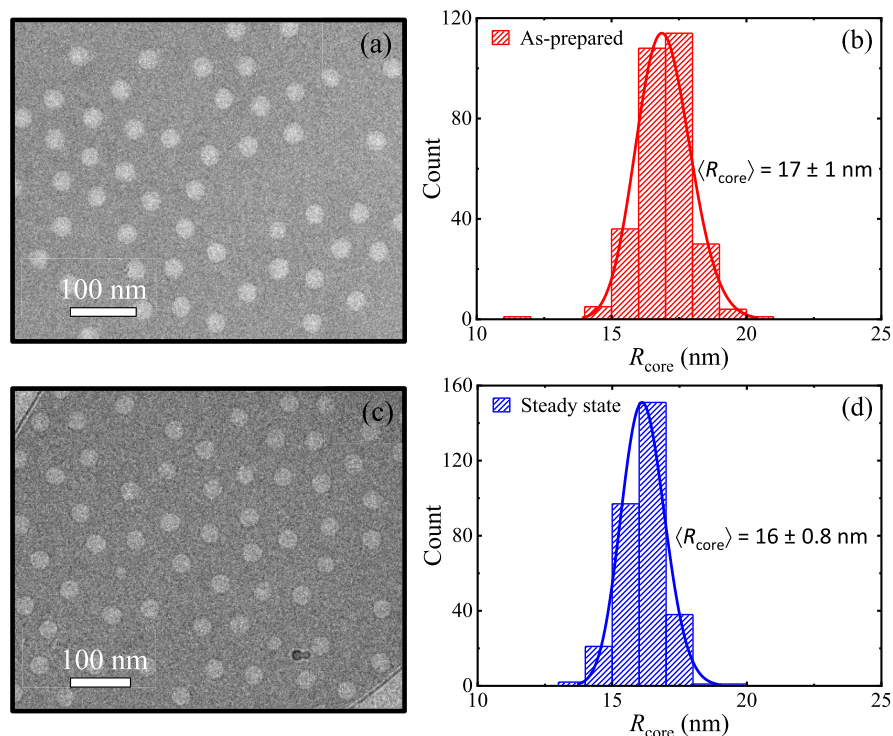


Figure 4. Cryo-TEM electron micrographs and their respective histograms of micellar core radius for 1 wt % BO(9–8) in [C₂mim][TFSI] (master solution). Micelle cores appear as bright regions: (a,b) before fragmentation and (c,d) after fragmentation.

