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Fragmentation of 1,2-Polybutadiene-block-poly(ethylene oxide) ² Micelles in Imidazolium-Based Ionic Liquids

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S Supporting Information 6

ABSTRACT: The effect of solvent selectivity on the fragmenta-7 8 tion kinetics of spherical micelles formed by a 1,2-polybutadieneblock-poly(ethylene oxide) "BO" copolymer in five 1-alkyl-3-9 methylimidazolium bis(trifluoromethylsulfonyl)imide-based 10 ionic liquids (ILs), ($[C_nMIM]$ [TFSI], where n = methyl, ethyl, 11 butyl, hexyl, and octyl) was investigated by temperature-jump 12 dynamic light scattering (T-jump DLS), small-angle X-ray 13 scattering (SAXS), and liquid-phase transmission electron 14 microscopy (LP-TEM). In this system, the core-forming block 15 is 1,2-polybutadiene (PB) and the corona-forming block is 16 poly(ethylene oxide). Micelle solutions prepared by direct 17 dissolution of the polymer into the IL resulted in large, 18 polydisperse spherical aggregates. For these micelles, with 19 aggregation numbers far from equilibrium, it was found that 20



fragmentation is the most favorable equilibration mechanism; previous measurements demonstrated that no single chain 21 22 exchange occurs under these conditions. T-jump DLS showed that the decay of $R_{\rm h}$ during annealing at 170 °C is, surprisingly, almost independent of the IL selectivity. This observation was confirmed by SAXS and LP-TEM, where the decay of R_{core} 23 during annealing at 170 °C was found to occur on the same timescale regardless of the solvent quality. For all relaxation 2.4 techniques used, and in all the ILs studied, the decay in micelle size could be well fit to the Avrami equation or "compressed 25 exponential" with an exponent (n) of 2, except for the decay in $R_{\rm h}$ in the most selective IL. Based on the change in the 26 aggregation number, Q, before and after a T-jump to 170 °C, the selectivity of the IL determines how far the initial micelles are 27 from equilibrium, but the fragmentation proceeds on the order of hundreds of minutes in all cases. SAXS of the bulk block 28 copolymer revealed a lamellar morphology with a domain size of the core-forming block of 21 nm, which is comparable to the 29 initial core radius of micelles prepared by direct dissolution, but well above the resulting core radii after fragmentation. We 30 discuss possible explanations for the functional form of the relaxation function, and the apparent independence of the rate on 31 interfacial tension. 32

INTRODUCTION 33

34 A-B diblock copolymers are known to self-assemble into a 35 variety of micellar structures when placed in a block selective 36 solvent. The self-assembly of block copolymers in solution has 37 been explored for numerous applications including drug or 38 gene delivery,¹⁻⁴ nanoreactors for small-molecule trans-39 formations,⁵ nanolithography,⁶ and viscosity modification.⁷ 40 Because of the versatility of block copolymer micelles from an 41 applications perspective, their dynamics and equilibration 42 kinetics in solution are of interest, yet remain less well 43 understood.^{8–10} Historically, the formation and equilibration 44 of block copolymer micelles is thought to occur by two 45 primary mechanisms, which were first described in the 46 Aniansson-Wall (AW) model for low-molecular weight 47 surfactants.¹¹ Specifically, the AW picture predicts that micelle 48 evolution and relaxation occurs via a combination of individual 49 chain exchange and micelle fusion/fragmentation.¹¹ Chain 50 exchange in block copolymer micelles has been explored in

detail, and the exchange kinetics have been quantified by time- 51 resolved small-angle neutron scattering (TR-SANS).^{8-10,12-21} 52 The influence of the Flory–Huggins interaction parameter, χ , ₅₃ between the core block and the solvent, and micelle core size 54 on the chain exchange kinetics was recently reported.^{8,10} 55 However, single-chain exchange is not the only process by 56 which micelles attain equilibrium. If the radius is large relative 57 to the equilibrium size, fragmentation is also possible. 58 Similarly, if the micelles are too small, fusion becomes 59 favorable; neither process has been studied in detail 60 experimentally. The existence of fusion/fragmentation mech- 61 anisms in block copolymer micelles has been debated for some 62 time.^{22,23} Recent reports showed that fusion and fragmentation 63

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64 occurs in various micellization scenarios, and some systems 65 even exhibit these phenomena at equilibrium.²⁴

There are several reports on fusion and fragmentation in low-molecular weight surfactants.^{25,26} Rharbi and Winnik used a fluorescent pyrene-derived probe to monitor the kinetics of fusion and fragmentation in aqueous solutions of surfactant micelles and found that the second-order kinetic process, identified as micelle fusion, occurs several orders of magnitude more slowly than a diffusion-controlled kinetic process.²⁵ The first report of fusion and fragmentation in block copolymer micelles was also conducted using excimer fluorescence, and the presence of both mechanisms in aqueous solutions of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene roxide) micelles was detected at equilibrium.²⁴ Additional work using excimer fluorescence spectroscopy to study ionic/ nonionic mixed micelles of Triton X-100 and sodium dodecyl sulfate provided a clear picture of the fusion and fragmentation process.²⁷

In this work, we exploit the approach used by Eisenberg et 82 83 al.,²⁸⁻³⁰ and later by Meli and Lodge,³¹ who demonstrated that 84 a range of micelle sizes could be obtained from a single block 85 copolymer by changing the solution preparation method. Meli 86 et al. prepared 1,2-polybutadiene-block-poly(ethylene oxide) 87 (BO) micelles in the ionic liquids (ILs) 1-ethyl-3-methyl-88 imidazolium bis(trifluoromethylsulfonyl)imide ([C₂MIM]-[TFSI]) or 1-butyl-3-methylimidazolium TFSI ([C₄MIM]-89 90 [TFSI]) by different dissolution methods. They noted that 91 micelles formed by direct dissolution (DD) of BO into the IL 92 formed large, polydisperse spherical aggregates, which 93 decreased in size when subjected to annealing at elevated 94 temperatures.^{31,32} They showed that BO micelle relaxation in 95 [C2MIM][TFSI] and [C4MIM][TFSI] was heavily dependent 96 on temperature, but the timescale for micelle equilibration at 97 170 °C remained on the order of 10³ s when changing the 98 solvent from $[C_2MIM]$ [TFSI] to $[C_4MIM]$ [TFSI]. Analysis of 99 this system by TR-SANS revealed that chain exchange did not 100 occur up to at least 200 $^{\circ}C_{,}^{32}$ indicating that micelle 101 equilibration must take place through some other mecha-102 nism(s). It was also found that the decay in BO micelle size is 103 well described by a compressed exponential with n = 2 in both 104 ILs and at various annealing temperatures.³² However, a 105 physical interpretation for this compressed exponential 106 behavior remains elusive. Although these results suggest that 107 the primary relaxation mechanism in BO/[C₂MIM][TFSI] is 108 micelle fragmentation, there are several questions that remain 109 unanswered, including the roles of solvent selectivity, initial 110 micelle size, core block degree of polymerization (N_{core}) , and 111 corona block degree of polymerization (N_{corona}) in fragmenta-112 tion kinetics.

To that end, a single BO block copolymer is studied here in 113 114 five different $[C_nMIM]$ [TFSI] ILs, where the same anion is 115 used, but the length of the alkyl chain on the IL cation is 116 varied. By changing the alkyl chain length, the selectivity 117 toward the 1,2-polybutadiene (PB) core block is tuned systematically, that is, the interfacial tension, which also 118 119 influences the initial size of the micelles prepared by DD. 120 Because larger micelles are formed initially in more selective 121 solvents, the influence of micelle size, and how far the system is 122 from the equilibrium size, was explored. Traditionally, studies 123 on micellization kinetics use jumps in temperature,³³ pH,³⁴ or 124 solvent³⁵ to perturb the system from equilibrium, and the time 125 required to relax to equilibrium is determined by some 126 detection method, such as light scattering. The method of T-

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jump dynamic light scattering (DLS) is used here to follow the ¹²⁷ evolution of the mean hydrodynamic radius (R_h) as a function ¹²⁸ of annealing time. When micelles equilibrate solely through ¹²⁹ chain exchange, the average R_h should not change much.⁸ ¹³⁰ Conversely, R_h is expected to change considerably when ¹³¹ fusion/fragmentation mechanisms dominate, so following the ¹³² evolution of micelle size throughout annealing is essential. ¹³³

An additional benefit of using ILs is that they have negligible 134 vapor pressures and extremely high boiling points.³⁶ These 135 properties were exploited here for imaging BO micelles in the 136 solution state by liquid-phase transmission electron micros- 137 copy (LP-TEM), which allowed for detailed analysis of the 138 evolution of the micelle core size following a T-jump to 170 139 °C. The core radius is not expected to change significantly by 140 chain exchange alone, so the ability to measure the PB core 141 size throughout the equilibration process provides more direct 142 evidence of micelle fragmentation. To complement LP-TEM, 143 small-angle X-ray scattering (SAXS) was used to determine the 144 micelle core radius and its distribution as a function of 145 annealing time. From these combined techniques, the kinetics 146 of fragmentation were determined for BO micelles in five 147 different ILs. 148

EXPERIMENTAL SECTION

Synthesis and Characterization. BO was synthesized previously 150 by two-step sequential anionic polymerization.³⁷ The diblock 151 copolymer used will be referred to as BO(8-7), where the numbers 152 in parentheses refer to the number average molar mass in kDa of each 153 block, respectively. The number average molecular weight (M_n) , 154 dispersity (D), and the poly(ethylene oxide) (PEO) block 155 composition (f_{PEO}) for BO(8-7) were determined by a combination 156 of size exclusion chromatography (SEC) with a multiangle laser light 157 scattering detector (Wyatt Dawn Heleos II) and ¹H nuclear magnetic 158 resonance spectroscopy in CDCl₃ (¹H NMR, Varian Inova 500). The 159 refractive index increment (dn/dc) for the diblock was estimated as 160 the weight average of the refractive index increments for PB in 161 tetrahydrofuran (THF) (dn/dc = 0.119 mL/g) and PEO in THF (dn/162dc = 0.068 mL/g.³⁸ For BO(8-7), M_n is 14.6 kDa and D = 1.10, with 163 $M_{n,PB} = 8.2 \text{ kDa}, M_{n,PEO} = 6.4 \text{ kDa}, \text{ and } f_{PEO} = 0.40.$ 164

