Equilibrium vs Metastability: High-Temperature Annealing of Spherical Block Copolymer Micelles in an Ionic Liquid

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Amphiphilic block copolymers are known to self-assemble into a variety of stable nanostructures when dissolved in a selective solvent due to the association of the insoluble core-forming blocks. The geometrical structures adopted by the micellar aggregates are determined by a free energy balance involving the stretching of the core chains, the intercoronal interactions, and the excess energy at the core−corona interface.[1,2] The typical progression of equilibrium micellar morphologies, from spheres to cylinders and bilayers (lamellae or vesicles) with decreasing corona block length (or, equivalently, with increasing solvent selectivity), has been well documented for block copolymers as well as for small molecule surfactants in both organic solvents[1,3] and aqueous solutions.[4−6] In addition, a myriad of near-equilibrium, metastable, and complex morphologies that are unique to macromolecular amphiphiles have been reported.[4,6,7] These kinetically controlled structures are thought to be a result of the slow chain exchange between micelles due to the high molecular weights of the polymers, their vanishingly small critical micelle concentrations (cmc), and by the possible entanglement and low mobility of the core chains.[6,7] Indeed, molecular exchange has been shown to be arrested over time scales of days[8,9] and even months[7,10] for a range of block copolymer micellar systems. In this context, it is evident that an unequivocal classification of the different morphologies observed in block copolymer solutions as equilibrium or nonequilibrium structures is a challenging task.

Fortunately, there are a large number of experimental variables that can help unravel the thermodynamic and kinetic parameters of micelle formation and equilibration. Some common schemes employed are changes in block composition,[4,11] polymer concentration[12] or pH, addition of salts,[6] homopolymers,[11] or common solvents,[13] and variations in temperature.[14] The last approach is desirable due to the relative simplicity of interpreting the morphological changes observed in terms of its effects in the kinetics of micellar formation and relaxation (often viewed as activated processes[15] that exhibit an Arrhenius type behavior) and in the strength of the polymer/solvent interactions[14] ($\chi \sim 1/T$, where χ is the interaction parameter between the "insoluble" core-forming block and the solvent). A frequent limitation to this procedure is the high vapor pressure of most organic solvents and of water, which allow only a narrow window of temperatures to be accessed at atmospheric pressure. A useful strategy to circumvent this limitation is to use ionic liquids as the solvent media for the block copolymer micelles. Ionic liquids are solvents with remarkable physicochemical properties, including extremely low vapor pressure, high thermal and chemical stability, and wide liquid temperature range.[16−20] It is anticipated that these ionic liquids will allow us to control micellar dynamics over a wide range of temperatures and time scales, such that thermodynamic vs kinetics aspects of micellar morphogenesis can be better understood.

In this work we investigate the formation of nonergodic micelles of polybutadiene−poly(ethylene oxide) (PB−PEO) diblock copolymers and their relaxation in an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI]). In particular, we focus on the path dependence of the micellar morphologies assumed by the PB−PEO block copolymers through modification of the preparation protocols as well as through extended thermal annealing at relatively high temperatures ($T > 120$ °C), using dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM).

It is has been previously shown that PB−PEO block copolymers form micellar aggregates in [EMI][TFSI] with an insoluble PB core and a well-solvated PEO corona.[21,22] This polymer has the advantage that the glass transition of the PB block is low ($T_g \sim -12$ °C), and thus aggregate formation should not be additionally encumbered by extremely slow core dynamics. The micellar solutions are prepared from a PB−PEO block copolymer designated BO(8−7), where the numbers in parentheses refer to the number-average molecular weights of the PB and PEO blocks in kg/mol, respectively. The molecular characteristics of the BO(8−7) block copolymer are listed in Table S1 of the Supporting Information. The Supporting Information also includes a detailed account of the preparation of the solutions as well as of the cryo-TEM and DLS experiments and data analysis.

Briefly, three protocols for the preparation of 0.5 wt % BO(8−7)/[EMI][TFSI] solutions were followed. In the direct dissolution protocol (DD), the appropriate amounts of bulk polymer are simply dissolved in [EMI][TFSI] by heating at a moderate temperature (70 °C). A variation of the DD procedure is the thin film method (TF), which involves the dissolution of the BO(8−7) copolymer in a good solvent (dichloromethane), followed by complete evaporation of the solvent such that a thin film of polymer is deposited on the walls of the vial. Afterward, the polymer is dissolved in [EMI][TFSI] as in the DD protocol. Finally, in the cosolvent procedure (CS) the copolymer is first dissolved in a good solvent mixture ([EMI][TFSI]/CH_2Cl_2), and micelle formation is then prompted by slow evaporation of the cosolvent until its complete removal is achieved.