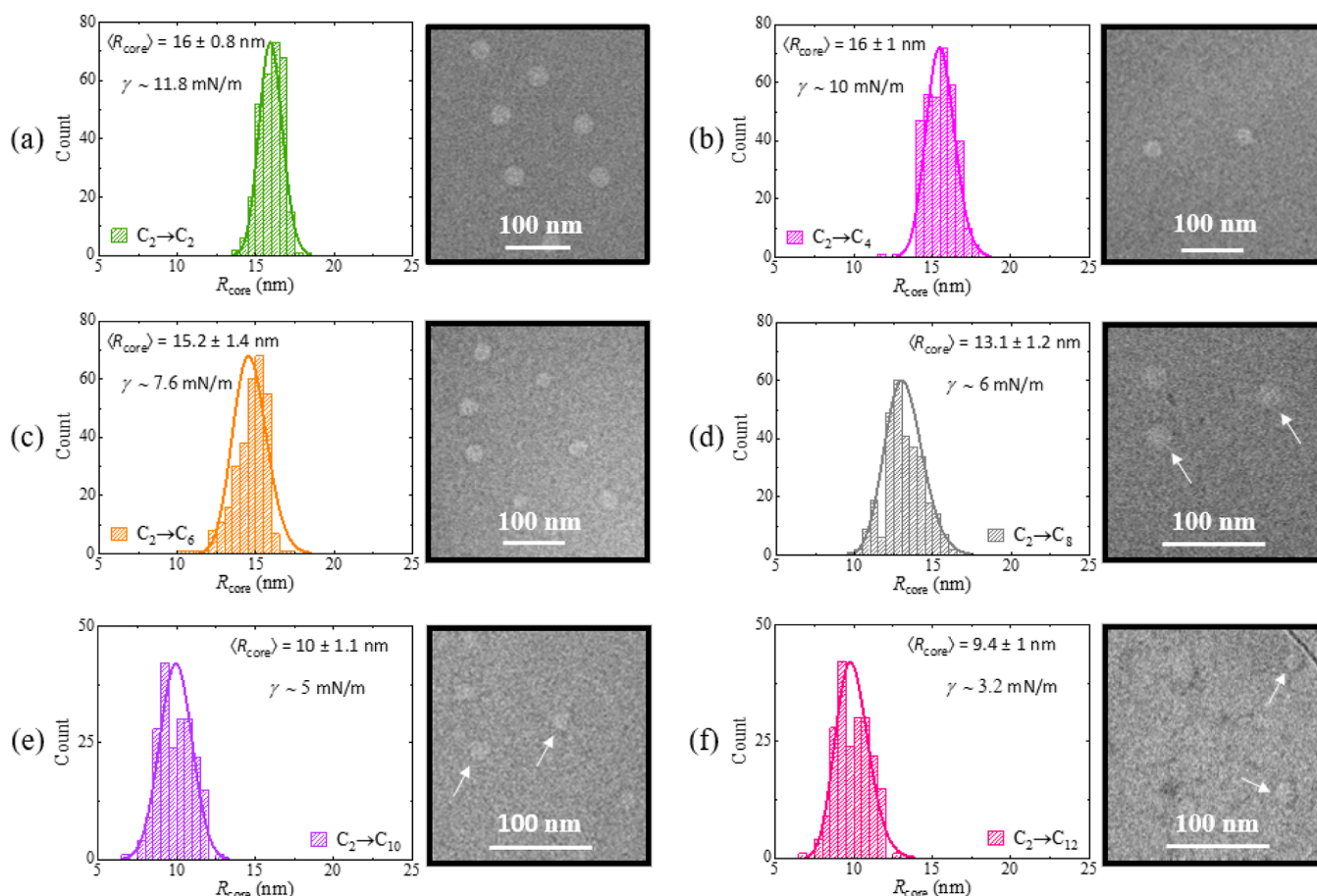


Figure 5. TEM micrographs and the corresponding histograms for the core radius distribution of 0.1 wt % BO(9–8) micelles after relaxation in mixed ILs. (a) $C_2 \rightarrow C_2$; (b) $C_2 \rightarrow C_4$; (c) $C_2 \rightarrow C_6$; (d) $C_2 \rightarrow C_8$; (e) $C_2 \rightarrow C_{10}$; and (f) $C_2 \rightarrow C_{12}$.

Table 3. Micelle Characteristics after Fragmentation from Cryo-TEM

(P + IL1) → IL2	$\langle R_{core} \rangle_f$ (nm)	σ_{core} (nm)	Q_{eq}	Q/Q_{eq}
C_2	16.1	0.8	1070	1.2
$C_2 \rightarrow C_2$	16	0.8	1040	1.2
$C_2 \rightarrow C_4$	16	1.1	1040	1.2
$C_2 \rightarrow C_6$	15.2	1.4	900	1.4
$C_2 \rightarrow C_8$	13.1	1.2	580	2.2
$C_2 \rightarrow C_{10}$	10	1.1	260	5
$C_2 \rightarrow C_{12}$	9.4	1.0	210	6

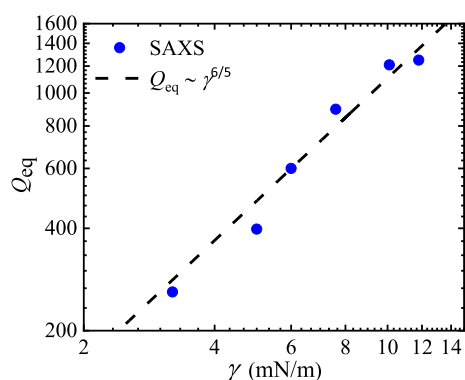


Figure 6. Dependence of equilibrium micelle size, Q_{eq} , on solvent quality γ . Symbols represent data obtained from SAXS. The dashed line represents scaling prediction for star-like micelles, $Q_{eq} \sim \gamma^{6/5}$.