The ILs 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)- 165 imide 99% ([C1MIM][TFSI]) and 1-hexyl-3-methylimidazolium 166 TFSI ([C₆MIM][TFSI]) 99.5% were purchased from IoLiTec. The 167 ILs [C₂MIM][TFSI], [C₄MIM][TFSI], and [C₈MIM][TFSI] were 168 synthesized by anion exchange reactions.³⁹ The typical procedure for 169 IL synthesis is as follows. For synthesis of $[C_2MIM]$ [TFSI], anion 170 exchange between 1-ethyl-3-methylimidazolium bromide ([C₂MIM]- 171 [Br]) and lithium TFSI was carried out in water at 70 °C for 24 h. 172 The reaction mixture was diluted with dichloromethane, the aqueous 173 layer was removed, and the organic layer was washed with water three 174 times. The organic layer was stirred in activated charcoal for 24 h 175 before passing the solution through an alumina column. Dichloro- 176 methane was removed in vacuo, and [C2MIM][TFSI] was dried 177 under vacuum (<100 mTorr) at 60 °C for 72 h. The same general 178 procedure was used to synthesize [C4MIM][TFSI] and [C8MIM]- 179 [TFSI], but [C₂MIM][Br] was replaced with [C₄MIM][Cl] and 180 [C₈MIM][Cl], respectively. All ILs were dried under vacuum (<100 181 mTorr) at 60 °C for 72 h prior to use and were characterized by ¹H, 182 ¹³C, and ¹⁹F NMR spectroscopy in DMSO-*d*₆. The ¹H NMR spectra 183 for all ILs are shown in Figures S1-S5. 184

Solution Preparation by DD. All solutions were prepared by the 185 DD method described here, unless noted otherwise. The desired 186 amounts of BO(8-7) and IL were combined by weight in a 20 mL 187 scintillation vial equipped with a stir bar to obtain a 0.5 wt % solution. 188 The vial was placed into an oil bath and stirred vigorously at 70 °C for 189 48 h. The resulting DD solutions were slightly blue-tinted in color 190 when $[C_1MIM][TFSI]$, $[C_2MIM][TFSI]$, or $[C_4MIM][TFSI]$ was 191 used as the solvent. Solutions prepared by DD in $[C_6MIM][TFSI]$ 192

193 and [C₈MIM[[TFSI] were clear and colorless. For the concentration 194 series of 0.5, 0.25, 0.1, and 0.05 wt % BO(8-7) in [C₂MIM][TFSI], a 195 1 wt % solution was prepared by the DD protocol described 196 previously and subsequently diluted with additional $[C_2MIM]$ [TFSI]. Dynamic Light Scattering. T-jump scattering measurements 197 198 were performed on a home-built light scattering setup equipped with Brookhaven BI-DS photomultiplier mounted to an adjustable 199 a 200 goniometer, a Lexel Ar⁺ laser (λ = 488 nm), and a Brookhaven BI-9000 correlator. During a typical T-jump experiment, the temperature 201 202 was controlled with an index-matching high-temperature silicone oil 203 bath to within ± 0.1 °C. To verify the size of the micelles before and 204 after a T-jump, multi-angle light scattering experiments were performed at T = 27 °C using a DLS instrument with a Brookhaven 205 206 BI-200SM goniometer, a Brookhaven BI-9000AT correlator, and a 637 nm laser with a range of scattering angles from 40° to 120° . 207

All micelle solutions (between 0.05 and 1 wt % copolymer) for 2.08 209 DLS were passed through a 0.45 μ m PTFE syringe filter to remove 210 any dust, and subsequently flame-sealed under vacuum (≤70 mTorr) 211 in a dust-free glass tube with an inner diameter of 0.51 cm to prevent 212 degradation of the block copolymer and to avoid contact with 213 moisture and dust. In a typical T-jump experiment, the oil bath 214 temperature was allowed to equilibrate for ~ 30 min prior to 215 introducing the sample. The normalized intensity autocorrelation 216 function, $g_2(t)$, was measured at a scattering angle of 90° as a function 217 of time. For each time point, $g_2(t)$ was acquired for 2–5 min. The 218 measured $g_2(t)$ was converted to the electric field autocorrelation 219 function, $g_1(t)$, via the Siegert relation,⁴⁰ which for single populations 220 was then fit to a second-order cumulant expansion to obtain the 221 average decay rate, $\overline{\Gamma}$, and the variance, $\mu_2/\overline{\Gamma}^2$ (also known as the 222 dispersity). The mutual diffusion coefficient, D_m, was obtained from 223 $D_{\rm m} = \overline{\Gamma}/q^2$, where q is the magnitude of the scattering vector defined 224 by $q = (4\pi n/\lambda_0)\sin(\theta/2)$, where *n* is the refractive index of the IL, λ_0 225 is the wavelength of light in a vacuum, and θ is the scattering angle. 226 For multi-angle light scattering experiments, D_m was estimated by 227 taking the slope of the line generated by plotting $\overline{\Gamma}$ versus q^2 with zero 228 intercept.

E29 For dilute solutions, $D_{\rm m}$ can be used as an approximation of the 230 tracer diffusion coefficient, $D_{\rm t}$. This is used to calculate the 231 hydrodynamic radius using the Stokes–Einstein equation

232

$$R_{\rm h} = \frac{k_{\rm B}T}{6\pi\eta_{\rm s}D_{\rm t}} \tag{1}$$

233 where $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature, and $\eta_s(T)$ is 234 the solvent viscosity. The temperature dependence of the viscosity is 235 well described by the Vogel–Fulcher–Tammann equation for these 236 (and many other) ILs.^{41–44} Additional analysis of the micelle size 237 distribution was performed by applying the regularized positive 238 exponential sum (REPES) Laplace inversion to the intensity 239 correlation function.⁴⁵ Application of this algorithm results in the 240 decay rate distribution, $G(\Gamma)$, which can be expressed in terms of the 241 hydrodynamic size from eq 1. When the REPES routine showed a 242 sample with a bimodal distribution, $g_1(t)$ was fit to a double-243 exponential function, shown in eq 2, to obtain the decay rates of each 244 population.

$$g_1(t) = A_1 \exp(-\overline{\Gamma}_1 t) + A_2 \exp(-\overline{\Gamma}_2 t)$$
 (2)

Liquid-Phase Transmission Electron Microscopy. The aver-247 age micelle core radius, $\langle R_{core} \rangle$, and the standard deviation of the core 248 size, σ_{core} at different time points during an annealing experiment 249 were determined using LP-TEM. The LP-TEM samples were passed 250 through a 0.45 μ m PTFE syringe filter to remove any dust or large 251 aggregates, and subsequently flame-sealed under vacuum (\leq 70 252 mTorr) in a glass tube to prevent degradation of the block copolymer 253 and to avoid contact with moisture and dust. The glass tubes were 254 submerged in an oil bath at T = 170 °C and held at this temperature 255 for the specified amount of time. Each glass tube was quenched to 256 room temperature in a water bath and opened to obtain a time-point 257 sample for LP-TEM imaging. Prior to imaging each sample, the 258 solutions were degassed under vacuum (<100 mTorr) for at least 20 min to prevent the appearance of air bubbles in the sample and then 259 immediately imaged. Approximately 0.5 μ L of solution was placed on 260 a 200 mesh copper grid coated with lacey Formvar stabilized with 261 carbon (Ted Pella Inc.), and the excess solution was manually blotted 262 from below the grid with filter paper until a thin film was left spanning 263 the holes of the lacey carbon support film. The images were obtained 264 at ambient temperatures using a FEI Tecnai G2 Spirit BioTWIN 265 operating at an accelerating voltage of 120 kV with an Eagle 4- 266 megapixel charge-coupled device (CCD) camera. To minimize any 267 effects of electron beam damage, the samples were imaged with a spot 268 size of 5 or larger, where the spot size is inversely related to the 269 strength of the first condenser lens. When the strength of the first 270 condenser lens is reduced, the beam current reaching the sample is 271 also reduced. $\langle R_{core} \rangle$ and σ_{core} were determined from measurements of 272 at least 400 individual micelles using ImageJ software.

Small-Angle X-ray Scattering. SAXS experiments were con- 274 ducted at the 5-ID-D beamline of the Dupont-Northwestern-Dow 275 Collaborative Access Team (DND-CAT) at the Advanced Photon 276 Source, Argonne National Laboratory. The same preparation method 277 used for the time-point samples in LP-TEM was also used for SAXS 278 experiments. Samples of 0.5 wt % BO(8-7) directly dissolved in ILs 279 were syringe-filtered into glass tubes, and then flame-sealed under 280 vacuum. The flame-sealed glass tubes were placed in an oil bath at 170 281 °C, removed at the designated time point, and quenched in a room 282 temperature water bath. The glass tubes were opened and taken into a 283 glovebox to load the micelle solutions into 1.5 mm diameter 284 borosilicate capillaries, sealed with epoxy under an argon atmosphere, 285 and then placed into a 16-capillary ambient temperature stage. SAXS 286 measurements were conducted at room temperature. Two-dimen- 287 sional scattering patterns were obtained using a Rayonix MX170-HS 288 CCD area detector using a 0.5 s exposure time to X-rays with a 289 wavelength of $\lambda = 0.729$ Å and a sample-to-detector distance of 8.5 m. 290 The 2D data were azimuthally averaged to yield 1D scattering 291 patterns as intensity versus q. The incoherent background (i.e., IL and 292 capillary scattering) exhibits a slight upturn at higher q values for the 293 ILs [C₆MIM][TFSI] and [C₈MIM][TFSI], which corresponds to 294 nanometer length scale ordering within the IL itself.⁴⁵⁻⁴⁸ The 295 incoherent background was fit to a power law $[I(q) = A + Bq^{-m} + Cq^2]$, 296 where $2 \le m \le 4$] and subtracted from the solution scattering data.⁴⁶ 297 For the solvents [C₁MIM][TFSI], [C₂MIM][TFSI], and [C₄MIM]- 298 [TFSI], no upturn at higher q is observed, and these solvents are fit to 299 a power law equation where the constant C is equal to zero. The 300 background-corrected intensity traces were analyzed using the 301 Pedersen model for block copolymer micelles with the Percus- 302 Yevick structure factor.49 303

