

Kinetics of polybutadiene-poly(ethylene oxide) micelles in an ionic liquid



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INTRODUCTION

Amphiphilic block copolymers can form micellar structures when dissolved in a selective solvent, which are of interest in a range of applications from advanced electronics¹ to drug delivery.²

Dynamic equilibrium is established in solution; however, incompatibility between block and solvent prevents equilibrium, leading to kinetically-frozen aggregates.^{3,4} Sufficient thermal energy may allow the locked-in micelle system to relax into a stable conformation.

Polybutadiene-poly(ethylene oxide) (PB-PEO) micelles were prepared in the ionic liquid 1-butyl-3-methyl imidazolium bis(trifluoromethyl sulfonyl) imide [BM][TFSI] via two methods: direct dissolution and cosolvent-aided dissolution using dichloromethane.

Ionic liquids exhibit versatility, wide-ranging stability, and have excellent solvation capabilities.^{5,6} [BM][TFSI] is selective towards the PEO block.

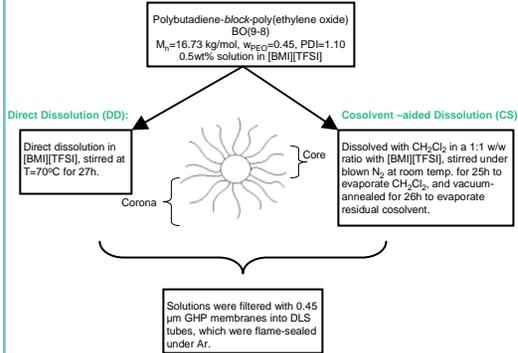
Measurements of hydrodynamic radii were conducted by dynamic light scattering. The thermally stable environment provided by [BM][TFSI] permitted annealing of both samples above 150°C.

MATERIALS AND METHODS

PB-PEO prepared via living anionic polymerization, provided by Sangwoo Lee.

[BM][TFSI] synthesized by anion exchange, using [BM][Br] and [Li][TFSI] purchased from Io-Li-Tec.

Two methods used to prepare PB-PEO micelles:



Dynamic light-scattering measurements of intensity correlation functions $[g_2(t)]$, taken at five angles from 60° to 120° . Samples were annealed at temperatures between 150°C – 170°C .

Seigert relation used to obtain electric field correlation functions $[g_1(t)]$:

$$g_2(t) = 1 + g_1^2(t)$$

Fitted by method of cumulants to extrapolate average relaxation rates $\langle \Gamma \rangle$.

Linear fit of $\langle \Gamma \rangle$ vs. scattering vector q^2 gave average diffusion coefficient D_0 , used in Stokes-Einstein equation to calculate hydrodynamic radius:

$$R_h = k_B T / (6\pi\eta D_0)$$

RESULTS AND DISCUSSION

METHOD-DEPENDENT MICELLAR MORPHOLOGY

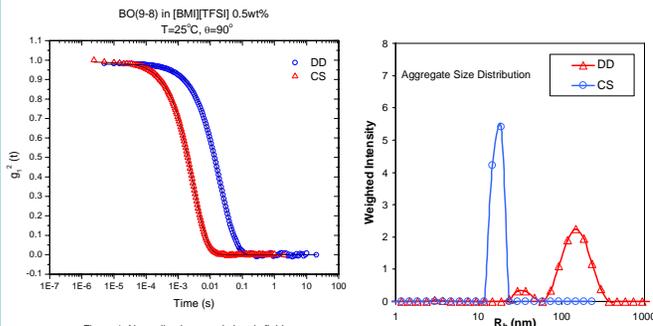


Figure 1: Normalized squared electric field correlation functions $[g_2(t)]$ for each preparation procedure at $T = 25^\circ\text{C}$ and $\theta = 90^\circ$.

Figure 2: Aggregate size distribution of each preparation procedure before annealing, at $T = 25^\circ\text{C}$ and $\theta = 90^\circ$.