the interfacial free energy (proportional to γ); however, the counterbalancing core and corona stretching entropy penalty differs between theoretical approaches.^{11,60,61} For star-like micelles (Halperin model¹⁰) $Q_{eq} \sim \gamma^{6/5}$, whereas for crew-cut micelles (planar brush model, based on work by de Gennes⁶¹ and Alexander⁶²), $Q_{eq} \sim \gamma^{18/11}$. In comparison, mean-field theory gives $Q_{eq} \sim \gamma^{5/12}$. In Figure 6, fitting Q_{eq} with γ reveals a power-law dependence, $Q_{eq} \sim \gamma^{1.2 \pm 0.1}$, consistent with the scaling prediction by Halperin for star-like micelles.¹⁰ The experimental data have been fitted with all three theoretical predictions for comparison, as displayed in Figure S17. Additionally, Q_{eq} vs γ correlation is consistent with our previous results,⁵⁴ as compared in Figure S18. Note that in the previous study, γ was varied in mixtures of two ILs attained by varying the amount of low γ solvent added (and thus polymer concentration), whereas in the present study, γ is varied by the addition of a second IL chosen from a homologous series with different-length alkyl groups on the imidazolium cation at fixed polymer concentration.

As noted above, for all pairs (except for $C_2 \rightarrow C_{12}$) of mixed ILs, the as-prepared micelles (in IL1) remain unaffected on dilution with IL2 at room temperature. Thus, the aggregation number before equilibration, denoted by Q is held nearly constant for all pairs of ILs studied. The reduction in Q_{eq} , therefore, allows systematic variation of the ratio Q/Q_{eq} , and thus the driving force for fragmentation. Figure 7 shows the variation in fragmentation time with Q/Q_{eq} . The fragmentation time decreases significantly, and monotonically, with increasing

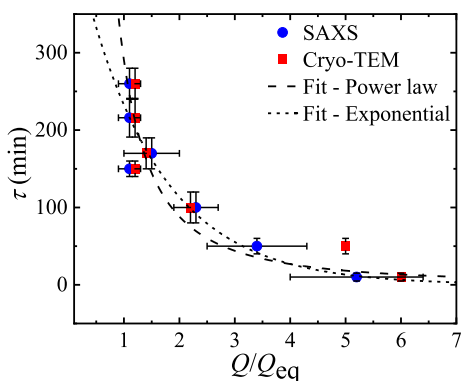


Figure 7. Dependence of characteristic fragmentation time, τ , on micelle size ratio Q/Q_{eq} . The error bars denote the standard error in τ and Q/Q_{eq} (propagated from R_{core}). Dashed and dotted lines represent power law and exponential fit to SAXS data.

driving force. Two empirical curve fits are also shown, one an exponential [$\tau \sim \exp(-0.3 Q/Q_{eq})$] and one a power-law ($\tau \sim (Q/Q_{eq})^{-1.7}$) both providing reasonable descriptions of the data; we are not aware of a theoretical model that might be compared to the results. The enhanced rate of fragmentation can be attributed to a greater thermodynamic drive to attain equilibrium as micelles much larger than the equilibrium size are energetically less stable. Kinetically, therefore, the relaxation process becomes faster for micelles farther from the equilibrium state.

TEM imaging provides the core size distribution of micelles before (as-prepared) and after equilibration (steady state). Figure 8a displays an overlay of the micelle count distributions as a function of Q (obtained from cryo-TEM) before and after fragmentation in pure $[C_2mim][TFSI]$ (no dilution). The as-prepared micelles exhibit a broad distribution in size. Prolonged thermal annealing at 170 °C drives the initial micelles to relax to approach Q_{eq} . In the case of no dilution, micelles are prepared and fragmented in the same IL. Hence, the initial size ratio Q/Q_{eq} which is calculated as 1.1 from SAXS, remains fixed. Since Q/Q_{eq} is not very high, the shift in micelle size distribution due to fragmentation is relatively small. In fact, as noted previously, a significant fraction of the initial micelle population does not undergo fragmentation. Unfortunately, DLS does not provide direct access to the fraction of micelles that have undergone fragmentation at any time point.

The present study aims to achieve a broader variation in Q/Q_{eq} which is realized by dilution of the as-prepared micelles