SAXS of the bulk BO(8-7) diblock copolymer was performed using 304 a Ganesha SAXSLAB instrument with sample-to-detector distance of 305 1050 mm, a Cu K α X-ray source with $\lambda = 1.54$ Å, covering a q range 306 of 0.007–0.25 Å⁻¹. The sample was placed in a Linkam heating stage, 307 and the temperature was held for 10 min to allow for thermal 308 equilibration. The acquisition time for each temperature was 5 min. 309 The 2D data were collected with a position-sensitive EIGER 1M 310 (Dectris) detector and azimuthally averaged to yield 1D scattering 311 patterns plotted as intensity versus q. 312

RESULTS

Effect of Micelle Concentration. To determine the effect 314 of concentration on micelle equilibration kinetics, a series of 315 BO(8-7) solutions ranging from 0.05 to 1.0 wt % in 316 $[C_2MIM][TFSI]$ was prepared and studied by *T*-jump DLS 317 at 170 °C. One indicator of micelle fusion is the presence of 318 second-order kinetics with respect to micelle concentration, 319 whereas fragmentation or chain exchange should be first- 320 order.^{23,24,51} It was found that the initial average micelle 321 hydrodynamic radius, $\langle R_h \rangle_0$, for all concentrations prepared by 322 the DD protocol were relatively large ($\langle R_h \rangle_0 \approx 60$ nm) and 323 disperse ($\mu_2/\overline{\Gamma}$]² \geq 0.18). The evolution of the R_h distribution 324 for 0.5 wt % BO(8-7) in [C_2MIM][TFSI] after a *T*-jump to 325 fi

313

f1



Figure 1. (a) REPES results for 0.5 wt % BO(8-7) in $[C_2MIM]$ -[TFSI] after a *T*-jump to 170 °C. Light scattering measurements were performed at a scattering angle of 90°. (b) Time dependence of normalized R_h for BO(8-7) in $[C_2MIM]$ [TFSI] at various polymer concentrations, a scattering angle of 90°, and a relaxation temperature of 170 °C. Solid lines represent best fits to eq 3, with n = 2.

328 the distribution begins to narrow and shift to a smaller $\langle R_h \rangle$ 329 after annealing for approximately 1100 min. The $\langle R_h \rangle$ for all 330 concentrations was determined by fitting the DLS autocorre-331 lation functions to a second-order cumulant expansion, and 332 these values were normalized by the initial value to compare 333 the decay in $\langle R_h \rangle$ across all concentrations. In all cases, $\langle R_h \rangle$ 334 decayed more rapidly than a single exponential function, as 335 shown in Figure 1b, leading to a steady-state size, $\langle R_h \rangle_{lp}$ of 336 approximately 34 nm. Note that relaxation curves for 0.5, 0.25, 337 0.1, and 0.05 wt % shown in Figure 1b are vertically shifted for 338 clarity.

In agreement with previous reports,^{31,32} the normalized hydrodynamic radius as a function of annealing time, R(t), and be well described by the Avrami equation, or compressed exponential, shown in eq 3

$$R(t) = \frac{\langle R_{\rm h} \rangle_t - \langle R_{\rm h} \rangle_{\rm f}}{\langle R_{\rm h} \rangle_0 - \langle R_{\rm h} \rangle_{\rm f}} = \exp[-(t/\tau)^n]$$
(3)

34

t1

344 where $\langle R_h \rangle_t$ is the average hydrodynamic radius of the micelles 345 at time, t, $\langle R_h \rangle_0$ is the initial hydrodynamic radius of the 346 micelles measured by multi-angle DLS at room temperature, 347 $\langle R_h \rangle_f$ is the final average hydrodynamic radius determined by 348 multi-angle DLS at room temperature after a *T*-jump, τ is the 349 characteristic relaxation time, and *n* is the exponent, which is 350 fixed at 2. When fits were performed with two adjustable 351 paraments, τ and *n*, the average value of the exponent was 352 found to be equal to 2.2 \pm 0.2.

The characteristic relaxation time τ was obtained from fitting the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized the *T*-jump DLS data to eq 3, and the results are summarized to eq 4, and the results are sum

Table 1. Concentration	Dependence of $\langle R_{\rm h} \rangle$ and τ
Determined by T-Jump	DLS at 170 °C for $BO(8-7)$ in
$[C_2MIM][TFSI]^a$	

concentration (wt %)	$\langle R_{ m h} angle_0$ (nm)	$\langle \mu_2/\Gamma^2 angle_0$	$\langle R_{\rm h} \rangle_{\rm f}$ (nm)	$\langle \mu_2/\Gamma^2\rangle_{\rm f}$	au (min)
1	70	0.28	38	0.09	$260~\pm~40$
0.5	85/62	bimodal	35	0.03	200 ± 20
0.25	58	0.22	35	0.09	240 ± 17
0.1	49	0.25	30	0.005	300 ± 82
0.05	58	0.18	30	0.006	440 ± 56
^{<i>a</i>} Relaxation times were determined by eq 3 with n fixed as 2.					

the relaxation times observed here (on the order of hundreds 358 of minutes). Therefore, we attribute these long relaxation times 359 to the fragmentation of large, disperse spherical micelles 360 formed by DD of BO(8-7) in ILs. The relaxation time only 361 varies by at most a factor of 2 over a 20-fold variation in 362 concentration, indicating that a first-order process is dominant. 363 The relaxation times do increase very slightly with decreasing 364 polymer concentration for polymer concentrations less than 1 365 wt %, which could indicate a minor contribution from a 366 second-order kinetic process.⁵² One process that could 367 account for the slightly concentration-dependent relaxation 368 times observed here is collisional aggregation and de- 369 aggregation. When micelle solutions are prepared by the DD 370 protocol, large aggregates consisting of multiple micelles could 371 undergo some type of sticky-collisional interactions, and then 372 disassociate upon heating. The time required for micelle 373 collisions would be expected to depend on polymer 374 concentration; however, the time required for dissociation 375 would not.^{22,53} Such micelle collision and fusion events have 376 been observed in the growth and evolution of amphiphilic 377 block copolymers in water by TEM, and this process was 378 reported to contribute to a concentration-dependent relaxation 379 process.54 380

Effect of Solvent. To understand the influence of solvent ³⁸¹ selectivity on fragmentation kinetics, five 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs were selected ³⁸³ as PEO-selective solvents. In general, the longer the alkyl chain ³⁸⁴ on the imidazolium cation, the less selective is the IL, that is, ³⁸⁵ the surface tension between the PB core block and the solvent ³⁸⁶ decreases and the PB block is more solvated by the IL. ^{55–58} ³⁸⁷ Thus, the five ILs chosen here have alkyl chain lengths of one, ³⁸⁸ two, four, six, and eight carbon chains. The effects of solvent ³⁸⁹ selectivity on the relaxation time were investigated for 0.5 wt % ³⁹⁰ BO(8-7) in these five ILs. ³⁹¹

The time-dependent normalized hydrodynamic radii for 0.5 392 wt % BO(8-7) in the five ILs after a T-jump to 170 °C are 393 shown in Figure 2. The dynamic traces obtained by T-jump 394 f2 DLS for 0.5 wt % BO(8-7) in four of the five ILs selected here 395 were fit to eq 3 with n = 2. However, relaxation in the most 396 selective IL, [C₁MIM][TFSI], was found to occur much more 397 slowly than the other four ILs, and the relaxation in $\langle R_{\rm h} \rangle$ was 398 fit to eq 3 with n = 3.3. To verify that n = 2 in 399 [C₂MIM][TFSI], [C₄MIM][TFSI], [C₆MIM][TFSI], and 400 $[C_8MIM]$ [TFSI], linear plots of log R(t) versus t^2 are shown 401 in Figure S11a of the Supporting Information. A nonlinear 402 curve is obtained for T-jump DLS results in $[C_1MIM]$ [TFSI] 403 (see the Supporting Information, Figure S11b). When fitting 404 the time-dependent normalized hydrodynamic radii for 0.5 wt 405 % BO(8-7) in [C₂MIM][TFSI], [C₄MIM][TFSI], [C₆MIM]- 406 [TFSI], and [C₈MIM][TFSI] with two adjustable parameters, 407

t2



Figure 2. Time-dependent normalized hydrodynamic radii for 0.5 wt % BO(8-7) in 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide based ILs. Solid lines represent the best fits to the relaxation function shown in eq 3, with n = 2 for all ILs except [C₁MIM][TFSI], where n = 3.3. DLS measurements were performed at a temperature of 170 °C and a scattering angle of 90°.

408 τ and *n*, the $\langle n \rangle = 2.2 \pm 0.1$ for the four ILs, which again 409 confirms that the exponent is essentially 2 in these solvents. Table 2 summarizes the fitting results of T-jump DLS at 170 410 411 °C, along with $\langle R_{\rm h} \rangle$ and the dispersity before and after the T-412 jump to 170 °C. When preparing micelle solutions by DD, the 413 $\langle R_h \rangle_0$ is expected to decrease as the cation alkyl chain length is 414 increased because the solvent becomes less selective for the 415 PEO block. Based on the solubility parameters of the PB (δ = 416 17.4 MPa^{1/2})³⁸ and PEO ($\delta = 20.2$ MPa^{1/2})³⁸ blocks at T =417 298 K, the largest aggregates would be formed by DD in $[C_1 MIM][TFSI]$ or $[\tilde{C}_2 MIM][TFSI]$ ($\delta = 27.6 \text{ MPa}^{1/2}$),⁵⁵ 418 419 and the smallest aggregates should form by DD in $[C_8MIM]$ -420 [TFSI] ($\delta = 25.0 \text{ MPa}^{1/2}$).⁵⁵ The results in Table 2 are 421 consistent with this expectation, in that $\langle R_{\rm h} \rangle_0 = 79$ nm in 422 [C₁MIM][TFSI] and $\langle R_h \rangle_0 = 38$ nm in [C₈MIM][TFSI].

423 As expected, the initial size of the micelles, determined by 424 multi-angle DLS at room temperature prior to a *T*-jump, 425 decreased when the solvent quality of the IL toward the PB 426 core becomes less poor. Surprisingly, the kinetics of 427 fragmentation seem to be very similar for most of the ILs 428 used here, except for $[C_1MIM][TFSI]$, which we consider to 429 be an outlier due to the SAXS and LP-TEM data for this 430 sample, which will be discussed in subsequent sections.