DLS measurements of the solutions at 25 °C over a range of scattering vectors (q) show the formation of large aggregates with average hydrodynamic radii ($\langle R_h \rangle$) of 85 and 54 nm for the TF and DD procedures, respectively (Table 1). The $\langle R_h \rangle$ values were obtained from cumulant fits of the normalized, squared electric field correlation functions, $g_1{}^2(t)$, as exemplified in Figure 1. The fits of $g_1{}^2(t)$ yield the average decay rate, $\bar{\Gamma}$, the second cumulant μ_2, and the ratio $\mu_2/\bar{\Gamma}^2$, which is a measure of the breadth of the distribution. The slopes of the linear plots $\bar{\Gamma}$ vs q^2 (inset in Figure 1) then give the diffusion coefficients (D_m) and ultimately $\langle R_h \rangle$ through the Stokes−Einstein equation. The relatively large values of $\mu_2/\bar{\Gamma}^2$ obtained for the DD and TF methods (Table 1) are indicative of a broad distribution of micelle sizes, strongly suggesting the formation of nonequilibrium aggregates.[23] In fact, it was found that different distributions of aggregate size were obtained when repeating the

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Table 1. Characteristics of the PB−PEO Block Copolymer Micelles Formed at a Concentration of 0.5 wt % in [EMI][TFSI][a]

preparation procedure[b]	D_m (cm^2/s)	$\langle R_h \rangle$ (nm)[c]	$\langle \mu_2/\Gamma^2 \rangle$
TF: as-prepared	7.4×10^{-10}	85 (159)[d]	0.53
TF: steady-state	2.0×10^{-9}	30	0.12
DD: as-prepared	1.2×10^{-9}	54 (82)[d]	0.27
DD: steady-state	2.2×10^{-9}	29	0.08
CS: as-prepared	3.8×10^{-9}	16	0.10
CS: steady-state	4.1×10^{-9}	15	0.07

[a] All DLS measurements were taken at 25 °C. [b] Solutions labeled "steady-state" were obtained after thermal annealing at 170 °C. [c] Hydrodynamic radii calculated from linear fits of Γ vs q^2 plots. [d] The numbers in parentheses refer to calculations of $\langle R_h \rangle$ from angular extrapolation of Γ/q^2 vs q^2 for aggregates where $qR_h > 1$.

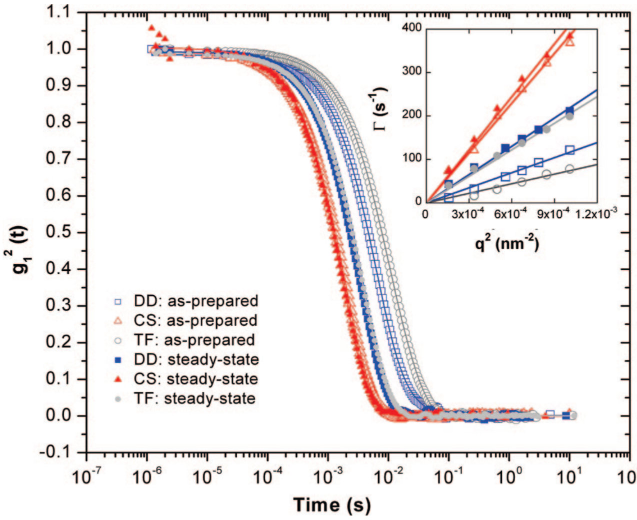

Figure 1. Normalized squared electric field correlation functions for 0.5 wt % solutions of BO(8−7) copolymer in [EMI][TFSI]. The DLS measurements were taken at $\theta = 90°$ and $T = 25$ °C and fitted with the cumulant method (solid lines). The curves vary in the preparation protocol of the copolymer solutions: open symbols show data for as-prepared solutions; filled symbols represent data taken after thermal relaxation at 170 °C. The inset shows the linear fits to the decay rate versus the square of the scattering vector from which the micelle diffusion coefficient is extracted.

preparation of the solutions using the same methodologies. In contrast, DLS measurements of the CS-prepared solution (Figure 1) reflect a narrow distribution of aggregate sizes with $\langle R_h \rangle$ = 16 nm, as shown in Table 1. In this case, good reproducibility of micelle size distribution was found after preparation of new solutions.

