

Direct Observation of Micelle Fragmentation via In Situ Liquid-Phase Transmission Electron Microscopy

Julia T. Early, Kevin G. Yager, and Timothy P. Lodge*



Cite This: <https://dx.doi.org/10.1021/acsmacrolett.0c00273>



Read Online

ACCESS |



Metrics & More

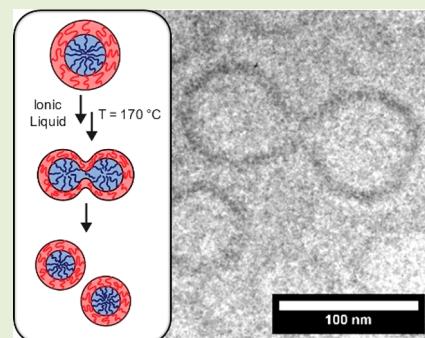


Article Recommendations



Supporting Information

ABSTRACT: Recently, attention has been directed toward understanding the dynamics and relaxation kinetics of block copolymer micelles, including mechanisms such as micelle fragmentation and fusion. The few prior studies on block copolymer micelle fragmentation relied on ensemble averaging techniques such as small-angle X-ray scattering and dynamic light scattering; some individual particles were imaged by ex situ transmission electron microscopy. Here we report the direct observation of fragmentation for three molecular weights of 1,2-polybutadiene-*block*-poly(ethylene oxide) (PB-PEO) micelles in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide using high-temperature liquid-phase transmission electron microscopy (LP-TEM). The use of in situ LP-TEM provides unique insights into the evolution of block copolymer micelles during fragmentation. Specifically, upon heating to 170 °C, a sequence of morphological transitions from a spherical micelle to a prolate ellipsoid, then a “peanut” shape, followed by a two-spherical-compartment micelle was observed, where the last is presumed to be the transition state.



A-B diblock copolymers self-assemble into micelles of various morphologies when placed in a block-selective solvent. These micelles are used in a range of applications such as viscosity modification,¹ oil recovery,^{2–4} nanoreactors,⁵ and drug or gene delivery.^{6–8} To fully realize the advantages of block copolymer micelles in more complex applications, the dynamics of micelle formation and equilibration should be better understood. Significant progress toward quantifying individual chain exchange kinetics has been reported for a variety of block copolymers in selective solvents, including organic solvents, water, and ionic liquids, where the micelle size is close to or at equilibrium.^{9–17} Yet, the equilibration dynamics for block copolymer micelles that are kinetically trapped at sizes far from equilibrium remain much less understood. The mechanisms of fusion or fragmentation are expected to contribute when the average micelle is, respectively, either much smaller than or larger than the equilibrium size.^{18–21} The mechanisms and kinetics of equilibration for low molecular weight surfactants in aqueous solutions have been studied extensively.^{22–29} However, direct experimental studies of block copolymer micelle fusion²¹ and fragmentation^{19,20,22,30,31} are rare. Previous work by Meli et al. showed that direct dissolution (DD) of 1,2-polybutadiene-*block*-poly(ethylene oxide) (PB-PEO) diblock copolymers in the ionic liquid 1-ethyl-2-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂MIM][TFSI]) resulted in kinetically trapped, large micelles.³² These micelles then became smaller, eventually reaching a steady state size, upon prolonged annealing at elevated temperatures. Similar evidence of fragmentation was

reported for PB-PEO micelles prepared by DD in various 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide-based ionic liquids.^{30,32,33} Although the as-prepared micelles decreased in size when subjected to annealing at 170 °C, time-resolved small-angle neutron scattering experiments revealed that no individual chain exchange occurred under these conditions.³⁰ Additionally, the kinetics of this process were found to be independent of polymer concentration. Because micelle fusion should be a second-order kinetic process with respect to polymer concentration,^{18,25,34} it was concluded that PB-PEO micelles in these ionic liquids equilibrate primarily by fragmentation.³⁰ This strong evidence for fragmentation notwithstanding, the equilibration kinetics were determined primarily by ensemble average methods such as dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS). Direct imaging ex situ by transmission electron microscopy (TEM) has also been employed.³³ Micelle fusion events have recently been observed for aqueous polymer solutions using in situ liquid cell transmission electron microscopy.²¹ To the best of our knowledge, direct observation of fragmentation has not been reported in any block copolymer/solvent system. Of particular interest is the nature of the transition state.