⁴³¹ To further investigate the process of micelle fragmentation, ⁴³² LP-TEM and SAXS were used to follow the evolution of ⁴³³ $\langle R_{core} \rangle$ following a *T*-jump to 170 °C. Previous workers have ⁴³⁴ used SAXS to study the kinetics of globule-to-cylinder ⁴³⁵ transitions,⁵⁹ the ordering kinetics of micelle-forming block ⁴³⁶ copolymers,⁶⁰ and the time-dependent evolution of block ⁴³⁷ copolymer micelles in THF/water mixtures.⁶¹ This technique ⁴³⁸ proves extremely useful in that specific structural details of the ⁴³⁹ micelles such as the core radius, corona thickness, dispersity of ⁴⁴⁰ the core, and the aggregation number (*Q*) can be obtained by fitting I(q) to analytical models.^{50,62,63} In addition to SAXS, 441 TEM is a valuable technique for determining micelle 442 morphology, including quantifying the core radius and its 443 distribution as a function of time. 444

SAXS curves for 0.5 wt % BO(8-7) micelles prepared by DD 445 in $[C_1MIM][TFSI]$ and $[C_2MIM][TFSI]$ are shown in Figure 446 f3 3a,b, respectively. SAXS data for 0.5 wt % BO(8-7) in 447 f3



Figure 3. Structural evolution of 0.5 wt % BO(8-7) (a) in $[C_1MIM][TFSI]$ and (b) in $[C_2MIM][TFSI]$ upon *T*-jump to 170 °C by TR-SAXS curves fit to the Pedersen model (solid black lines). The curves are shifted vertically for clarity. Measurements were acquired at room temperature after quenching each sample in a room temperature water bath.

[C₄MIM][TFSI], [C₆MIM][TFSI], and [C₈MIM][TFSI] are 448 included in Supporting Information. In the figures, the dark 449 purple traces indicate the first time point (30 min) obtained 450 for these samples, that is, the sample was annealed at 170 °C 451 for 30 min before the sample was quenched to room 452 temperature and loaded into glass capillaries for SAXS. This 453 process was repeated for all indicated time points. From the 454 scattering patterns shown in Figure 3a,b, the average micelle 455 core radius decreases substantially upon annealing at 170 °C. 456 The *q* value of the first minimum in the SAXS curves is 457 inversely proportional to the micelle core radius.^{50,63} The first 458 minimum in Figure 3a,b shifts to larger *q* values with time, 459 indicative of a decrease in $\langle R_{core} \rangle$. 460

Table 2. $\langle R_h \rangle$ and τ Determined by T-Jump DLS at 170 °C for 0.5 wt % BO(8-7) in Imidazolium-Based ILs^{*a*}

IL cation	$\langle R_{\rm h} \rangle_0 \ ({\rm nm})$	$\langle \mu_2/\Gamma^2 angle_0$	$\langle R_{\rm h} \rangle_{\rm f} ({\rm nm})$	$\langle \mu_2/\Gamma^2 angle_{ m f}$	n	τ (min)
$[C_1MIM]$	79	0.24	39	0.13	3.3	1340 ± 220
$[C_2MIM]$	85/62	bimodal	35	0.03	2.4	200 ± 20
$[C_4MIM]$	51	0.19	34	0.13	2.2	110 ± 30
$[C_6MIM]$	43	0.12	34	0.014	2.1	70 ± 15
[C ₈ MIM]	38	0.17	32	0.008	1.9	130 ± 22

^{*a*}The relaxation times were determined by eq 3.

f4

t3

⁴⁶¹ The time evolution of $\langle R_{core} \rangle$ in the five ILs from SAXS was ⁴⁶² also fit to the Avrami equation. Normalization of $\langle R_{core} \rangle$ was ⁴⁶³ carried out as in the *T*-jump DLS data analysis, where R(t) is ⁴⁶⁴ calculated according to eq 4. Figure 4 shows the normalized



Figure 4. Normalized $\langle R_{core} \rangle$ from SAXS upon *T*-jump to 170 °C for 0.5 wt % BO(8-7) in 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide-based ILs. The curves are shifted vertically for clarity. Solid lines represent the fits to the standardized relaxation function shown in eq 4 with an Avrami exponent of n = 2.

⁴⁶⁵ core radii from SAXS as determined by fitting the 1D ⁴⁶⁶ scattering data to the Pedersen model,^{49,50} and the relaxation ⁴⁶⁷ functions are well described by eq 4, with fixed n = 2. Table 3

Table 3. Summary of $\langle R_{\text{core}} \rangle$, σ_{core} , and τ Obtained by *T*-Jump SAXS at 170 °C for 0.5 wt % BO(8-7) in Imidazolium-Based ILs^{*a*}

IL	$\langle R_{\rm core} \rangle_0 \ ({\rm nm})$	$\sigma_{ m core} \ ({ m nm})$	${\langle R_{\rm core} angle_{\rm f} \over ({\rm nm})}$	$\sigma_{ m core} \ (m nm)$	au (min)
[C ₁ MIM] [TFSI]	25	5.0	19	3.6	190
[C ₂ MIM] [TFSI]	23	4.6	18	3.4	171
[C ₄ MIM] [TFSI]	20	4.5	16	3.2	100
[C ₆ MIM] [TFSI]	18	4.2	14	3.6	100
[C ₈ MIM] [TFSI]	16	3.9	13	3.1	150

^{*a*}The relaxation times were determined by fitting the normalized $\langle R_{core} \rangle$ to eq 4 with n = 2.

468 shows the results for all five ILs including the initial core size 469 and standard deviation, the final core size and standard 470 deviation, and the relaxation times determined by SAXS. It was 471 found that the time required to reach steady-state is generally 472 unaffected by the IL selectivity, in agreement with the results 473 from *T*-jump DLS.

$$R(t) = \frac{\langle R_{\text{core}} \rangle_t - \langle R_{\text{core}} \rangle_f}{\langle R_{\text{core}} \rangle_0 - \langle R_{\text{core}} \rangle_f} = \exp[-(t/\tau)^n]$$
(4)

To gain more insight into how the core size distribution 476 changes with annealing time, LP-TEM was used to measure 477 the mean and standard deviation of the micelle core radius 478 distribution at different time points following a *T*-jump to 170 479 °C. The change in $\langle R_{\rm core} \rangle$ for 0.5 wt % BO(8-7) in 480 [C₁MIM][TFSI] and [C₂MIM][TFSI] after a *T*-jump to 481 170 °C was 6 and 5 nm, respectively, as shown by SAXS and 482 LP-TEM results in Figures 3 and 5. The electron micrographs 483 of the as-prepared and steady-state micelles in [C₁MIM]-



Figure 5. (a) LP-TEM of 0.5 wt % BO(8-7) in $[C_1MIM][TFSI]$ asprepared by DD, and (b) LP-TEM of the solution after annealing at 170 °C for 1800 min. (c) LP-TEM of 0.5 wt % BO(8-7) in $[C_2MIM][TFSI]$ as-prepared by DD, and (d) LP-TEM of the solution after annealing at 170 °C for 1800 min. In these images, the IL appears darker than the PB micelle core because of the higher electron density of the IL.

[TFSI] and $[C_2MIM]$ [TFSI] are shown in Figure 5a,b, and 484 5c,d, respectively. In the electron micrographs, the densely 485 packed PB blocks form the micelle cores, which appear lighter 486 than the IL medium. As shown in Figure 5a,c, the micelles 487 prepared by DD are all apparently spherical, but with large 488 variations in radius. The images in Figure 5b,d are 489 representative images of the micelles in $[C_1MIM]$ [TFSI] and 490 $[C_2MIM]$ [TFSI], respectively, after annealing at 170 °C for 491 1800 min. Qualitatively, the steady-state images show that the 492 micelle radius decreases noticeably after annealing. 493

To quantify the evolution of $\langle R_{\rm core} \rangle$ and the standard 494 deviation ($\sigma_{\rm core}$), LP-TEM was employed to image the change 495 in micelle structure throughout a T-jump at 170 °C for the 496 same five ILs. The resulting time point images are shown in 497 Figure S16 for 0.5 wt % BO(8-7) in [C₂MIM][TFSI]. As 498 shown in the figure, the PB core size decreases after heating at 499 170 °C for just 90 min. Additional structural details were 500 obtained through image analysis of each time point. By 501 measuring the radius of several hundred micelle cores 502 (specifically, 600 micelles were measured for the as-prepared 503 samples, and 400 micelles were measured for the other time 504 points), a core radius distribution was obtained for each time 505 point in the annealing process. From these measurements, the 506 histograms in Figure 6 were constructed, where the bin width 507 f6 was set to 3 nm, and the solid lines are overlays of a lognormal 508 distribution with the mean and standard deviation denoted in 509 each histogram. Clearly, $\langle R_{\rm core} \rangle$ and $\sigma_{\rm core}$ decrease substantially 510 throughout a *T*-jump to 170 °C, and the size distribution of 511 the micelles in [C₂MIM][TFSI] narrows considerably when 512 comparing the histogram of the steady-state micelles to that of 513 the as-prepared micelles. Furthermore, the larger size wing of 514 the distribution changes much more significantly than the 515 lower size wing, suggesting an increasing preference to undergo 516

f5

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Figure 6. Histograms of data obtained by image analysis from LP-TEM showing the evolution in $\langle R_{core} \rangle$ for 0.5 wt % BO(8-7) in [C₂MIM][TFSI] during *T*-jump at 170 °C. The solid curves shown in each histogram corresponds to a log normal distribution function with the corresponding average and standard deviation indicated for each time point.

517 fragmentation, the further from equilibrium a particular micelle 518 is.