with a lower γ solvent before thermal annealing. Figure 8b demonstrates the shift in micelle core size distribution due to fragmentation under altered solvent quality vis-à-vis as-prepared micelles. Figure 8b displays the overlaid micelle size distributions from cryo-TEM at equilibrium (after fragmentation) for different pairs of IL1–IL2. It should be noted that for all solvent pairs, the initial micelle distribution is the same, indicated by the dashed curve. The distribution shifts toward lower Q after fragmentation. While the shift is less prominent for dilution with IL2 having $\alpha = 2$, it becomes progressively more and more prominent when the solution is diluted by the addition of lower γ ILs ($\alpha > 2$). As confirmed in Figure 6, the smaller equilibrium micelle size for dilution with IL having higher α is correlated with the reduction in γ . The relatively small shifts in size distribution upon dilution with either $[C_2mim][TFSI]$ ($\alpha = 2$) or $[C_4mim][TFSI]$ ($\alpha = 4$) indicate that only a small fraction of micelles experience fragmentation, presumably the ones with $Q/Q_{eq} > 1$; micelles with size $Q \leq Q_{eq}$ remain intact. However, when micelles are diluted with IL2 having $\alpha = 6, 8, 10$, or 12, the value of Q_{eq} decreases significantly, and hence, most or all micelles across the initial distribution undergo fragmentation. In fact, for dilution with $[C_{10}mim][TFSI]$ or $[C_{12}mim][TFSI]$, the entire initial distribution shifts to lower Q . This corresponds to a significant enhancement in the average size ratio Q/Q_{eq} , from 1.1 to 5.2. A significant shift in Q and its distribution suggests that micelles far above the equilibrium size undergo a series of fragmentation events to achieve equilibrium. For example, if $Q/Q_{eq} \approx 4$, it is possible that a given micelle fragments once to give two micelles with $Q/Q_{eq} \approx 2$, and these “daughter” micelles then undergo secondary fragmentation events to yield four micelles with $Q \approx Q_{eq}$. In this scenario, one might expect the net fragmentation time to be greater than, or equal to, that for micelles prepared with $Q/Q_{eq} \approx 2$, with equality corresponding to the situation where a micelle with $Q/Q_{eq} \approx 4$ fragments much more rapidly than one with $Q/Q_{eq} \approx 2$. The data in Figure 7 do not support this mechanism; however, micelles with $Q/Q_{eq} \geq 4$ achieve equilibrium more rapidly than those with $Q/Q_{eq} \approx 2$, suggesting that the process for $Q/Q_{eq} \geq 4$ bypasses an intermediate state with $Q/Q_{eq} \approx 2$. Possibilities include a large micelle “extruding” multiple daughter micelles with $Q/Q_{eq} \approx 1$ or spontaneously breaking into more than two daughter micelles. To explore these possibilities, in situ time-resolved liquid-phase TEM measurements are an attractive option. While it is confirmed that the chain-exchange process is very slow compared to fragmentation of BO(9–8) micelles in $[C_2mim][TFSI]$,⁴⁵ for lower γ solvents, especially $[C_{12}mim]$ -

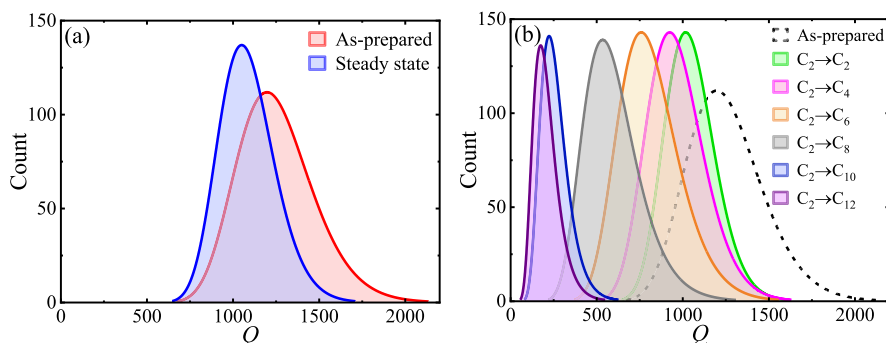


Figure 8. Overlaid count distributions of BO(9–8) micelles as a function of Q from cryo-TEM: (a) in pure $[C_2mim][TFSI]$ and (b) in different pairs of IL1–IL2 after fragmentation.

[TFSI], the role of chain-exchange processes in micellar relaxation needs to be investigated separately. Even though the relaxation of big micelles of size $Q/Q_{eq} \gg 1$ is believed to be driven mainly by micellar fragmentation, the presence of chain exchange in solution diluted with $[C_{12}mim][TFSI]$ cannot be completely ruled out.

