Mechanism of Molecular Exchange in Diblock Copolymer Micelles: Hypersensitivity to Core Chain Length

Soo-Hyung Choi,[1] Timothy P. Lodge,[1,2,*] and Frank S. Bates[1,†]

[1]*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA*
[2]*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, USA*

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Molecular exchange between spherical micelles formed from isotopically labeled diblock copolymers was investigated using time-resolved small-angle neutron scattering measurements. Temperature changes affect the micelle exchange rate $R(t)$ consistent with melt dynamics for the core polymer. Varying the core block length N produces gigantic changes in $R(t)$ due to the thermodynamic penalty associated with ejecting a core block into the surrounding solvent. This hypersensitivity, combined with modest polydispersity in N, leads to an approximately logarithmic $R(t)$.

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Self-assembly of amphiphilic molecules such as lipids, surfactants, and soaps constitutes a central theme in the development of structure and properties in soft materials [1]. Living cell membranes, complex fluids containing long wormlike micelles, and detergents that sequester and disperse oily impurities are representative examples of technologically important systems that rely on this class of compounds. For more than a decade amphiphilic block copolymers have been investigated as potentially superior alternatives to low molecular weight surfactants [2]. Increasing the overall molecular weight provides access to a wide range of micelle and vesicle dimensions, along with additional property advantages such as controlled solute release, mechanical robustness, and versatility in targeting aqueous or hydrocarbon media. Extensive experimentation with diblock and multiblock copolymers [3–5], supported by predictive theory [6,7], has produced an expansive literature regarding the static structure of block copolymers when dispersed in water or oil; a typical dispersion contains spherical or cylindrical micelles, or bilayer based vesicles.

Much less is known about the dynamics of block copolymer dispersions, particularly the mechanism(s) governing molecular exchange between micelles, yet this is the fundamental process that must underlay the attainment of thermodynamic equilibrium. Several experimental techniques have been applied to this problem including sedimentation [8], fluorescence quenching spectroscopy [9,10], and small-angle neutron scattering [11–14]. Using time-resolved small-angle neutron scattering (TR-SANS) measurements Won and co-workers [11] demonstrated a complete lack of exchange, over an 8 d period, of poly(butadiene-*b*-ethylene oxide) (PB-PEO) molecules assembled as spherical or cylindrical micelles dispersed in water (1 wt %). The sphere forming diblocks contained $\langle N_{\mathrm{PB}} \rangle = 71$ hydrophobic and $\langle N_{\mathrm{PEO}} \rangle = 139$ hydrophilic repeat units, leading to a thermodynamic state of very strong segregation. Lund and co-workers [12–14] have investigated a similar system, poly(ethylene-*alt*-propylene-*b*-ethylene oxide) (PEP-PEO), also by TR-SANS, and shown an unusual logarithmic time dependence to the micelle chain exchange kinetics in water-DMF solutions. Here chain exchange was facilitated by reducing the length of the hydrophobic block ($\langle N_{\mathrm{PEP}} \rangle = 16.5$), while increasing the length of the hydrophilic block ($N_{\mathrm{PEO}} = 497$). These authors suggested that their findings may reflect a coupling between the core (PEP) block molecular dynamics and the geometric constraints imposed by the micelle structure.

We have addressed this issue using poly(styrene-*b*-ethylene-*alt*-propylene) (PS-PEP) diblock copolymers dispersed in squalane, an oligomeric hydrocarbon solvent ($C_{30}H_{62}$) with a segment structure identical to PEP. Squalane is a poor solvent for PS and accordingly PS-PEP diblock copolymers form micelles with a PS core and a PEP corona when dispersed at low concentrations. Since the thermodynamic interactions governing this purely hydrocarbon system are significantly weaker than those associated with aqueous based mixtures, molecular exchange dynamics can be characterized at higher molecular weights and more symmetric compositions. Two pairs of structurally matched PS-PEP compounds, i.e., with nearly equal molecular weights and compositions, were synthesized using established techniques. Each pair includes polymers with a fully deuterated (dPS-PEP) and a normal (hPS-PEP) PS blocks, and all four diblock copolymers form spherical micelles as determined by static small-angle neutron and x-ray scattering (SANS and SAXS) [15]. Table I lists the PS and PEP block lengths and overall polydispersities, along with the micelle core radius (R_c) and aggregation number (N_{agg}), for each compound in squalane.

TR-SANS specimens were prepared by dispersing the copolymers in a mixture of deuterated and protonated squalane, formulated to exactly contrast match a perfectly mixed dPS and hPS (50/50) micelle core. Each specimen

TABLE I. Diblock copolymer and micelle characteristics.

Polymer	Number of repeat units $N_{\rm PS}$	$N_{\rm PEP}$	Polydispersity N_w/N_n	Core radius R_c (Å)[a]	Aggregation number $N_{\rm agg}$[a]
hPS-PEP-1	250	970	1.04	87	67
dPS-PEP-1	260	985	1.10	89	72
hPS-PEP-2	400	880	1.05	105	77
dPS-PEP-2	423	926	1.10	102	78

[a] Detailed fitting model is described in Ref. [15].

was annealed at 180 °C then cooled to room temperature, where the micelle cores are glassy, hence thoroughly immobilized. Subsequently, dPS-PEP and hPS-PEP dispersions were combined (post mixed) and stored at room temperature; molecular exchange is completely suppressed at this temperature. Premixed specimens were created by codissolving dPS-PEP and hPS-PEP in dichloromethane, followed by dissolution in squalane and removal of the volatile solvent by vacuum drying.