The difference between the final and initial $\langle R_{core} \rangle$ 519 determined by LP-TEM agrees closely with the results from 520 SAXS. For 0.5 wt % BO(8-7) in [C₂MIM][TFSI], the initial 521 $\langle R_{core} \rangle$ is 22 and 23 nm by LP-TEM and SAXS, respectively. 522 The steady-state $\langle R_{core} \rangle$ in [C₂MIM][TFSI] is 18 and 15 nm as 523 determined by LP-TEM and SAXS, respectively. The differ-524 ence in the absolute values of $\langle R_{core} \rangle$ by LP-TEM and SAXS is 525 within the standard deviation of the core radius obtained by 526 each technique. In general, the LP-TEM results support the 527 conclusion from SAXS, which is that the change in $\langle R_{core} \rangle$ after 528 *T*-jump to 170 °C occurs on the order of 100 min. 529

⁵³⁰ The comparison of R(t) based on the $\langle R_{\text{core}} \rangle$ determined by ⁵³¹ SAXS and the $\langle R_{\text{h}} \rangle$ determined by DLS is shown in Figure 7. ⁵³² In the figure, filled circles represent the normalized $\langle R_{\text{h}} \rangle$ as ⁵³³ determined by *T*-jump DLS to 170 °C, filled triangles ⁵³⁴ represent the normalized $\langle R_{\text{core}} \rangle$ from SAXS, and solid lines

f7



Figure 7. Normalized $\langle R_{\rm h} \rangle$ (filled in circles) and normalized $\langle R_{\rm core} \rangle$ (filled in triangles) for 0.5 wt % BO(8-7) at 170 °C in [C₁MIM][TFSI] (red points and lines), [C₂MIM][TFSI] (blue points and lines), [C₄MIM][TFSI] (green points and lines), [C₆MIM][TFSI] (purple points and lines), and [C₈MIM][TFSI] (orange points and lines). The solid lines represent the fits to eq 3 and the dashed lines represent fits to eq 4, both with n fixed at 2 except for *T*-jump DLS in [C₁MIM][TFSI], where the best fit was obtained when n is 3.3. The plots are shifted vertically for clarity.

represent best fits to eq 3 with n = 2 for all ILs except for the 535 normalized $\langle R_{\rm h} \rangle$ in [C₁MIM][TFSI], where n = 3.3. The 536 dashed lines in Figure 7 represent best fits to eq 4 with n fixed 537 at 2. The results for [C₂MIM][TFSI], [C₄MIM][TFSI], 538 $[C_6MIM]$ [TFSI], and $[C_8MIM]$ [TFSI] agree quite well across 539 the two techniques, but larger deviations are observed in 540 $[C_1MIM]$ [TFSI]. This discrepancy could be explained by the 541 existence of additional relaxation mechanisms for micelles 542 prepared by DD in [C₁MIM][TFSI] including the disassoci- 543 ation of larger aggregates consisting of multiple micelles. The 544 difference in the exponent determined by DLS (n = 3.3) and 545 SAXS (n = 2) for relaxation in $[C_1MIM]$ [TFSI] indicates that 546 the change in size observed between the two techniques is 547 likely dominated by two different mechanisms. This conclusion 548 would also support the large differences in au for SAXS and DLS 549 in [C₁MIM][TFSI].^{64,65} However, additional experiments on 550 this system may be required to determine the exact cause of 551 the different time scales observed in T-jump DLS and SAXS 552 for BO(8-7) micelles in $[C_1MIM][TFSI]$. 553

Effect of the Micelle Preparation Protocol. To 554 determine the effect of solution preparation on $\langle R_{\rm h} \rangle_0$ and 555 $\langle R_{\rm h} \rangle_{\rm f}$ for BO(8-7) in [C₂MIM][TFSI], a 0.5 wt % solution was 556 prepared by the cosolvent (CS) method, following the 557 approach described previously by Meli et al.³² All components 558 were dissolved in dichloromethane (DCM), and after stirring 559 to ensure all components are well dissolved, the DCM was 560 slowly evaporated under a nitrogen purge over 24 h. The 561 complete procedure for the CS method is described in 562 Supporting Information. The $\langle R_h \rangle_0$ for 0.5 wt % BO(8-7) in 563 [C₂MIM][TFSI] prepared by this method was found to be 26 564 nm with a dispersity of 0.08. Thus, the initial size of the CS 565 micelles is less than half that of the micelles prepared by DD. 566 Additionally, when CS micelles are annealed at 170 °C for a 567 day (see Supporting Information, Figure S9), $\langle R_{\rm h} \rangle$ remains 568 constant. Thus, the $\langle R_h \rangle_f$ obtained for the CS micelles remain 569 significantly smaller than the steady state size for solutions 570 prepared by DD (35 nm). Similar results were obtained by 571 Meli, et al., who conjectured that the annealed DD micelle size 572 was closer to equilibrium than CS micelles. They argued that 573 (a) it is clear that the CS protocol generates micelles that are at 574

IL cation	$\delta^{b}~(\mathrm{MPa}^{1/2})^{55}$	$\delta^c~(\mathrm{MPa}^{1/2})^{58}$	$\Delta R_{\rm h}~({\rm nm})$	$\Delta R_{\rm core} \ ({\rm nm})$	Q_0^{a}	$Q_{\rm f}^{\ a}$	$Q_0/Q_{\rm f}$
$[C_1MIM]$		21.5	40	6	4480	1970	0.44
$[C_2MIM]$	27.6	21.1	27	5	3490	1670	0.48
$[C_4MIM]$	26.7	19.4	17	4	2300	1180	0.51
$[C_6MIM]$	25.6		9	4	1670	790	0.47
$[C_8MIM]$	25.0		6	3	1180	630	0.53

Table 4. Effects of Solvent Quality on Micelle Size and Aggregation Number (Q) for 0.5 wt % BO(8-7) in ILs before and after a T-Jump to 170 °C

^{*a*}Aggregation number (Q_x), where x = 0, f denoting initial and final values, calculated as $4\pi \langle R_{core} \rangle_x^{3/} (3V_{PB})$, assuming that the core is devoid of solvent, and V_{PB} is the volume per core chain. ^{*b*}Hildebrand solubility parameters reported for T = 298 K. ^{*c*}Hildebrand solubility parameters reported for T = 303 K. For reference, the average solubility parameters for PB and PEO are $\delta = 17.4$ MPa^{1/2} and $\delta = 20.2$ MPa^{1/2}, respectively.³⁸

575 equilibrium with a much less selective, mixed solvent at the 576 time of formation and should therefore be much smaller than 577 equilibrium micelles in the IL; (b) to reduce the number 578 density of micelles is an extremely time-consuming process, so 579 it is difficult for CS micelles to coarsen with time; (c) DD 580 micelles annealed at different temperatures relaxed to the same 581 final size.

582 DISCUSSION

We now consider four general questions about these results. 583 1. Is the change in micelle size due to fragmentation? 584 The fact that the micelles are deliberately prepared to be 585 586 significantly larger than their equilibrium size favors relaxation 587 by fragmentation. The fact that the relaxation process is first-588 order in micelle concentration is consistent with fragmenta-589 tion. However, it is worth noting that we have no direct proof 590 of fragmentation, such as clear TEM evidence of an 591 intermediate state. Direct evidence that fragmentation is 592 occurring in this system is currently being pursued via 593 temperature-controlled LP-TEM of BO micelles in ILs. The 594 one aspect of the results that raises a possible doubt is the 595 compressed exponential relaxation function, which might 596 imply some kind of a cooperative process. It is hard to 597 conceive of a strictly first-order process that gives this 598 functional form. Nevertheless, the presence of micelle 599 fragmentation is consistent with the theory presented by 600 Dormidontova, which predicts that micelles with aggregation 601 numbers that lie very far from equilibrium are more likely to 602 relax via fusion or fragmentation mechanisms.²³ We assume 603 that the steady-state aggregation number, $Q_{\rm fr}$ obtained for each 604 sample is the equilibrium aggregation number, Q_{eq}. Based on 605 the arguments posed by Dormidontova,²³ fragmentation into 606 two equally sized micelles is favored when $Q \ge 1.5Q_{eq}$. In this 607 work, the aggregation numbers for each sample were 608 determined assuming a dry PB core and calculated according 609 to $Q = (4\pi \langle R_{core} \rangle^3)/3V_{core}$, where $\langle R_{core} \rangle$ is taken from the 610 model fits to SAXS data, and $V_{\rm core} = M_{\rm n}/\rho N_{\rm av}$ where ρ is the 611 amorphous density of PB ($\rho = 0.91$ g/cm³),³⁸ and $N_{\rm av}$ is 612 Avogadro's constant. From Table 4, the equilibrium 613 aggregation number can be estimated as $Q_{eq} \approx Q_{fr}$ and 614 1.5Qeq is equal to 2960, 2500, 1770, 1185, and 945 for BO(8-615 7) micelles in [C₁MIM], [C₂MIM], [C₄MIM], [C₆MIM], and 616 [C_8 MIM], respectively. From Q_0 in Table 4, all as-prepared 617 micelles are significantly larger, 1.5 times Q_{eq} , supporting 618 micelle fragmentation as the dominant pathway. The ratio of 619 $Q_{\rm f}$ to Q_0 for the 5 ILs are shown in Table 4. Regardless of the 620 solvent, the average aggregation number is approximately 621 halved after heating at 170 °C. It is likely that the largest 622 micelles (i.e., those with $Q \ge 1.5Q_{eq}$) account for the observed 623 decrease in Q, as the micelles that are at or near the

equilibrium aggregation number are not expected to undergo 624 fragmentation. Experimentally, this is consistent with the 625 histograms shown in Figure 6, where the number of micelles 626 with $\langle R_{\rm core} \rangle$ greater than 18 nm decreases significantly over 627 time, but the number of micelles with $\langle R_{\rm core} \rangle \leq 18$ nm remains 628 relatively constant.

2. Why does the relaxation follow a compressed exponential? 630

In all ILs, excluding $[C_1MIM]$ [TFSI], the timescales and the 631 exponents from fits to the data from *T*-jump DLS and SAXS 632 agree well. We do not have a physical interpretation for the 633 origin of n = 2 in the BO/ $[C_nMIM]$ [TFSI] samples studied 634 here, but the results are consistent with previous reports on 635 this system.^{31,32} The use of compressed exponential (n > 1) 636 functions to describe block copolymer dynamics is docu- 637 mented in other reports,^{64–67} and in at least one instance has 638 been attributed to the spontaneous breakup of pre-formed 639 structures.⁶⁵ The similarity to the Avrami form, typically used 640 to describe a nucleation and growth kinetics, hints at a 641 nucleation-limited or cooperative kinetic process, but the 642 independence of the experimental rate on concentration 643 suggests that any cooperativity is confined to a single micelle. 644

3. What sets the characteristic relaxation time? 645

We speculate that the experimental fragmentation times 646 follow an Arrhenius expression, shown in eq 5 647

$$\tau = \tau_0 \exp(E_{\rm b}/kT) \tag{5}_{648}$$

where $E_{\rm b}$ is the activation barrier for fragmentation and τ_0 is 649 the characteristic attempt time to form the transition state. 650 This attempt time is likely dependent on the viscosity of the 651 PB core and driven by the corona crowding and core stretching 652 (both of which are significant). The corona crowding exerts a 653 stress, σ , on the cross-sectional area of the core, given by f/ 654 $\pi \langle R_{\rm core} \rangle_0^2$, where f is the force. This force can be estimated 655 using the theory by Sheiko, et al.⁶⁸ which gives the force 656 exerted on a linking unit by a star polymer grafted to a hard 657 surface, and here choosing the linker length to be $\langle R_{\rm core} \rangle_0/2$. 658 Using this model to determine the stress from corona 659 crowding, eq 6 shows an estimate for τ_0 . 660

$$\tau_0 \approx \frac{\eta_{\text{core}}}{\sigma} = \frac{\eta_{\text{core}} \pi \langle R_{\text{core}} \rangle_0^3}{\sqrt{2} k T Q_0^{3/2}} \tag{6} 66$$