SUMMARY

Fragmentation kinetics of spherical micelles of 1,2-polybutadiene-*b*-poly(ethylene oxide) diblock copolymers have been investigated in strategically mixed solvents made of imidazolium-based ILs. The jump in solvent quality achieved by the addition of a second solvent after the formation of micelles in a first solvent influences the equilibrium micelle size and hence the fragmentation behavior. Relatively large ($\langle R_h \rangle_i \approx 70$ nm) and dispersed ($D_i \approx 1.27$) initial micelles were prepared by the direct dissolution of BO(9–8) in a higher γ IL ($[C_2mim][TFSI]$), followed by dilution with a second IL with a lower γ ($[C_xmim][TFSI]$ with $x > 2$). Micelles under the altered solvent medium attain equilibrium after prolonged thermal annealing at 170 °C, resulting in smaller and narrowly dispersed micelles after equilibration. In particular, progressive reduction in γ , achieved by selecting a second IL with an increasing value of x , tends to decrease the equilibrium micelle size, characterized by $\langle R_h \rangle_f$ by DLS, $\langle R_{core} \rangle_f$ by SAXS, and cryo-TEM, and therefore Q_{eq} . In situ DLS experiments demonstrate that the characteristic fragmentation time of BO(9–8) micelles can be lowered substantially by decreasing γ of the surrounding medium after micelle formation. An increase in size ratio Q/Q_{eq} , which represents the extent of driving force for fragmentation, is responsible for faster fragmentation. Micelle fragmentation in a single IL, irrespective of its γ value, exhibits only a narrow Q/Q_{eq} around 1.1–1.5 in the absence of γ -jump. However, a notable variation in the micelle size ratio Q/Q_{eq} from 1.1 to 5.2 was achieved using the γ -jump strategy adopted in the present study. A significant decrease in micelle core size indicates fragmentation to be the primary mechanism for equilibration. While for micelles close to equilibrium (with Q/Q_{eq} just above unity), only a fraction of micelles experience fragmentation, and for larger micelles (with $Q/Q_{eq} > 2$), the entire population of the as-prepared micelle appears to undergo fragmentation. Fragmentation of such big micelles may take place through a series of multiple fragmentation events or by a more concerted process; there is some evidence for the latter. Finally, the study indicates that the fragmentation time can be tuned by controlled variation in solvent quality after micelle preparation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.3c00580>.

Pendant drop profiles of ILs, $R(t)$ versus time of 1% BO(9–8) in pure $[C_2mim][TFSI]$, micelle size distributions using REPES, SAXS profile of BO(9–8) in bulk, 1H NMR spectra of BO(9–8) and all ILs, SEC-RI traces of PB(4.8k) and BO(9–8) in tetrahydrofuran, IL parameters, Q_{eq} vs γ and τ vs Q/Q_{eq} for BO(9–8) in mixed ILs, core-shell model equations, and contrast values (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Gohy, J. F. Block Copolymer Micelles. *Adv. Polym. Sci.* **2005**, 190, 65–136.
- (2) Mai, Y.; Eisenberg, A. Self-Assembly of Block Copolymers. *Chem. Soc. Rev.* **2012**, 41, 5969–5985.
- (3) Tritschler, U.; Pearce, S.; Gwyther, J.; Whittell, G. R.; Manners, I. 50th Anniversary Perspective: Functional Nanoparticles from the Solution Self-Assembly of Block Copolymers. *Macromolecules* **2017**, 50, 3439–3463.
- (4) Gupta, S.; Chokshi, P. Self-Organization of a 4-Miktoarm Star Block Copolymer Induced by Cylindrical Confinement. *Soft Matter* **2021**, 17, 4929–4941.
- (5) Noolandi, J.; Hong, K. M. Theory of Block Copolymer Micelles in Solution. *Macromolecules* **1983**, 16, 1443–1448.
- (6) Lodge, T. P. Block Copolymers: Long-Term growth with Added Value. *Macromolecules* **2020**, 53, 2–4.
- (7) Bates, F. S.; Fredrickson, G. H. Block Copolymers—Designer Soft Materials. *Phys. Today* **1999**, 52, 32–38.
- (8) Matsen, M. W.; Schick, M. Stable and Unstable Phases of a Diblock Copolymer Melt. *Phys. Rev. Lett.* **1994**, 72, 2660–2663.
- (9) Fredrickson, G. H. *The Equilibrium Theory of Inhomogeneous Polymers*; Oxford University Press, 2013.