Received: April 7, 2020

Accepted: May 4, 2020

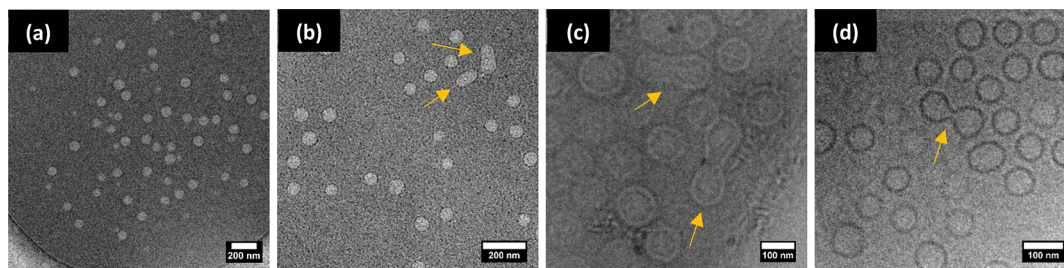


Figure 1. In situ LP-TEM images of 0.25 wt % BO(25–22) in $[C_2MIM][TFSI]$ annealing at $T = 170\text{ }^{\circ}\text{C}$ for (a) 2, (b) 20, (c) 180, and (d) 400 min. Orange arrows indicate micelles referenced in the text. The electron dose rate was $9.8\text{ e}^-/\text{\AA}^2\text{ s}$ at a magnification of 15000 $\times$.

In this work, we exploit the high thermal stability and nonvolatility of ionic liquids to conduct high-temperature liquid-phase TEM (LP-TEM) to observe in situ fragmentation of PB–PEO micelles in $[C_2MIM][TFSI]$. Because the ionic liquid does not evaporate under the high vacuum conditions in the microscope, liquid samples can be imaged directly without the need for a hermetically sealed sample chamber.^{35–38} Using a temperature-controlled sample holder for LP-TEM allows T -jump experiments to be conducted directly in the microscope, and images of the change in the PB core morphology during fragmentation were collected. Additionally, time-resolved SAXS (TR-SAXS) experiments were performed to corroborate changes in the average core radius $\langle R_{\text{core}} \rangle$ after a T -jump to 170 $^{\circ}\text{C}$.

Three molecular weights of PB–PEO were synthesized by two-step sequential anionic polymerization, as described previously,³⁹ with a constant volume fraction of PEO, $f_{\text{PEO}} \cong 0.40$.³⁹ PB–PEO diblocks and 0.1 wt % butylated hydroxytoluene as an antioxidant were dissolved in benzene and freeze-dried under vacuum prior to use. Each molecular weight of PB–PEO used in this work is referred to as BO(x – y), where x and y denote the number-average molecular weight in kDa (M_n) of the PB and PEO blocks, respectively. Size exclusion chromatography with multiangle light scattering detection showed that the three polymers studied, BO(8–7), BO(25–22), and BO(27–27), had low dispersities ($\mathcal{D} \leq 1.09$); see Supporting Information for further molecular characterization. Micelle solutions were prepared by the direct dissolution (DD) method. The desired amounts of PB–PEO and $[C_2MIM][TFSI]$ were combined by weight in a 20 mL scintillation vial equipped with a stir bar to obtain a 0.25 wt % solution. The vial was placed into an oil bath and stirred vigorously at 70 $^{\circ}\text{C}$ for 48 h. The micelle core dimensions were then studied in situ via high-temperature liquid-phase transmission electron microscopy (LP-TEM) and time-resolved synchrotron small-angle X-ray scattering (TR-SAXS), as discussed in the Supporting Information.