Given that the viscosity of 8.2 kDa PB at 170 °C is 662 approximately 0.6 Pa·s (see Figure S17 in Supporting 663 Information) and knowing the experimental relaxation times 664 range from 6000 to 11 000 s, then E_b is on the order of 25–30 665 kT per micelle. The barrier per chain is obtained by dividing E_b 666 by Q_0 resulting in a barrier on the order of 0.01 kT per chain. 667 This is very small and makes it difficult to resolve in terms of 668 calculating possible contributions from core stretching, corona 669

670 stretching, and interfacial tension. A transition state for micelle 671 fragmentation is not as easily identified.^{26,69,70} As the 672 fragmentation process increases the net surface area of the 673 core blocks, it is tempting to infer that the barrier involves a 674 transition state with a larger area. However, the independence 675 of the fragmentation rate on IL selectively argues strongly 676 against interfacial tension as rate-limiting. A previous report on 677 the fusion and fragmentation kinetics of ionic/nonionic mixed 678 micelles proposed that fragmentation arises from surface 679 instabilities, which leads to bending of the micelle surface, 680 pinching, and finally breaking into two or more micelles.²⁷ The 681 authors concluded that one of the main barriers to 682 fragmentation would arise from the solvophobic core block, 683 which is likely exposed to the solvent in the final stage of 684 breaking. This is inconsistent with our results. Another 685 potential barrier to fragmentation could arise from additional 686 corona crowding during a "pinch-off" process. Because the 687 total surface area of the micelle increases by only about 26% after fragmentation, the corona crowding could be quite severe 688 in the transition state during a fragmentation event. If this 689 690 interpretation is correct, this could explain why the 691 fragmentation kinetics are independent of solvent selectivity. 692 The fragmentation process begins when separation of the 693 micelle core occurs, which will increase the total surface free energy. Further corona separation will decrease the free energy 694 via entropic gain of the corona chains, which allows the core 695 chains to adopt a less-stretched conformation after fragmenta-696 tion.²³ This is likely the case for $BO(8-7)/[C_nMIM]$ [TFSI], 697 considering the extremely large values of Q_0 obtained for the 698 699 as-prepared micelles. To accommodate such high aggregation 700 numbers, the PB blocks in the core must adopt a highly 701 stretched conformation, which further drives the corona 702 crowding. An estimate of the degree of core block stretching 703 using $R_{\rm core}$ divided by the mean square end-to-end distance of 704 the core block for as-prepared micelles in $[C_2MIM]$ [TFSI] shows the PB chains are initially stretched to approximately 1/705 706 3 of the fully extended length. Using this same estimate for the steady-state core radius, the PB chains relax to 1/4 of the fully 707 extended length, which is still substantial. 708

709 4. How are the initial micelles formed?

Table 4 summarizes the change in R_h and R_{core} , the initial 710 711 aggregation number (Q_0) , and the final aggregation number $(Q_{\rm f})$ for BO(8-7) micelles before and after a *T*-jump at 170 °C, 712 713 along with the Hildebrand solubility parameters for each IL ⁷¹⁴ and the PB and PEO blocks. The χ parameter can be estimated 715 using solubility parameters based on the following equation, 716 $\chi_{\text{PB-IL}} = (V/RT)(\delta_1 - \delta_2)^2$, where V is a reference volume, in 717 this case the molar volume of the IL, R is the gas constant, and 718 δ_i are the solubility parameters of the core block and the IL. 719 From the difference in solubility parameters between PB and $_{\rm 720}$ the IL, the $\chi_{\rm PB-IL}$ parameter is expected to decrease with 721 increasing IL cation alkyl chain length. When preparing 722 micelles by the DD protocol, the higher the $\chi_{\text{PB-IL}}$, the larger 723 and more disperse are the resulting micelles. Additionally, the 724 relatively large χ restricts typical equilibration mechanisms observed in diblock copolymer micelles such as individual 725 chain exchange.^{8,10} 726

Figure 8a demonstrates the large dependence of ΔQ on response solvent selectivity. As shown in the figure and in Table 4, the response selective ILs show a larger change in the as-prepared and response selective aggregation numbers in comparison to the least response solvent, [C₈MIM][TFSI]. This trend is also observed response when comparing the as-prepared and steady-state



Figure 8. (a) Initial and final aggregation numbers versus IL cation alkyl chain length. The aggregation numbers are calculated from the $\langle R_{core} \rangle$ determined by SAXS assuming a dry micelle core. (b) Dependence of $\langle R_h \rangle_0$ and $\langle R_{core} \rangle_0$ (filled circles) and $\langle R_h \rangle_f$ and $\langle R_{core} \rangle_f$ (filled triangles) on the IL cation alkyl chain length. The $\langle R_h \rangle_0$ for 0.5 wt % BO(8-7) in [C₂MIM][TFSI] was calculated by taking the average of the two R_h values obtained by fitting DLS results to a double exponential.

 $\langle R_{\rm h} \rangle$ and $\langle R_{\rm core} \rangle$ as a function of the IL selectivity. Specifically, 733 the overall change in $\langle R_{\rm h} \rangle$ and $\langle R_{\rm core} \rangle$ increases with increasing 734 solvent selectivity. In general, the effects of the solvent 735 selectivity on the fragmentation kinetics are minimal; however, 736 the results show that regardless of the IL selectivity, DD of 737 BO(8-7) in these solvents lead to micelles that are not at 738 equilibrium, and this preparation protocol results in structures 739 that are just large enough to equilibrate by fragmentation and 740 not by chain exchange. 741

The poor solubility of the core block is anticipated to give 742 rise to a micellization scenario where the nucleation of micelles 743 is overcome by the speed of micelle growth, resulting in large, 744 polydisperse micelles. Additionally, it has been suggested that 745 the morphology of micelles prepared by DD will depend on 746 the morphology of the bulk polymer.^{30,71} SAXS of the bulk 747 BO(8-7) polymer was conducted. The scattering data, shown 748 in Supporting Information Figure S18, confirms that BO(8-7) 749 exhibits a lamellar morphology at 70 °C, which is the 750 temperature used for DD of BO(8-7) in ILs. The domain 751 size of the PB lamellae was estimated to be approximately 21 752 nm, which is comparable to the initial micelle core size. It is 753 possible that in DD, the solvent penetrates the PEO domains, 754 and surface instabilities of the lamellae begin to pinch off to 755 give large, polydisperse spherical aggregates in solution. This 756 behavior is analogous to the Rayleigh instability and is 757 referenced in computations of surfactant-based micelles,⁶⁹ 758 and experimentally in cylinder-to-sphere transitions⁷² in block 759 copolymer micelles. A schematic illustration of this process is 760 depicted in Figure 9. However, the interfacial tension between 761 f9 the core-forming block and the solvent also plays a role in the 762 initial micelle size. This is shown in Table 3, where $\langle R_h \rangle_0$ 763 decreases as the solvent is changed from [C₁MIM][TFSI] to 764



Figure 9. Schematic illustration of the DD process. In the bulk, BO(8-7) exhibits a lamellar morphology, with a PB domain size of 21 nm, and a PEO domain size of 14 nm. When IL, vigorous stirring, and heat are introduced to the bulk polymer, the lamella begin to tear apart into sheets, or potentially cylinders, and each lamella breaks off into either cylinders and then into spherical aggregates, or the lamella break off to form large spherical aggregates. This results in spherical micelles with $\langle R_{core} \rangle_0 \approx 21$ nm.

⁷⁶⁵ $[C_8MIM][TFSI]$. Based on this view, it is reasonable that the ⁷⁶⁶ size and polydispersity of micelles prepared by the DD ⁷⁶⁷ protocol can be tuned based on the initial domain size of the ⁷⁶⁸ core- and corona-forming blocks in the bulk polymer in one ⁷⁶⁹ solvent. As the solvent selectivity toward the core block is ⁷⁷⁰ changed, the as-prepared micelle size will also be determined ⁷⁷¹ by the interfacial tension between the core-forming block and ⁷⁷² the solvent, but the domain size in the bulk sample can also ⁷⁷³ play a role.

774 SUMMARY

775 In this work, the equilibration kinetics were studied for BO(8-776 7) micelles prepared by DD in five 1-alkyl-3-methylimidazo-777 lium bis(trifluoromethylsulfonyl)imide-based ILs using T-jump 778 DLS, SAXS, and LP-TEM. From the combined techniques, it 779 was found that the micelle size $(\langle R_h \rangle$ and $\langle R_{core} \rangle)$ decreased 780 significantly after prolonged annealing at 170 °C; the final 781 aggregation number was about half of the original. The decay 782 in $\langle R_{\rm h} \rangle$ and $\langle R_{\rm core} \rangle$ could be well described by a compressed exponential with an exponent of 2 in almost all cases. The 783 784 origin of this functional form is not yet apparent. The characteristic relaxation times determined by fits to this 785 786 equation for DLS for BO(8-7) in $[C_2MIM][TFSI]$ were essentially independent of concentration, indicating a 787 relaxation process that is first-order with respect to polymer 788 concentration. The effects of solvent selectivity on the 789 790 equilibration kinetics were investigated by using five different 791 ILs with varying cation alkyl chain lengths. In this case, the 792 decay of $\langle R_{\rm h} \rangle$ occurs on a similar timescale regardless of the 793 solvent quality. To verify that micelle fragmentation was taking place, LP-TEM and SAXS were used to monitor the evolution 794 795 in micelle core size after annealing at 170 °C. The large decrease in the core radius indicates that fragmentation is most 796 797 likely the primary equilibration mechanism observed in this system, as individual chain exchange would not be expected to 798 change the core radius to that extent. 799

In general, these experiments indicate that the solvent sol selectivity plays a significant role in how far the as-prepared micelles are from the equilibrium size. Specifically, the more micelles are from the equilibrium size. Specifically, the more micelles solvents result in micelles much larger aggregation micelles that are closer to the equilibrium size. However, the solvent selectivity was found to play essentially no role in the fragmentation kinetics, as nearly all the BO micelles in 807 imidazolium-based ILs fragmented on the order of hundreds 808 of minutes. Because the fragmentation kinetics are independ- 809 ent of solvent quality, the primary barrier to micelle 810 fragmentation is most likely not from the exposure of the 811 micelle core to the solvent in the transition state. We speculate 812 that the corona crowding in the transition state is quite severe, 813 which could be the main barrier to fragmentation. 814