- (10) Halperin, A. Polymeric Micelles: A Star Model. *Macromolecules* **1987**, *20*, 2943–2946.
- (11) Halperin, A.; Tirrell, M.; Lodge, T. P. Tethered Chains in Polymer Microstructures. *Adv. Polym. Sci.* **1992**, *100*, 31–71.
- (12) Nagarajan, R.; Ganesh, K. Block Copolymer Self-Assembly in Selective Solvents: Spherical Micelles with Segregated Cores. *J. Chem. Phys.* **1989**, *90*, 5843–5856.
- (13) Zhulina, E. B.; Adam, M.; LaRue, I.; Sheiko, S. S.; Rubinstein, M. Diblock Copolymer Micelles in a Dilute Solution. *Macromolecules* **2005**, *38*, 5330–5351.
- (14) Hubbell, J. A. Enhancing Drug Function. *Science* **2003**, *300*, 595–596.
- (15) Elsababy, M.; Heo, G. S.; Lim, S. M.; Sun, G.; Wooley, K. L. Polymeric Nanostructures for Imaging and Therapy. *Chem. Rev.* **2015**, *115*, 10967–11011.
- (16) Ge, Z.; Liu, S. Functional Block Copolymer Assemblies Responsive to Tumor and Intracellular Microenvironments for Site-Specific Drug Delivery and Enhanced Imaging Performance. *Chem. Soc. Rev.* **2013**, *42*, 7289–7325.
- (17) Gupta, S.; Chokshi, P. Self-Assembly of Polymer Grafted Nanoparticles within Spherically Confined Diblock Copolymers. *J. Phys. Chem. B* **2020**, *124*, 11738–11749.
- (18) Krishnamoorthy, S.; Pugin, R.; Brugger, J.; Heinzlmann, H.; Hinderling, C. Nanopatterned Self-Assembled Monolayers by Using Diblock Copolymer Micelles as Nanometer-Scale Adsorption and Etch Masks. *Adv. Mater.* **2008**, *20*, 1962–1965.
- (19) Wang, T. Y.; Tsiang, R. C. C.; Liou, J. S.; Wu, J.; Sheu, H. C. Preparation and Characterization of a Star-Shaped Polystyrene-*b*-Poly(Ethylene-co-Propylene) Block Copolymer as a Viscosity Index Improver of Lubricant. *J. Appl. Polym. Sci.* **2001**, *79*, 1838–1846.
- (20) Lodge, T. P.; Seitzinger, C. L.; Seeger, S. C.; Yang, S.; Gupta, S.; Dorfman, K. D. Dynamics and Equilibration Mechanisms in Block Copolymer Particles. *ACS Polym. Au* **2022**, *2*, 397–416.
- (21) Lodge, T. P. A Unique Platform for Materials Design. *Science* **2008**, *321*, 50–51.
- (22) He, Y.; Li, Z.; Simone, P.; Lodge, T. P. Self-Assembly of Block Copolymer Micelles in an Ionic Liquid. *J. Am. Chem. Soc.* **2006**, *128*, 2745–2750.
- (23) Zana, R. Dynamics in Micellar Solutions of Amphiphilic Block Copolymers. In *Dynamics of Surfactant Self-Assemblies: Micelles, Microemulsions, Vesicles, and Lyotropic Phases*; Hubbard, A. T., Ed.; Taylor & Francis Group/CRC Press: Boca Raton, 2005; pp 161–231.
- (24) Aniansson, E. A. G.; Wall, S. N. Kinetics of Step-Wise Micelle Association. *J. Phys. Chem.* **1974**, *78*, 1024–1030.
- (25) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. Theory of the Kinetics of Micellar Equilibria, and Quantitative Interpretation of Chemical Relaxation Studies of Micellar Solutions of Ionic Surfactants. *J. Phys. Chem.* **1976**, *80*, 905–922.
- (26) Wang, Y.; Balaji, R.; Quirk, R. P.; Mattice, W. L. Detection of the Rate of Exchange of Chains between Micelles Formed by Diblock Copolymers in Aqueous Solution. *Polym. Bull.* **1992**, *28*, 333–338.
- (27) Cao, T.; Munk, P.; Ramireddy, C.; Tuzar, Z.; Webber, S. E. Fluorescence Studies of Amphiphilic Poly(Methacrylic Acid)-Block-Polystyrene-Block-Poly(Methacrylic Acid) Micelles. *Macromolecules* **1991**, *24*, 6300–6305.
- (28) Smith, C. K.; Liu, G. Determination of the Rate Constant for Chain Insertion into Poly(Methyl Methacrylate)-Block-Poly(Methacrylic Acid) Micelles by a Fluorescence Method. *Macromolecules* **1996**, *29*, 2060–2067.
- (29) Willner, L.; Poppe, A.; Allgaier, J.; Monkenbusch, M.; Richter, D. Time-Resolved SANS for the Determination of Unimer Exchange Kinetics in Block Copolymer Micelles. *Europhys. Lett.* **2001**, *55*, 667–673.
- (30) Halperin, A.; Alexander, S. Polymeric Micelles: Their Relaxation Kinetics. *Macromolecules* **1989**, *22*, 2403–2412.
- (31) Halperin, A. On Micellar Exchange: The Role of the Insertion Penalty. *Macromolecules* **2011**, *44*, 5072–5074.