Prior to a T -jump to 170 $^{\circ}\text{C}$, the PB core size for micelles as prepared by DD in $[C_2MIM][TFSI]$ was characterized by room-temperature LP-TEM and SAXS. The initial average core radius ($\langle R_{\text{core}} \rangle_0$) for 0.25 wt % BO(8–7) in $[C_2MIM][TFSI]$ was found to be approximately 20 nm, with a standard deviation ($\sigma_{\text{core},0}$) of 6 nm by TEM image analysis. The 1D scattering patterns for BO(8–7) by SAXS at room temperature were fit to the Pedersen form factor for block copolymer micelles with the Percus–Yevick structure factor.^{40,41} From the fits, $\langle R_{\text{core}} \rangle_0 = 19.5 \pm 2.0\text{ nm}$ for BO(8–7), in excellent agreement with TEM. As shown in Figure S7, all micelles observed for BO(8–7) by TEM were spherical. From Figure S4, the form factor scattering for BO(8–7) micelles, as

prepared by DD and after a T -jump to 170 $^{\circ}\text{C}$, are consistent with a spherical core. The initial sizes of BO(25–22) and BO(27–27) micelles in $[C_2MIM][TFSI]$ were also determined in this manner and by TEM image analysis, $\langle R_{\text{core}} \rangle_0 = 45 \pm 5\text{ nm}$ for BO(25–22) and $\langle R_{\text{core}} \rangle_0 = 50 \pm 7\text{ nm}$ for BO(27–27). Again, the TEM images and SAXS data of these samples in the Supporting Information confirm that the as-prepared micelles are spherical.

As noted above, prior work on the equilibration kinetics of PB–PEO in ionic liquids relied on ensemble average methods to determine the evolution of micelle size during a T -jump, and while the observed substantial decrease in the hydrodynamic radius and core radius is consistent with fragmentation, this phenomenon has yet to be observed in situ.^{30,32,33} By annealing the solutions directly in the electron microscope, a series of images were obtained throughout the micelle relaxation process, and the evolution of the core morphology was monitored during fragmentation. Representative in situ high-temperature LP-TEM images are shown in Figure 1 for 0.25 wt % BO(25–22) in $[C_2MIM][TFSI]$ at 170 $^{\circ}\text{C}$. Ideally, the time evolution of individual micelles would be recorded during annealing, but there are significant constraints on this experiment. First, the characteristic equilibration times for the polymers studied here are on the order of 10^2 to 10^3 min, making it difficult to track a single micelle in the TEM without causing significant electron beam damage. Second, the particles observed in LP-TEM are mobile and able to diffuse out of the image frame throughout the experiment. Thus, while the time series of images shown here are obtained for the same area of the sample grid, it is difficult to establish how many micelles remained within in the field of view throughout the annealing process.

From Figure 1, the BO(25–22) micelle cores appear to be spherical, yet the distribution of core radii is quite significant after heating at 170 $^{\circ}\text{C}$ for 2 min (Figure 1a). After 20 min of annealing, some micelles become distinctly elliptical, and the core appears elongated compared to the image at 2 min; this is presumably the first stage of fragmentation (Figure 1b). After 180 min of annealing, the elongated cores appear more like a “peanut” with the formation of a shallow neck, which we interpret as the second major morphological change to the micelle structure during fragmentation (Figure 1c). After annealing for 400 min at 170 $^{\circ}\text{C}$, a finer neck is observed in one micelle core undergoing fragmentation (Figure 1d). This fine neck formation was the last anisotropic morphology observed in BO(25–22) micelles during the experiment and is, therefore, likely close to the final step in fragmentation, that is, the transition state, before the complete separation of the core into two smaller spherical micelles.

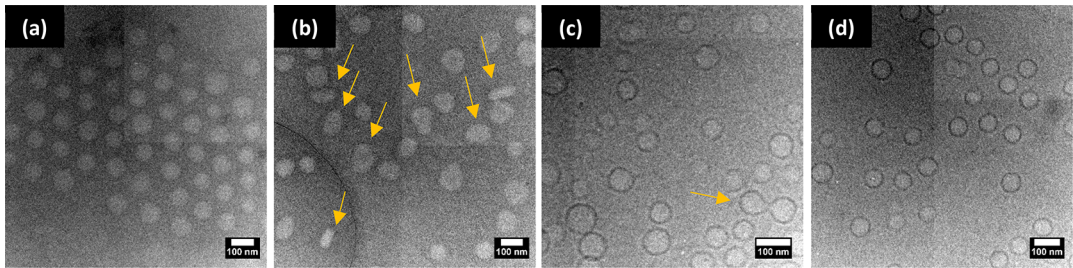


Figure 2. In situ LP-TEM images of 0.25 wt % BO(27–27) in [C₂MIM][TFSI] annealing at $T = 170\text{ }^{\circ}\text{C}$ for (a) 5, (b) 45, (c) 320, and (d) 450 min. Orange arrows indicate micelles referenced in the text. The electron dose rate was $9.8\text{ e}^{-}/\text{\AA}^2\text{ s}$ at a magnification of 15000 $\times$.