ASSOCIATED CONTENT

S Supporting Information

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The Supporting Information is available free of charge on the 817 ACS Publications website at DOI: 10.1021/acs.macro- 818 mol.9b01530. 819

Thermal equilibration in $[C_2MIM][TFSI]$, CS dissolu- ⁸²⁰ tion, SEC-RI trace of BO(8-7) in THF, ¹H NMR spectra ⁸²¹ of BO(8-7), $[C_1MIM][TFSI]$, $[C_2MIM][TFSI]$, ⁸²² $[C_4MIM][TFSI]$, $[C_6MIM][TFSI]$, and $[C_8MIM]$ - ⁸²³ [TFSI], Arrhenius plots for 0.5 wt % BO(8-7) in ⁸²⁴ $[C_2MIM][TFSI]$, R_h versus time at 170 °C for 0.5 wt % ⁸²⁵ BO(8-7) in $[C_2MIM][TFSI]$ by DD and CS protocols, ⁸²⁶ linearized R(t) plots, LP-TEM and background ⁸²⁷ subtracted SAXS profiles of 0.5 wt % BO(8-7) micelles ⁸²⁸ in $[C_4MIM][TFSI]$, $[C_6MIM][TFSI]$, and $[C_8MIM]$ - ⁸²⁹ [TFSI], complex viscosity versus frequency for 8.2 kDa ⁸³⁰ PB homopolymer, and SAXS of BO(8-7) in the bulk ⁸³¹ (PDF) ⁸³²

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The authors declare no competing financial interest.	839

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862 **REFERENCES**

863 (1) Tyrrell, Z. L.; Shen, Y.; Radosz, M. Fabrication of Micellar 864 Nanoparticles for Drug Delivery through the Self-Assembly of Block 865 Copolymers. *Prog. Polym. Sci.* 2010, 35, 1128–1143.

866 (2) Hubbell, J. A. Enhancing Drug Function. *Science* 2003, 300, 867 595–596.

868 (3) Meier, W. Polymer Nanocapsules. *Chem. Soc. Rev.* 2000, *29*, 869 295–303.

870 (4) Park, T.; Jeong, J.; Kim, S. Current Status of Polymeric Gene 871 Delivery Systems. *Adv. Drug Deliv. Rev.* **2006**, *58*, 467–486.

872 (5) Cotanda, P.; Lu, A.; Patterson, J. P.; Petzetakis, N.; O'Reilly, R.

873 K. Functionalized Organocatalytic Nanoreactors: Hydrophobic 874 Pockets for Acylation Reactions in Water. *Macromolecules* **2012**, *45*,

875 2377–2384.

876 (6) Krishnamoorthy, S.; Pugin, R.; Brugger, J.; Heinzelmann, H.;

877 Hinderling, C. Nanopatterned Self-Assembled Monolayers by Using 878 Diblock Copolymer Micelles as Nanometer-Scale Adsorption and 879 Etch Masks. *Adv. Mater.* **2008**, *20*, 1962–1965.

880 (7) Anderson, W. Block Copolymers as Viscosity Index Improvers 881 for Lubrication Oils. U.S. Patent 3,763,044 A, 1973.

(8) Zhao, D.; Ma, Y.; Lodge, T. P. Exchange Kinetics for a Single
883 Block Copolymer in Micelles of Two Different Sizes. *Macromolecules*884 2018, *51*, 2312–2320.

885 (9) Zinn, T.; Willner, L.; Pipich, V.; Richter, D.; Lund, R. Molecular
886 Exchange Kinetics of Micelles: Corona Chain Length Dependence.
887 ACS Macro Lett. 2016, 5, 884–888.

888 (10) Ma, Y.; Lodge, T. P. Chain Exchange Kinetics in Diblock 889 Copolymer Micelles in Ionic Liquids: The Role of χ . *Macromolecules* 890 **2016**, 49, 9542–9552.

891 (11) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.;

892 Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. Theory of 893 the Kinetics of Micellar Equilibria and Quantitative Interpretation of 894 Chemical Relaxation Studies of Micellar Solutions of Ionic

895 Surfactants. J. Phys. Chem. 1976, 80, 905–922.
896 (12) Willner, L.; Poppe, A.; Allgaier, J.; Monkenbusch, M.; Richter,

897 D. Time-Resolved SANS for the Determination of Unimer Exchange
898 Kinetics in Block Copolymer Micelles. *Europhys. Lett.* 2001, 55, 667–

899 673.
900 (13) Lund, R.; Willner, L.; Stellbrink, J.; Radulescu, A.; Richter, D.
901 Tuning of Structure and Kinetics of Chain Exchange in Star-like PEP902 PEO Block Copolymer Micelles. *Phys. B* 2004, 350, E909–E912.

903 (14) Lund, R.; Willner, L.; Stellbrink, J.; Lindner, P.; Richter, D. 904 Logarithmic Chain-Exchange Kinetics of Diblock Copolymer 905 Micelles. *Phys. Rev. Lett.* **2006**, *96*, 049902.

906 (15) Lund, R.; Willner, L.; Richter, D.; Dormidontova, E. E. 907 Equilibrium Chain Exchange Kinetics of Diblock Copolymer Micelles: 908 Tuning and Logarithmic Relaxation. *Macromolecules* **2006**, *39*, 4566– 909 4575.

910 (16) Lund, R.; Willner, L.; Stellbrink, J.; Richter, D. Equilibrium 911 Exchange Kinetics in PEP-PEO Block Copolymer Micelles. A Time 912 Resolved SANS Study. *Phys. B* **2006**, 385–386, 735–737.

913 (17) Lund, R.; Willner, L.; Richter, D.; Iatrou, H.; Hadjichristidis, 914 N.; Lindner, P. Unraveling the Equilibrium Chain Exchange Kinetics 915 of Polymeric Micelles Using Small-Angle Neutron Scattering -916 Architectural and Topological Effects. *J. Appl. Crystallogr.* **2007**, *40*, 917 s327-s331.

918 (18) Lund, R.; Willner, L.; Pipich, V.; Grillo, I.; Lindner, P.; 919 Colmenero, J.; Richter, D. Equilibrium Chain Exchange Kinetics of 920 Diblock Copolymer Micelles: Effect of Morphology. *Macromolecules* 921 **2011**, *44*, 6145–6154.

922 (19) Choi, S.-H.; Lodge, T. P.; Bates, F. S. Mechanism of Molecular 923 Exchange in Diblock Copolymer Micelles: Hypersensitivity to Core 924 Chain Length. *Phys. Rev. Lett.* **2010**, *104*, 047802.

925 (20) Lu, J.; Bates, F. S.; Lodge, T. P. Chain Exchange in Binary 926 Copolymer Micelles at Equilibrium: Confirmation of the Independent 927 Chain Hypothesis. *ACS Macro Lett.* **2013**, *2*, 451–455.

928 (21) Wang, E.; Lu, J.; Bates, F. S.; Lodge, T. P. Effect of Corona 929 Block Length on the Structure and Chain Exchange Kinetics of Block 930 Copolymer Micelles. *Macromolecules* **2018**, *51*, 3563–3571. (22) Halperin, A.; Alexander, S. Polymeric Micelles: Their 931 Relaxation Kinetics. *Macromolecules* **1989**, 22, 2403–2412. 932

(23) Dormidontova, E. E. Micellization Kinetics in Block Copolymer 933 Solutions: Scaling Model. *Macromolecules* **1999**, *32*, 7630–7644. 934

(24) Rharbi, Y. Fusion and Fragmentation Dynamics at Equilibrium 935 in Triblock Copolymer Micelles. *Macromolecules* **2012**, *45*, 9823–936 9826. 937

(25) Rharbi, Y.; Winnik, M. A.; Hahn, K. G. Kinetics of Fusion and 938 Fragmentation Nonionic Micelles: Triton X-100. *Langmuir* **1999**, *15*, 939 4697–4700. 940

(26) Rharbi, Y.; Li, M.; Winnik, M. A.; Hahn, K. G. Temperature 941 Dependence of Fusion and Fragmentation Kinetics of Triton X-100 942 Micelles. J. Am. Chem. Soc. 2000, 122, 6242–6251. 943

(27) Rharbi, Y.; Karrouch, M.; Richardson, P. Fusion and Fission 944 Inhibited by the Same Mechanism in Electrostatically Charged 945 Surfactant Micelles. *Langmuir* **2014**, *30*, 7947–7952. 946

(28) Zhang, L.; Eisenberg, A. Thermodynamic vs Kinetic Aspects in 947 the Formation and Morphological Transitions of Crew-Cut 948 Aggregates Produced by Self-Assembly of Polystyrene-b-Poly(Acrylic 949 Acid) Block Copolymers in Dilute Solution. *Macromolecules* **1999**, *32*, 950 2239–2249. 951

(29) Desbaumes, L.; Eisenberg, A. Single-Solvent Preparation of 952 Crew-Cut Aggregates of Various Morphologies from an Amphiphilic 953 Diblock Copolymer. *Langmuir* **1999**, *15*, 36–38. 954

(30) Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. E.W.R. Steacie 955 Award Lecture Asymmetric Amphiphilic Block Copolymers in 956 Solution: A Morphological Wonderland. *Can. J. Chem.* **1999**, 77, 957 1311–1326. 958

(31) Meli, L.; Lodge, T. P. Equilibrium vs Metastability: High- 959 Temperature Annealing of Spherical Block Copolymer Micelles in an 960 Ionic Liquid. *Macromolecules* **2009**, *42*, 580–583. 961

(32) Meli, L.; Santiago, J. M.; Lodge, T. P. Path-Dependent 962 Morphology and Relaxation Kinetics of Highly Amphiphilic Diblock 963 Copolymer Micelles in Ionic Liquids. *Macromolecules* **2010**, *43*, 964 2018–2027. 965

(33) Honda, C.; Abe, Y.; Nose, T. Relaxation Kinetics of 966 Micellization in Micelle-Forming Block Copolymer in Selective 967 Solvent. *Macromolecules* **1996**, *29*, 6778–6785. 968