Characterization of the "as-prepared" solutions was followed by thermal relaxation experiments, where the samples are placed in an oil bath at high temperatures (typically 170 °C), and the evolution of the micelle size was monitored as a function of time using DLS. The samples were flame-sealed in glass tubes under an argon atmosphere to inhibit degradation. In the case of the directly dissolved solution we observed a continuous decrease in the scattered intensity, signaling a decrease in R_h. Indeed, the $\langle R_h \rangle$ decayed exponentially with time to a steady-state value of $\langle R_{h\text{-}DD} \rangle \approx 29$ nm, as illustrated in Figure 2. Similar measurements taken at $T = 145$ °C show a comparable exponential decay with a much longer relaxation time, but with approximately the same final micelle size ($\langle R_h \rangle \approx 30$ nm). In fact, within experimental uncertainty, a constant value of hydrodynamic radius was obtained after annealing over a 60 °C temperature range ($T = 120-180$ °C, data not shown). The latter observation is a clear indication that the temperature dependence of the PB/[EMI][TFSI] interfacial energy ($\gamma(T)$) is not responsible for the large decrease in micelle size, but that it is rather caused by a relaxation of the kinetically trapped, as-prepared structures. Furthermore, the polydispersity of the size distribution is shown to decrease considerably, judging from the values of $\mu_2/\bar{\Gamma}^2$ reported in Table 1. This is graphically displayed in Figure 3c, where the distributions of aggregate sizes, obtained from the application of inverse Laplace transformation (REPES routine) directly to the correlation functions, are shown for the DD solution before and after thermal treatment. In Figure 3a we also show a representative cryo-TEM image of the DD micelles after thermal treatment, exhibiting a spherical morphology with a core radius, $\langle R_{c\text{-}DD} \rangle \approx 15 \pm 2$ nm and a mean aggregation number, $p \approx 950$. In the image, the bright spheres correspond to the PB cores with their lower electron density, while the darker, higher electron density matrix corresponds to the [EMI][TFSI].

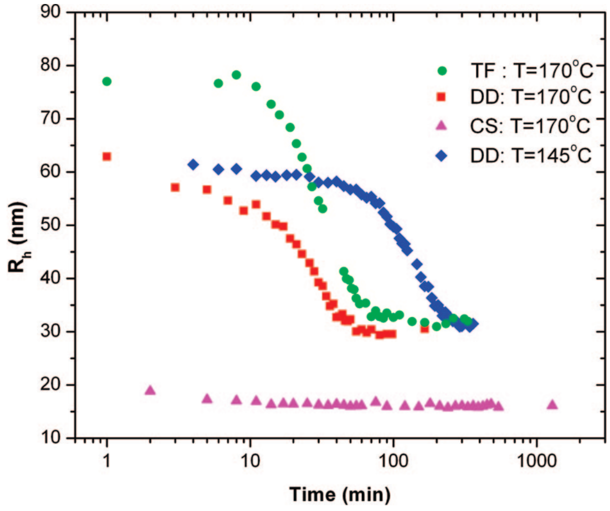

Figure 2. Hydrodynamic radii (R_h) vs time for the BO(8−7) micelles taken at $\theta = 90°$. Diamonds and squares represent micelles prepared by the direct dissolution protocol (DD) at 145 and 170 °C, respectively. Circles and triangles are data for micelles prepared by the thin film (TF) and cosolvent procedure (CS), respectively, and annealed at 170 °C.

A thermal relaxation experiment at 170 °C was also carried out for the micelle solution prepared via the TF procedure. Once again, we notice an exponential decay of the average micelle size to $\langle R_{h\text{-}TF} \rangle \approx 30$ nm (Figure 2), with a concomitant decrease in polydispersity (Table 1). This experiment illustrates the point that micelles prepared through methodologies in which the polymer is dissolved directly in the ionic liquid ultimately reach the same steady-state size upon heat treatment, regardless of the initial aggregate size distribution. This strongly suggests that there is a global minimum in the free energy of the system yielding equilibrium spherical micelles of roughly 30 nm in radius.