Table 1. Automated Image Analysis of In Situ LP-TEM Images for 0.25 wt % PB–PEO in [C₂MIM][TFSI] While Annealing at $T = 170\text{ }^{\circ}\text{C}$

t (min)	$\langle R_{\text{core}} \rangle^a$ (nm)	σ_{core}^b (nm)	Q^c	A^d (nm ²)	ϵ^e	$P \times R_{\text{core}}/A^f$	s_{core}^g
BO(8–7)							
5	20	2	1750	1230	0.5	2.1	2.2
20	18	2	1270	986	0.6	2.1	1.9
50	18	3	1340	1040	0.5	2.2	2.0
100	16	2	972	814	0.3	2.1	1.8
BO(25–22)							
2	43	9	6840	5700	0.4	2.1	2.9
20	35	11	3890	5180	0.6	2.5	2.4
180	33	8	3270	5780	0.5	2.7	2.3
400	30	5	2440	2930	0.1	2.1	2.0
BO(27–27)							
5	46	5	7520	6580	0.4	2.1	3.0
45	48	7	8720	7320	0.5	2.2	3.1
320	34	7	3000	3660	0.4	2.2	2.2
450	35	2	3450	3880	0.3	2.1	2.3

^a $\langle R_{\text{core}} \rangle = (A/\pi)^{1/2}$. ^bOne standard deviation from $\langle R_{\text{core}} \rangle$. ^cAggregation number (Q) calculated as $4\pi(R_{\text{core}})^3/(3V_{\text{PB}})$, assuming the core is devoid of solvent, and V_{PB} is the volume per core chain. ^dSurface area measured by automated image analysis. ^eEccentricity calculated by fitting an ellipse to the object, determined as $\epsilon = (1 - b^2/a^2)^{1/2}$; for a perfect circle, $\epsilon = 0$, and for an infinitely long object, $\epsilon = 1$. ^fPerimeter $\times$ average radius/area is equal to 2 for a perfectly spherical boundary, and the boundary is less spherical if this value is greater than 2. ^g s_{core} is the degree of core block stretching calculated as $\langle R_{\text{core}} \rangle$ divided by the root-mean-square end-to-end distance of the core block.

As shown in Figure 2, a similar evolution of the core morphology was observed for 0.25 wt % BO(27–27) in [C₂MIM][TFSI]. Note that the equilibration kinetics for this sample are slightly slower than for BO(25–22) micelles at 170 °C and about an order of magnitude slower than for BO(8–7) micelles. A more quantitative study of the effect of molecular weight on fragmentation kinetics is currently in progress. The PB core remains spherical after annealing at 170 °C for 5 min (Figure 2a), but a variety of more elongated micelles emerge after annealing for 45 min (Figure 2b). It is interesting to note the variety of anisotropic core morphologies observed in the 45 min image, and some particles appear to have formed a slight necking point. The fine-neck formation in one micelle was also observed for this sample after 320 min of annealing (Figure 2c), and after 450 min of annealing, the PB core morphology again appears spherical, but distinctly smaller (Figure 2d). The evolution of BO(8–7) micelles in [C₂MIM][TFSI] during annealing at 170 °C proceeds by the same general mechanism observed for BO(25–22) and BO(27–27) micelles, and in situ LP-TEM images for this polymer are shown in the Supporting Information, Figure S10.

It is important to address the contrast variation observed in the in situ LP-TEM images. At short annealing times, the micelle cores appear bright, with minimal appearance of Fresnel fringes. During high-temperature annealing, the

changes in sample height cause a variation of focus, which is likely the cause for the appearance of darker Fresnel fringes at longer times. This change in sample thickness is relatively common in the LP-TEM literature, particularly for the open environmental chamber used here.^{36,42–44} Due to the short lifetime of the fragmenting micelles, such as the one highlighted in Figure 2c, focus adjustments were difficult to perform. However, we conclude that this change in focus and the appearance of dark Fresnel fringes in some of the images is due to the experimental setup and not due to changes in the mass distribution of the micelle core.