- (32) Dormidontova, E. E. Micellization Kinetics in Block Copolymer Solutions: Scaling Model. *Macromolecules* **1999**, *32*, 7630–7644.
- (33) Won, Y. Y.; Davis, H. T.; Bates, F. S. Molecular Exchange in PEO–PB Micelles in Water. *Macromolecules* **2003**, *36*, 953–955.
- (34) van Stam, J.; Creutz, S.; De Schryver, F. C.; Jérôme, R. Tuning of the Exchange Dynamics of Unimers between Block Copolymer Micelles with Temperature, Cosolvents, and Cosurfactants. *Macromolecules* **2000**, *33*, 6388–6395.
- (35) Lu, J.; Bates, F. S.; Lodge, T. P. Remarkable Effect of Molecular Architecture on Chain Exchange in Triblock Copolymer Micelles. *Macromolecules* **2015**, *48*, 2667–2676.
- (36) Choi, S.; Lodge, T. P.; Bates, F. S. Mechanism of Molecular Exchange in Diblock Copolymer Micelles: Hypersensitivity to Core Chain Length. *Phys. Rev. Lett.* **2010**, *104*, 047802.
- (37) Zhao, D.; Ma, Y.; Lodge, T. P. Exchange Kinetics for a Single Block Copolymer in Micelles of Two Different Sizes. *Macromolecules* **2018**, *51*, 2312–2320.
- (38) Ma, Y.; Lodge, T. P. Chain Exchange Kinetics in Diblock Copolymer Micelles in Ionic Liquids: The Role of χ . *Macromolecules* **2016**, *49*, 9542–9552.
- (39) Seeger, S. C.; Dorfman, K. D.; Lodge, T. P. Free Energy Trajectory for Escape of a Single Chain from a Diblock Copolymer Micelle. *ACS Macro Lett.* **2021**, *10*, 1570–1575.
- (40) Wang, E.; Zhu, J.; Zhao, D.; Xie, S.; Bates, F. S.; Lodge, T. P. Effect of Solvent Selectivity on Chain Exchange Kinetics in Block Copolymer Micelles. *Macromolecules* **2019**, *53*, 417–426.
- (41) Lund, R.; Willner, L.; Stellbrink, J.; Radulescu, A.; Richter, D. Role of Interfacial Tension for the Structure of PEP–PEO Polymeric Micelles. A Combined SANS and Pendant Drop Tensiometry Investigation. *Macromolecules* **2004**, *37*, 9984–9993.
- (42) Lund, R.; Willner, L.; Richter, D.; Dormidontova, E. E. Equilibrium Chain Exchange Kinetics of Diblock Copolymer Micelles: Tuning and Logarithmic Relaxation. *Macromolecules* **2006**, *39*, 4566–4575.
- (43) Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. 1998 E.W.R. Steacie Award Lecture Asymmetric amphiphilic block copolymers in solution: a morphological wonderland. *Can. J. Chem.* **1999**, *77*, 1311–1326.
- (44) Meli, L.; Lodge, T. P. Equilibrium vs Metastability: High-Temperature Annealing of Spherical Block Copolymer Micelles in an Ionic Liquid. *Macromolecules* **2009**, *42*, 580–583.
- (45) Meli, L.; Santiago, J. M.; Lodge, T. P. Path-Dependent Morphology and Relaxation Kinetics of Highly Amphiphilic Diblock Copolymer Micelles in Ionic Liquids. *Macromolecules* **2010**, *43*, 2018–2027.
- (46) Early, J. T.; Lodge, T. P. Fragmentation of 1,2-Polybutadiene-Block-Poly(Ethylene Oxide) Micelles in Imidazolium-Based Ionic Liquids. *Macromolecules* **2019**, *52*, 7089–7101.
- (47) Early, J. T.; Yager, K. G.; Lodge, T. P. Direct Observation of Micelle Fragmentation via In Situ Liquid-Phase Transmission Electron Microscopy. *ACS Macro Lett.* **2020**, *9*, 756–761.
- (48) Lund, R.; Willner, L.; Richter, D.; Lindner, P.; Narayanan, T. Kinetic Pathway of the Cylinder-to-Sphere Transition in Block Copolymer Micelles Observed in Situ by Time-Resolved Neutron and Synchrotron Scattering. *ACS Macro Lett.* **2013**, *2*, 1082–1087.
- (49) Wang, L.; Huang, H.; He, T. Rayleigh Instability Induced Cylinder-to-Sphere Transition in Block Copolymer Micelles: Direct Visualization of the Kinetic Pathway. *ACS Macro Lett.* **2014**, *3*, 433–438.
- (50) Parent, L. R.; Bakalis, E.; Ramírez-Hernández, A.; Kammeyer, J. K.; Park, C.; de Pablo, J.; Zerbetto, F.; Patterson, J. P.; Gianneschi, N. C. Directly Observing Micelle Fusion and Growth in Solution by Liquid-Cell Transmission Electron Microscopy. *J. Am. Chem. Soc.* **2017**, *139*, 17140–17151.
- (51) Rharbi, Y. Fusion and Fragmentation Dynamics at Equilibrium in Triblock Copolymer Micelles. *Macromolecules* **2012**, *45*, 9823–9826.
- (52) Landazuri, G.; Fernandez, V. V. A.; Soltero, J. F. A.; Rharbi, Y. Length of the Core Forming Block Effect on Fusion and Fission