Additional thermal relaxation experiments were performed with the micelle solution prepared through the cosolvent procedure. Figure 2 clearly shows that the hydrodynamic radius of the CS micelles annealed at 170 °C remains approximately constant over a period of more than 20 h. Moreover, the distribution of micelle sizes is virtually unchanged by the heating process (Figure 3d). The cryo-TEM image of the micelles after heat treatment reveals that the morphology of these micelles is also spherical, but their core size ($\langle R_{c\text{-}CS} \rangle = 8 \pm 1$ nm, $p \approx 130$) is significantly smaller than the one obtained with the DD protocol (Figure 3a,b). Thus, we observe a strong path dependence in the morphology of PB−PEO micelles such that two separate distributions of spherical aggregates are obtained

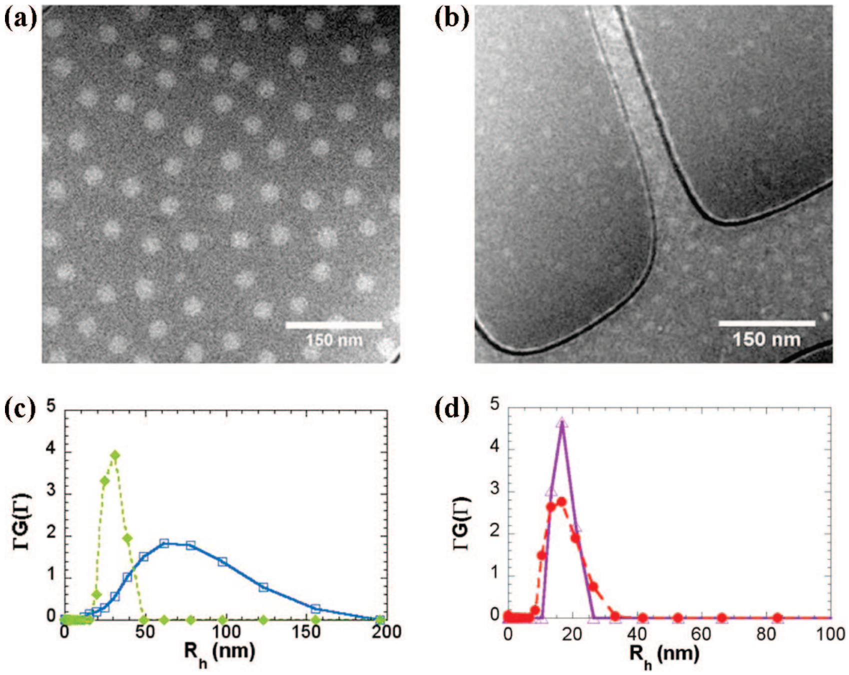

Figure 3. Cryo-TEM images of 0.5 wt % solutions of BO(8−7) in [EMI][TFSI] after thermal relaxation at 170 °C. The measured core radius is $\langle R_c\rangle = 15$ nm for micelles prepared through DD method (a) and $\langle R_c\rangle = 7.5$ nm for CS-prepared micelles (b). Hydrodynamic radius distributions for the DD- (c) and CS-prepared micelles (d). In each panel, open and filled symbols show the distributions for the as-prepared and steady-state aggregates, respectively.

after thermal treatment, both with a very low polydispersity but with a substantial difference in their average size ($\langle R_{\text{h-CS}}\rangle \sim {}^1/_2\langle R_{\text{h-DD}}\rangle$). To confirm that the extended annealing did not cause extensive degradation, a sample subjected to the DD protocol, followed by 10 h of annealing at 170 °C, was then subjected to the CS preparation procedure; the resulting micelles were identical to CS micelles that had never been annealed at high temperature.

The two steady-state size distributions obtained must be a consequence of the active mechanisms of micelle formation and relaxation[9,13,15,24−31] in each preparation procedure. In analogy to kinetic models for surfactant systems,[32,33] Halperin and Alexander[2,34] first proposed that the main route for micelle formation and equilibration in block copolymer systems is the consecutive incorporation/expulsion of unimers (unimer exchange). The rate of unimer exchange in a micellar solution is known to be strongly influenced by the degree of incompatibility between the insoluble block and the solvent, leading to frozen micellar structures when the solvent is very poor. It is widely accepted that precipitant methods, such as the CS procedure, can optimize exchange of polymer chains, since the content of precipitant at the onset of aggregation is low (high CH_2Cl_2 contents, in our case) and the core/solvent incompatibility is therefore weak.[6] As such, the kinetics of chain exchange will be rapid and micellization will be under thermodynamic control. However, as the solvent becomes progressively poorer for the core block during evaporation, the rate of chain exchange decreases and the micellar structure may become frozen if the exchange kinetics are slower than the rate of cosolvent evaporation. Thus, it is possible that the size of our CS-prepared micelles is representative of the morphology formed at a relatively low interfacial energy between the PB and the [EMI][TFSI]/CH_2Cl_2 solvent mixture, for which a smaller aggregation number is anticipated ($p \sim \gamma^{\alpha}$, where $\alpha = 1$ for crew-cut-type micelles, as obtained from scaling approaches[1]), and are unable to achieve equilibrium thereafter.