Additionally, the influence of beam damage on the micelle structure is thought to be negligible compared to the effect of the electron beam on the stability of the free-standing ionic liquid films.^{33,36} We observed that the ionic liquid films become less stable at higher magnifications (>20000 $\times$) and at elevated temperatures, where the formation of holes in the liquid films becomes common. At higher temperatures and magnification, the liquid layers can burst and adhere to the holey carbon support. This phenomenon has been reported previously for ionic liquids in an open environment LP-TEM,³⁶ and some examples of beam-damaged ionic liquid films are provided in the Supporting Information.

To quantify the change in the core dimensions during fragmentation, an automated image analysis routine was

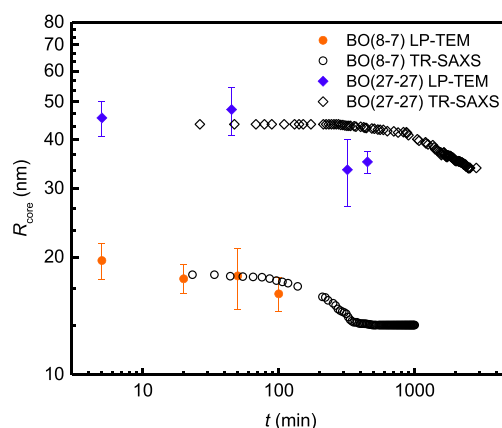


Figure 3. Image analysis of in situ LP-TEM of 0.25 wt % BO(8–7) (orange circles) and BO(27–27) (blue diamonds) in [C₂MIM][TFSI] at 170 °C. The change in $\langle R_{\text{core}} \rangle$ is determined using an automated image analysis program, where several micelles were measured for each time point. The error bars represent one standard deviation from the average value. Data points in black were determined by fitting the 1D scattering intensity obtained by TR-SAXS to the Pedersen model with the Percus–Yevick hard sphere structure factor.

a reasonable interval over which to conduct the LP-TEM experiment. The $\langle R_{\text{core}} \rangle$ obtained by each experiment for BO(27–27) micelles agrees within the errors of the two techniques at early times, but the $\langle R_{\text{core}} \rangle$ values from LP-TEM at 320 and 450 min are slightly smaller than the averages obtained by TR-SAXS. As the number of micelles measured in Figure 2 to obtain this average is relatively small (~20–30 micelles), this is presumably not an adequate representation of the ensemble $\langle R_{\text{core}} \rangle$. Nevertheless, the kinetic information from TR-SAXS supports the statistics obtained through analysis of the LP-TEM images.

To rationalize the fragmentation kinetics reported previously for BO(8–7) in ionic liquids^{30,32,33} and to understand the morphological evolution of the PB micelle core during fragmentation observed here, we consider the degree of chain stretching in the core (s_{core}) and the corona (s_{corona}), along with the extent of corona crowding in the transition state for fragmentation. The proposed transition state of a “two-spherical-compartment” micelle is illustrated in Figure 4 as structure IV. The equilibrium size and morphology of a micelle is governed by the free energy balance among the core, corona, and the interface.⁴⁵ The as-prepared micelles and those imaged at the shortest annealing times exhibit a relatively high degree of stretching in the core chains, as shown in Table 1, where s_{core} was calculated as $\langle R_{\text{core}} \rangle$ divided by the root-mean-square end-to-end distance of the PB block. The relative stability of the intermediates proposed in Figure 4 can explain the observation of a small number of anisotropic micelles with a neck for BO(25–22) and BO(27–27). It is likely that the stability of the micelles illustrated in Figure 4 decreases as I > II > III > IV. Therefore, the number of micelles observed in the experiment decreases in that order. Previous reports on the fragmentation kinetics of BO(8–7) in [C₂MIM][TFSI] found that the change in $\langle R_{\text{core}} \rangle$ with annealing time is well described by a compressed exponential with a compression exponent of 2.^{30,33} Although the mechanism of fragmentation was observed here, the origin of the compressed exponential behavior remains to be determined. The first stage of fragmentation proceeds via the elongation of spherical micelles into a 320