- 767 Dynamics at Equilibrium in PEO–PPO–PEO Triblock Copolymer
768 Micelles in the Spherical Regime. *Macromolecules* **2021**, *54*, 2494–
769 2505.
- 770 (53) Early, J. T.; Block, A.; Yager, K. G.; Lodge, T. P. Molecular
771 Weight Dependence of Block Copolymer Micelle Fragmentation
772 Kinetics. *J. Am. Chem. Soc.* **2021**, *143*, 7748–7758.
- 773 (54) Gupta, S.; Lodge, T. P. Effect of Changing Interfacial Tension
774 on Fragmentation Kinetics of Block Copolymer Micelles. *Macro-*
775 *molecules* **2023**, *56*, 2137–2148.
- 776 (55) Araque, J. C.; Hettige, J. J.; Margulis, C. J. Modern Room
777 Temperature Ionic Liquids, a Simple Guide to Understanding Their
778 Structure and How It May Relate to Dynamics. *J. Phys. Chem. B* **2015**,
779 *119*, 12727–12740.
- 780 (56) Guinier, A.; Fournet, G.; Yudowitch, K. L. *Small-Angle*
781 *Scattering of X-Rays*; Wiley: New York, 1955.
- 782 (57) Pedersen, J. S. Determination of size distribution from small-
783 angle scattering data for systems with effective hard-sphere
784 interactions. *J. Appl. Crystallogr.* **1994**, *27*, 595–608.
- 785 (58) Berry, J. D.; Neeson, M. J.; Dagastine, R. R.; Chan, D. Y.;
786 Tabor, R. F. Measurement of Surface and Interfacial Tension using
787 Pendant Drop Tensiometry. *J. Colloid Interface Sci.* **2015**, *454*, 226–
788 237.
- 789 (59) Bashforth, F.; Adams, J. C. *An Attempt to Test the Theories of*
790 *Capillary Action by Comparing the Theoretical and Measured Forms of*
791 *Drops of Fluid*; University Press, 1883.
- 792 (60) Izzo, D.; Marques, C. M. Formation of Micelles of Diblock and
793 Triblock Copolymers in a Selective Solvent. *Macromolecules* **1993**, *26*,
794 7189–7194.
- 795 (61) de Gennes, P.-G. Scaling Theory of Polymer Adsorption. *J.*
796 *Phys. (Paris)* **1976**, *37*, 1445–1452.
- 797 (62) Alexander, S. Adsorption of Chain Molecules with a Polar Head
798 a Scaling Description. *J. Phys. (Paris)* **1977**, *38*, 983–987.