It might be expected that the high thermal energy imparted to the system during annealing would allow faster unimer exchange kinetics that would in turn enable coarsening of the CS micelles to achieve their equilibrium size. However, in the absence of high unimer concentrations, micelle growth inevitably requires a net *decrease* in the number density of aggregates, through either coalescence or micelle evaporation. The former is highly unlikely due to the strong steric repulsion between opposing coronas. On the other hand, micelle evaporation (i.e., complete dissolution) is an activated process with a large energy barrier.[15] Furthermore, in the CS micellar solution the expulsion of chains from a given sphere opposes its driving force for growth, thus preventing equilibration. Cavicchi et al. have observed a similar phenomenon in the equilibration of the domain spacing of a poly(ethylene-*alt*-propylene)−poly(dimethylsiloxane) (PEP−PDMS) block copolymer in the body-centered-cubic ordered phase.[35] Namely, they demonstrate that the equilibration times for the spheres were remarkably long (i.e., months), particularly upon cooling within the ordered state, despite the fact that measurements of tracer diffusion showed significant chain mobility on a time scale of seconds. The authors concluded that the rate-limiting step for equilibration on cooling must be a large kinetic barrier for micelle evaporation. It is interesting to note that upon heating within the ordered state the PEP−PDMS spheres were able to equilibrate, forming smaller domains.

Let us now focus our attention on the TF and DD preparation protocols, both of which involve the dissolution of the polymer directly in the ionic liquid. Direct dissolution methods are generally considered poor methods for micelle preparation, specifically for crew-cut micelles in which the core block is longer than the corona block, since the polymer is scarcely soluble in the selective solvent.[6,12,36] In fact, it is expected that the highly selective ionic liquid will severely restrict exchange of the PB–PEO chains between micelles. Accordingly, the morphologies of the large, as-prepared aggregates obtained through these procedures are likely to be controlled by the speed of micellar growth, which overrides the rate of generation of new micelles, and consequently lie far from equilibrium.

Once again, equilibration of the DD- and TF-prepared micelles upon thermal annealing requires not only an increased rate of chain exchange but also a change in the number density of aggregates in solution. In this case, the increase in micelle number density should proceed through either fission of the large aggregates or nucleation and growth of new micelles. Even though the possibility of attaining equilibrium by means of a fission process cannot be completely discarded, theoretical studies suggest that both fusion and fission mechanisms are inefficient kinetic pathways to micelle formation and relaxation.[15] As suggested for the mechanism of micelle evaporation, the process of nucleation of a micelle can also pose a significant kinetic barrier. However, in the DD and TF micellar solutions the expulsion of unimers from a given aggregate should be a more energetically favorable process, since it complements the tendency of the micelle to shrink. This should provide an increased concentration of free chains in solution and enhance the rate of formation of new micelles by lowering the barrier to nucleation. Our observations are, once more, consistent with the mechanism proposed by Cavicchi and Lodge for the equilibration of the PEP–PDMS spheres upon heating the copolymer within the ordered phase.[35]

In this work, we have investigated the occurrence and relaxation of nonergodic states in PB–PEO micelles as a relevant and widespread phenomenon in dispersions of block copolymer amphiphiles. Our approach was to take advantage of the wide liquid temperature ranges characteristic of ionic liquids to prepare block copolymer dispersions that could be allowed to relax at high annealing temperatures. Interestingly, our results show that despite the ample thermal energy imparted to the systems, the steady-state structures remain highly path dependent, wherein two distinct yet narrow distributions of spherical micelles are obtained depending on the preparation procedure. We propose that both an enhanced rate of unimer exchange and a change in the number density of micelles are necessary to achieve equilibrium in the solutions. A strong concentration dependence of the activation energy for micelle evaporation might explain why ergodicity is not realized in certain preparation protocols, even after extended thermal treatment. However, a greater mechanistic understanding of the micelle formation and relaxation processes is necessary to unequivocally conclude whether either of the steady-state morphologies observed has attained equilibrium.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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