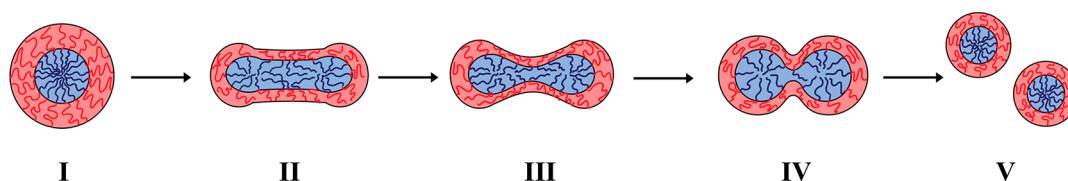


Figure 4. Schematic illustration of block copolymer micelle fragmentation, where the as-prepared micelles begin to elongate at short annealing times to relieve chain stretching in the larger, as-prepared micelles, followed by necking at longer annealing times and the thinning of the neck, which is believed to be the rate-limiting step to this process, and finally, separation of the micelle core and corona into two smaller micelles.

cylindrical morphology. This change in core area is entropically favorable due to the relief of both core and corona chain stretching in the as-prepared micelles, but opposed by the increased surface area. Previous measurements of fragmentation in five different ionic liquids revealed that the kinetics were largely independent of surface tension, indicating that the transition state does not involve exposing the core to the solvent.³³ Rather, the kinetic barrier most likely results from increased corona crowding during the neck formation in “two-compartment” micelles. In this scenario, the thinning of the neck, represented as the fourth structure in Figure 4, causes increased corona crowding for the polymer chains near the necking point and is presumably close to the transition state. In summary, we report the direct observation of block copolymer micelle fragmentation for PB–PEO in [C₂MIM]–[TFSI]. Due to the nonvolatility of ionic liquids, high-temperature LP-TEM allows imaging of dynamic processes of soft matter in solution. From this work, we identified three distinct changes in micelle core morphology during fragmentation. Initially, the micelles prepared by direct dissolution are spherical, and upon heating to 170 °C, the micelles begin to elongate. The elliptical micelles then begin to form a slight neck, or peanut shape, and then the neck thins out to connect two nearly spherical core compartments, which we hypothesize is the rate limiting step in micelle fragmentation; further annealing results in the necked micelles to fragment into two smaller micelles.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00273>.

Synthesis and characterization of BO(8–7), BO(25–22), BO(27–27), and [C₂MIM][TFSI], SEC-RI trace of BO polymers in THF, ¹H NMR spectra of BO polymers and [C₂MIM][TFSI], experimental details for in situ and ex situ LP-TEM and SAXS, background subtracted SAXS profiles of 0.25 wt % BO(8–7), BO(25–22), and BO(27–27) micelles in [C₂MIM][TFSI], ex situ LP-TEM images of 0.25 wt % BO(8–7), BO(25–22), and BO(27–27) in [C₂MIM][TFSI], as prepared by DD and steady-state after a *T*-jump to 170 °C, in situ LP-TEM images of 0.25 wt % BO(8–7) in [C₂MIM][TFSI] at *T* = 170 °C, automated image analysis results for 0.25 wt % BO(27–27) in [C₂MIM][TFSI], experimental details for dynamic light scattering, and dynamic light scattering of 0.25 wt % BO(27–27) in [C₂MIM][TFSI], as prepared by DD and steady-state after a *T*-jump to 170 °C (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Timothy P. Lodge – Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States; orcid.org/0000-0001-5916-8834; Email: lodge@umn.edu

Authors

Julia T. Early – Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States
Kevin G. Yager – Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States; orcid.org/0000-0001-7745-2513

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00273>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported primarily by the National Science Foundation (DMR-1707578) and by the U.S. Department of Energy (DOE), Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by ORAU under Contract No. DE-SC0014664. Portions of this work were performed at the Center for Functional Nanomaterials, and the National Synchrotron Light Source II, Brookhaven National Laboratory, which are supported by the U.S. DOE Office of Science under Contract No. DE-SC0012704. Data were collected using an instrument funded by the National Science Foundation under Award No. 0960140. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from NSF through the MRSEC program (DMR-1420013). We thank Dr. Ruipeng Li and Dr. Esther Tsai for assistance with TR-SAXS measurements at the 11-BM CMS beamline at the NSLS-II and Dr. Lihua Zhang for insightful discussions on high temperature LP-TEM.