Preparation Procedure	R_h (nm)	$\langle w_p \Gamma^2 \rangle$
DD (2nd run)	109	0.538
CS	17	0.016

Micelle size and polydispersity $\langle w_p \Gamma^2 \rangle$ differed for each protocol, displayed in Figure 2.

Incompatibility between core-forming PB block and [BM][TFSI] resulted in large aggregates in directly dissolved micelle solutions.

MICELLE STRUCTURE DEVELOPMENT AFTER ANNEALING

R_h of direct dissolution samples decreased in size, reaching a steady state.

Direct Dissolution				
T applied	180°C	170°C	160°C	150°C
R_h , after annealing (nm)	29	31	31	29
t_a (min)	212	360	1470	1457

Cosolvent samples did not change after 48 h at 170°C .

Cosolvent	
T applied	170°C
R_h , after annealing (nm)	17

Directly dissolved micelles distinctly larger than cosolvent micelles.

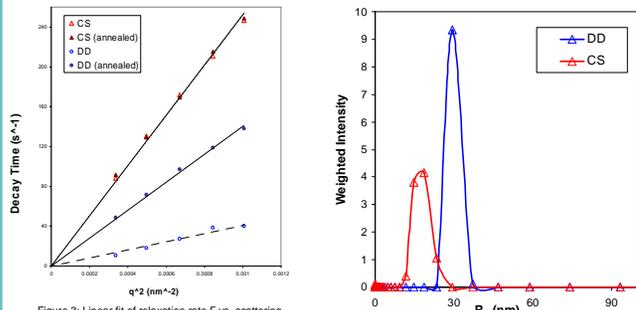


Figure 3: Linear fit of relaxation rate Γ vs. scattering vector q^2 for both DD and CS, before and after annealing at $T = 170^\circ\text{C}$ and $\theta = 90^\circ$.

Figure 4: Aggregate size distribution of each preparation procedure upon annealing at $T = 170^\circ\text{C}$, measurements taken at $T = 25^\circ\text{C}$ and $\theta = 105^\circ$.

MICELLE SIZE REDUCTION IN DIRECT DISSOLUTION SAMPLES

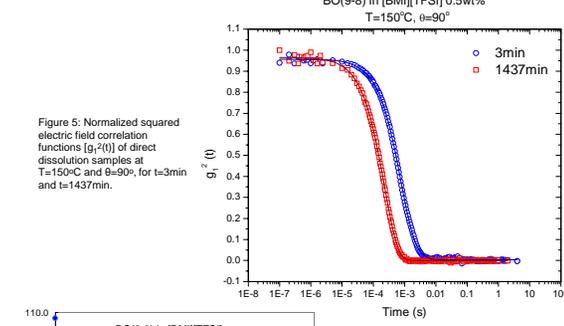


Figure 5: Normalized squared electric field correlation functions $[g_2(t)]$ of direct dissolution samples at $T = 150^\circ\text{C}$ and $\theta = 90^\circ$, for $t = 3\text{min}$ and $t = 1437\text{min}$.

Figure 6: Evolution of R_h over time at $T = 150^\circ\text{C}$, 160°C , and 170°C and $\theta = 90^\circ$.

The directly dissolved samples appear to follow an exponential decay.

A common reduced R_h is approached upon annealing.

CONCLUSIONS AND FUTURE DIRECTIONS

Highly amphiphilic block copolymer BO(9-8) was dissolved in [BM][TFSI] and self-assembled in dilute solution. Thermal stability of the ionic liquid allowed both samples to be annealed at high temperatures.

Preparation method of BO(9-8) micelles strongly influenced structures formed. When directly dissolved in [BM][TFSI], polymer associated into large aggregates with broad size distribution. Upon applying heat, micelles diminished in size and polydispersity. Cosolvent-dissolved polymer formed stable structures and retained morphology even after annealing over time. Two different micelle sizes resulted from each protocol.

Further investigations of PB-PEO include quantification of characteristic size decay exhibited by directly dissolved micelles, and also changing ionic liquid to observe effects of varying selectivity of solvent.

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