(34) Zhang, J.; Xu, J.; Liu, S. Chain-Length Dependence of Diblock 969 Copolymer Micellization Kinetics Studied by Stopped-Flow PH- 970 Jump. J. Phys. Chem. B 2008, 112, 11284–11291. 971

(35) Patist, A.; Kanicky, J. R.; Shukla, P. K.; Shah, D. O. Importance 972 of Micellar Kinetics in Relation to Technological Processes. J. Colloid 973 Interface Sci. 2002, 245, 1–15. 974

(36) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; 975 Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor 976 Pressures of 1-Alkyl-3-Methylimidazolium Bis-977 (Trifluoromethylsulfonyl)Imides and a Correlation Scheme for 978 Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys.* 979 *Chem. A* 2006, *110*, 7303–7306. 980

(37) Hillmyer, M. A.; Bates, F. S. Synthesis and Characterization of 981 Model Polyalkane-Poly(Ethylene Oxide) Block Copolymers. *Macro-* 982 *molecules* **1996**, *29*, 6994–7002. 983

(38) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; 984 Wiley-Interscience: New York, 1999. 985

(39) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, 986 K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temper- 987 ature Molten Salts. *Inorg. Chem.* **1996**, 35, 1168–1178. 988

(40) Brown, W. Dynamic Light Scattering: The Method and Some 989 Applications (Monographs on the Physics and Chemistry of Materials; 990 49); Clarendon Press; Oxford University Press: Oxford (England); 991 New York, 1993. 992

(41) Bai, Z.; He, Y.; Lodge, T. P. Block Copolymer Micelle Shuttles 993 with Tunable Transfer Temperatures between Ionic Liquids and 994 Aqueous Solutions. *Langmuir* **2008**, *24*, 5284–5290. 995

(42) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; 996 Watanabe, M. Physicochemical Properties and Structures of Room 997 Temperature Ionic Liquids . 1 . Variation of Anionic Species. *J. Phys.* 998 *Chem. B* **2004**, *108*, 16593–16600. 999 (43) Nazet, A.; Sokolov, S.; Sonnleitner, T.; Makino, T.; Kanakubo,
1001 M.; Buchner, R. Densities, Viscosities, and Conductivities of the
1002 Imidazolium Ionic Liquids [Emim][Ac], [Emim][FAP], [Bmim]1003 [BETI], [Bmim][FSI], [Hmim][TFSI], and [Omim][TFSI]. J. Chem.
1004 Eng. Data 2015, 60, 2400–2411.

1005 (44) Zhao, N.; Jacquemin, J.; Oozeerally, R.; Degirmenci, V. New 1006 Method for the Estimation of Viscosity of Pure and Mixtures of Ionic 1007 Liquids Based on the UNIFAC – VISCO Model. *J. Chem. Eng. Data* 1008 **2016**, *61*, 2160–2169.

1009 (45) Jakeš, J. Testing of the constrained regularization method of 1010 inverting Laplace transform on simulated very wide quasielastic light 1011 scattering autocorrelation functions. *Czech. J. Phys.* **1988**, *38*, 1305– 1012 1316.

1013 (46) Kharel, A.; Lodge, T. P. Coil Dimensions of Poly(Ethylene 1014 Oxide) in an Ionic Liquid by Small-Angle Neutron Scattering. 1015 *Macromolecules* **2017**, *50*, 8739–8744.

1016 (47) Araque, J. C.; Hettige, J. J.; Margulis, C. J. Modern Room 1017 Temperature Ionic Liquids, a Simple Guide to Understanding Their 1018 Structure and How It May Relate to Dynamics. *J. Phys. Chem. B* **2015**, 1019 *119*, 12727–12740.

(48) Kharel, A.; Lodge, T. P. Effect of Ionic Liquid Components on
the Coil Dimensions of PEO. *Macromolecules* 2019, 52, 3123–3130.
(49) Pedersen, J. S.; Svaneborg, C.; Almdal, K.; Hamley, I. W.;
Young, R. N. A Small-Angle Neutron and x-Ray Contrast Variation
Scattering Study of the Structure of Block Copolymer Micelles:
Corona Shape and Excluded Volume Interactions. *Macromolecules*2003, 36, 416–433.

1027 (50) Pedersen, J. S. Determination of Size Distributions from Small-1028 Angle Scattering Data for Systems with Effective Hard-Sphere 1029 Interactions. *J. Appl. Crystallogr.* **1994**, *27*, 595–608.

1030 (51) Rharbi, Y.; Kitaev, V.; Winnik, M. A.; Hahn, K. G. 1031 Characterizing Aqueous Micellar Triton X-100 Solutions of a 1032 Fluorescent Model Triglyceride. *Langmuir* **1999**, *15*, 2259–2266.

1033 (52) Zana, R. Dynamics in Micellar Solutions of Amphiphilic Block 1034 Copolymers. In *Dynamics of Surfactant Self-Assemblies: Micelles*, 1035 *Microemulsions, Vesicles, and Lyotropic Phases*; Hubbard, A. T., Ed.; 1036 Taylor & Francis Group/CRC Press: Boca Raton, 2005; pp 161–231. 1037 (53) Li, Z.; Dormidontova, E. E. Kinetics of Diblock Copolymer 1038 Micellization by Dissipative Particle Dynamics. *Macromolecules* **2010**, 1039 43, 3521–3531.

(54) Parent, L. R.; Bakalis, E.; Ramírez-Hernández, A.; Kammeyer, J.
(54) Parent, L. R.; Bakalis, E.; Ramírez-Hernández, A.; Kammeyer, J.
1041 K.; Park, C.; De Pablo, J.; Zerbetto, F.; Patterson, J. P.; Gianneschi, N.
1042 C. Directly Observing Micelle Fusion and Growth in Solution by
1043 Liquid-Cell Transmission Electron Microscopy. J. Am. Chem. Soc.
1044 2017, 139, 17140–17151.

1045 (55) Marciniak, A. The Solubility Parameters of Ionic Liquids. *Int. J.* 1046 *Mol. Sci.* **2010**, *11*, 1973–1990.

1047 (56) Lee, S. H.; Lee, S. B. The Hildebrand Solubility Parameters, 1048 Cohesive Energy Densities and Internal Energies of 1-Alkyl-3-1049 Methylimidazolium-Based Room Temperature Ionic Liquids. *Chem.* 1050 *Commun.* **2005**, *27*, 3469–3471.

1051 (57) Marciniak, A. The Hildebrand Solubility Parameters of Ionic 1052 Liquids-Part 2. *Int. J. Mol. Sci.* **2011**, *12*, 3553–3575.

1053 (58) Yoo, B.; Afzal, W.; Prausnitz, J. M. Solubility Parameters for 1054 Nine Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 9913–9917.

1055 (59) Jensen, G. V.; Lund, R.; Narayanan, T.; Pedersen, J. S. 1056 Transformation from Globular to Cylindrical Mixed Micelles through 1057 Molecular Exchange That Induces Micelle Fusion. *J. Phys. Chem. Lett.* 1058 **2016**, *7*, 2039–2043.

(60) Liu, Y.; Spring, J. D.; Steinhart, M.; Bansil, R. Pressure Jump
Kinetics of Disorder to BCC Ordering in Diblock Copolymer
Micelles in a Selective Solvent. *Macromolecules* 2012, 45, 9147–9154.
(61) Kelley, E. G.; Murphy, R. P.; Seppala, J. E.; Smart, T. P.; Hann,
S. D.; Sullivan, M. O.; Epps, T. H. Size Evolution of Highly
Amphiphilic Macromolecular Solution Assemblies via a Distinct
Bimodal Pathway. *Nat. Commun.* 2014, 5, 3599.

1066 (62) Pedersen, J. S.; Svaneborg, C. Scattering from Block Copolymer 1067 Micelles. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 158–166. (63) Pedersen, J. S. Analysis of Small-Angle Scattering Data from 1068 Micelles and Microemulsions: Free-Form Approaches and Model 1069 Fitting. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 190–196. 1070

(64) Falus, P.; Borthwick, M. A.; Narayanan, S.; Sandy, A. R.; 1071 Mochrie, S. G. J. Crossover from Stretched to Compressed 1072 Exponential Relaxations in a Polymer-Based Sponge Phase. *Phys.* 1073 *Rev. Lett.* **2006**, *97*, 066102.

(65) Ruegg, M. L.; Patel, A. J.; Narayanan, S.; Sandy, A. R.; Mochrie, 1075 S. G. J.; Watanabe, H.; Balsara, N. P. Condensed Exponential 1076 Correlation Functions in Multicomponent Polymer Blends Measured 1077 by X-Ray Photon Correlation Spectroscopy. *Macromolecules* **2006**, *39*, 1078 8822–8831. 1079

(66) Lewis, R. M.; Arora, A.; Beech, H. K.; Lee, B.; Lindsay, A. P.; 1080 Lodge, T. P.; Dorfman, K. D.; Bates, F. S. Role of Chain Length in the 1081 Formation of Frank-Kasper Phases in Diblock Copolymers. *Phys. Rev.* 1082 *Lett.* **2018**, *121*, 208002. 1083

(67) Oparaji, O.; Narayanan, S.; Sandy, A.; Ramakrishnan, S.; 1084 Hallinan, D. Structural Dynamics of Strongly Segregated Block 1085 Copolymer Electrolytes. *Macromolecules* **2018**, *51*, 2591–2603. 1086

(68) Sheiko, S. S.; Panyukov, S.; Rubinstein, M. Bond Tension in 1087 Tethered Macromolecules. *Macromolecules* **2011**, *44*, 4520–4529. 1088

(69) Sammalkorpi, M.; Karttunen, M.; Haataja, M. Micelle Fission 1089
through Surface Instability and Formation of an Interdigitating Stalk. 1090
J. Am. Chem. Soc. 2008, 130, 17977–17980. 1091

(70) Pool, R.; Bolhuis, P. G. Prediction of an Autocatalytic 1092 Replication Mechanism for Micelle Formation. *Phys. Rev. Lett.* 1093 **2006**, *97*, 018302. 1094

(71) Webber, S. E.; Munk, P.; Tuzar, Z. Solvents and Self- 1095 Organization of Polymers. *NATO Science Series E*; Springer, 1996; 1096 Vol. 327. 1097

(72) Wang, L.; Huang, H.; He, T. Rayleigh Instability Induced 1098 Cylinder-to-Sphere Transition in Block Copolymer Micelles: Direct 1099 Visualization of the Kinetic Pathway. *ACS Macro Lett.* **2014**, *3*, 433–1100 438. 1101