■ REFERENCES

- (1) Anderson, W. *Block Copolymers as Viscosity Index Improvers for Lubrication Oils*; 1973, 3763044.
- (2) Raffa, P.; Broekhuis, A. A.; Picchioni, F. Polymeric Surfactants for Enhanced Oil Recovery: A Review. *J. Pet. Sci. Eng.* **2016**, *145*, 723–733.
- (3) Wever, D. A. Z.; Picchioni, F.; Broekhuis, A. A. Polymers for Enhanced Oil Recovery: A Paradigm for Structure-Property Relationship in Aqueous Solution. *Prog. Polym. Sci.* **2011**, *36*, 1558–1628.

- (4) Pavía-Sanders, A.; Zhang, S.; Flores, J. A.; Sanders, J. E.; Raymond, J. E.; Wooley, K. L. Robust Magnetic/Polymer Hybrid Nanoparticles Designed for Crude Oil Entrapment and Recovery in Aqueous Environments. *ACS Nano* **2013**, *7*, 7552–7561.
- (5) Cotanda, P.; Lu, A.; Patterson, J. P.; Petzetakis, N.; O'Reilly, R. K. Functionalized Organocatalytic Nanoreactors: Hydrophobic Pockets for Acylation Reactions in Water. *Macromolecules* **2012**, *45*, 2377–2384.
- (6) Tyrrell, Z. L.; Shen, Y.; Radosz, M. Fabrication of Micellar Nanoparticles for Drug Delivery through the Self-Assembly of Block Copolymers. *Prog. Polym. Sci.* **2010**, *35*, 1128–1143.
- (7) Hubbell, J. A. Enhancing Drug Function. *Science (Washington, DC, U. S.)* **2003**, *300*, 595–596.
- (8) Meier, W. Polymer Nanocapsules. *Chem. Soc. Rev.* **2000**, *29*, 295–303.
- (9) 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.
- (10) Zinn, T.; Willner, L.; Pipich, V.; Richter, D.; Lund, R. Molecular Exchange Kinetics of Micelles: Corona Chain Length Dependence. *ACS Macro Lett.* **2016**, *5*, 884–888.
- (11) Ma, Y.; Lodge, T. P. Chain Exchange Kinetics in Diblock Copolymer Micelles in Ionic Liquids: The Role of χ . *Macromolecules* **2016**, *49*, 9542–9552.
- (12) 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.
- (13) Lund, R.; Willner, L.; Stellbrink, J.; Lindner, P.; Richter, D. Logarithmic Chain-Exchange Kinetics of Diblock Copolymer Micelles. *Phys. Rev. Lett.* **2006**, *96*, 1–4.
- (14) 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.
- (15) Choi, S. H.; Lodge, T. P.; Bates, F. S. Mechanism of Molecular Exchange in Diblock Copolymer Micelles: Hypersensitivity to Core Chain Length. *Phys. Rev. Lett.* **2010**, *104*, 1–4.
- (16) Lu, J.; Bates, F. S.; Lodge, T. P. Chain Exchange in Binary Copolymer Micelles at Equilibrium: Confirmation of the Independent Chain Hypothesis. *ACS Macro Lett.* **2013**, *2*, 451–455.
- (17) Wang, E.; Lu, J.; Bates, F. S.; Lodge, T. P. Effect of Corona Block Length on the Structure and Chain Exchange Kinetics of Block Copolymer Micelles. *Macromolecules* **2018**, *51*, 3563–3571.
- (18) Dormidontova, E. E. Micellization Kinetics in Block Copolymer Solutions: Scaling Model. *Macromolecules* **1999**, *32*, 7630–7644.
- (19) Rharbi, Y. Fusion and Fragmentation Dynamics at Equilibrium in Triblock Copolymer Micelles. *Macromolecules* **2012**, *45*, 9823–9826.
- (20) Rharbi, Y.; Karrouch, M.; Richardson, P. Fusion and Fission Inhibited by the Same Mechanism in Electrostatically Charged Surfactant Micelles. *Langmuir* **2014**, *30*, 7947–7952.
- (21) 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.
- (22) Rharbi, Y.; Li, M.; Winnik, M. A.; Hahn, K. G. Temperature Dependence of Fusion and Fragmentation Kinetics of Triton X-100 Micelles. *J. Am. Chem. Soc.* **2000**, *122*, 6242–6251.
- (23) Rharbi, Y.; Winnik, M. A. Salt Effects on Solute Exchange and Micelle Fission in Sodium Dodecyl Sulfate Micelles below the Micelle-to-Rod Transition. *J. Phys. Chem. B* **2003**, *107*, 1491–1501.
- (24) Rharbi, Y.; Kitaev, V.; Winnik, M. A.; Hahn, K. G. Characterizing Aqueous Micellar Triton X-100 Solutions of a Fluorescent Model Triglyceride. *Langmuir* **1999**, *15*, 2259–2266.
- (25) Rharbi, Y.; Winnik, M. A.; Hahn, K. G. Kinetics of Fusion and Fragmentation Nonionic Micelles: Triton X-100. *Langmuir* **1999**, *15*, 4697–4700.
- (26) Rharbi, Y.; Winnik, M. A. Salt Effects on Solute Exchange in Sodium Dodecyl Sulfate Micelles. *J. Am. Chem. Soc.* **2002**, *124*, 2082–2083 see Chart 1: (a) Exchange via Water Mechanism, (b) Collision-Exchange-Separation Mechanism, and (c) Fragmentation-Growth Mechanism.
- (27) 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.
- (28) 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, FL, 2005; pp 161–231.
- (29) Michels, B.; Waton, G.; Zana, R. Dynamics of Micelles of Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Block Copolymers in Aqueous Solutions. *Langmuir* **1997**, *13*, 3111–3118.
- (30) 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.
- (31) Zakharov, A. I.; Adzhemyan, L. T.; Shchekin, A. K. Relaxation Times and Modes of Disturbed Aggregate Distribution in Micellar Solutions with Fusion and Fission of Micelles. *J. Chem. Phys.* **2015**, *143*, 124902.
- (32) 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.
- (33) 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.
- (34) Halperin, A.; Alexander, S. Polymeric Micelles: Their Relaxation Kinetics. *Macromolecules* **1989**, *22*, 2403–2412.
- (35) Kim, P. Y.; Ribbe, A. E.; Russell, T. P.; Hoagland, D. A. Visualizing the Dynamics of Nanoparticles in Liquids by Scanning Electron Microscopy. *ACS Nano* **2016**, *10*, 6257–6264.
- (36) Mansfeld, U.; Hoepfner, S.; Schubert, U. S. Investigating the Motion of Diblock Copolymer Assemblies in Ionic Liquids by in Situ Electron Microscopy. *Adv. Mater.* **2013**, *25*, 761–765.
- (37) Kuwabata, S.; Tsuda, T.; Torimoto, T. Room-Temperature Ionic Liquid. A New Medium for Material Production and Analyses under Vacuum Conditions. *J. Phys. Chem. Lett.* **2010**, *1*, 3177–3188.
- (38) Uematsu, T.; Baba, M.; Oshima, Y.; Tsuda, T.; Torimoto, T.; Kuwabata, S. Atomic Resolution Imaging of Gold Nanoparticle Generation and Growth in Ionic Liquids. *J. Am. Chem. Soc.* **2014**, *136*, 13789–13797.
- (39) Hillmyer, M. A.; Bates, F. S. Synthesis and Characterization of Model Polyalkane-Poly(Ethylene Oxide) Block Copolymers. *Macromolecules* **1996**, *29*, 6994–7002.
- (40) 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.
- (41) Pedersen, J. S. Determination of Size Distributions from Small-Angle Scattering Data for Systems with Effective Hard-Sphere Interactions. *J. Appl. Crystallogr.* **1994**, *27*, 595–608.
- (42) De Jonge, N.; Ross, F. M. Electron Microscopy of Specimens in Liquid. *Nat. Nanotechnol.* **2011**, *6*, 695–704.
- (43) Helveg, S.; López-Cartes, C.; Sehested, J.; Hansen, P. L.; Clausen, B. S.; Røstrup-Nielsen, J. R.; Abild-Pedersen, F.; Nørskov, J. K. Atomic-Scale Imaging of Carbon Nanofibre Growth. *Nature* **2004**, *427*, 426–429.
- (44) Dai, L. L.; Sharma, R.; Wu, C. Y. Self-Assembled Structure of Nanoparticles at a Liquid-Liquid Interface. *Langmuir* **2005**, *21*, 2641–2643.

554 (45) Zhulina, E. B.; Adam, M.; Larue, I.; Sheiko, S. S.; Rubinstein,
555 M. Diblock Copolymer Micelles in a Dilute Solution. *Macromolecules*
556 **2005**, 38, 5330–5351.