TR-SANS experiments were performed with the NG7 30 m instrument at the National Institute of Standards and Technology, with a neutron wavelength of $\lambda = 7$ Å and a wavelength spread $\Delta\lambda/\lambda = 0.11$ [16]. Post mixed specimens containing 50% dPS-PEP and 50% hPS-PEP were heated to a target temperature above the glass transition of the core polymer in squalane, $T_{g,\rm PS\ core} \cong 70\,^\circ$C [17], and then monitored by SANS in 5 min intervals. As copolymers are exchanged between the hPS-PEP and dPS-PEP micelles, the magnitude of the neutron contrast between the PS cores and the matrix decreases, resulting in a reduction in the neutron scattering intensity. Figure 1 illustrates representative SANS data acquired during the time evolution of the dPS-PEP-2/hPS-PEP-2 system (1 vol % PS-PEP) at 135 °C. More than 30 h were required to achieve a statistical distribution of dPS and hPS across the micelle cores. (For times greater than about 3 h the specimens were maintained at the target temperature outside the SANS instrument and periodically reinserted for measurement).

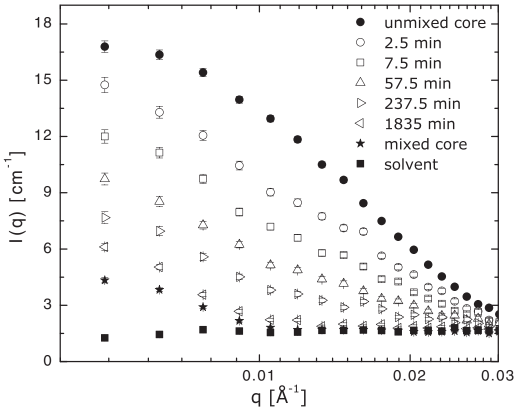

FIG. 1. Time dependence of SANS patterns obtained from a 1 vol % dPS-PEP-2/hPS-PEP-2 50/50 mixture at 135 °C. Initial measurements were made at 30 °C (filled circles) and followed by the acquisition of SANS data every 5 min (shown in the legend). The mixed core data were obtained from a premixed specimen.

The SANS intensity is proportional to the contrast factor, $I(t) \sim \{[b(t)/V]_{\rm core} - (b/V)_{\rm matrix}\}^2$, where $[b(t)/V]_{\rm core}$ is the time-dependent scattering length density of the micelle cores; $(b/V)_{\rm matrix}$, which is fixed primarily by the isotopic squalane mixture (and to a very minor extent the hydrogenous PEP corona), remains constant throughout the process. Since $[b(t)/V]_{\rm core}$ is proportional to the volume fraction of hPS chains in the core the instantaneous state of exchange can be represented by the time correlation function $R(t) = \{[I(t) - I(\infty)]/[I(0) - I(\infty)]\}^{1/2}$, where $I(0)$ and $I(\infty)$ are the scattering intensities at $t = 0$ (i.e., the unmixed core sample) and $t = \infty$ (i.e., a completely mixed and contrast matched core sample), respectively [12,13].

$R(t)$ is plotted versus $\log(t)$ in Fig. 2(a) for PS-PEP-1 at 100 °C, 110 °C, and 115 °C, and in Fig. 2(b) for PS-PEP-2 at 135 °C, 140 °C, and 145 °C. Consistent with the findings of Lund *et al.* [12,13], $R(t)$ is nearly linear on a logarithmic time scale. These results also demonstrate that two parameters strongly impact the micelle exchange dynamics: temperature and the core degree of polymerization N. We have accounted for the effects of temperature by exploiting the time-temperature superposition principle, routinely used to correlate polymer melt dynamics based on the shift factor, $a_T = \tau(T)/\tau_{\rm ref}(T_{\rm ref})$, which accounts for changes in the molecular relaxation time τ at temperature T relative to a reference temperature $T_{\rm ref}$ [18]. Recognizing that the temperature dependence of the micelles will reflect primarily core (plasticized polystyrene) dynamics, we have shifted the TR-SANS data along the time axis using $T_{\rm ref} = 125\,^\circ$C, i.e., $R(t, T) = R(t/a_T, T_{\rm ref})$. Figure 3 illustrates that each set of data, $\langle N_{\rm PS}\rangle = 255$ and $\langle N_{\rm PS}\rangle = 412$, can be shifted onto individual master curves using a single a_T function (consistent in form with the WLF equation [18]; inset of Fig. 3) with $T_{\rm ref} = 125\,^\circ$C, confirming the origin of the temperature dependence of $R(t)$. This procedure also exposes an extreme sensitivity of $R(t)$ to N, e.g., for $R(t) = 0.5$ a 62% increase in N inflates the time constant for micelle exchange by roughly 4 orders of magnitude (Fig. 3).

Moving a diblock copolymer from one micelle to another involves three steps: (i) extraction of a core block, (ii) transport of the macromolecule through the solvent matrix including the corona, and (iii) absorption of the core block by another micelle [19,20]. (In agreement with Lund *et al.* [13], we ignore exchange due to micelle fusion or fission based on the equivalence of TR-SANS results obtained at various copolymer concentrations). The first step in this sequence (i) is assumed to be rate limiting, with the net flux of deuterated (and protonated) PS blocks from a core proportional to the concentration, $K(t, N) = [c(t) - c(0)]/[c(\infty) - c(0)] = \exp[-t/\tau(N)]$, where $\tau(N)$ is the characteristic exchange time. For unentangled poly-

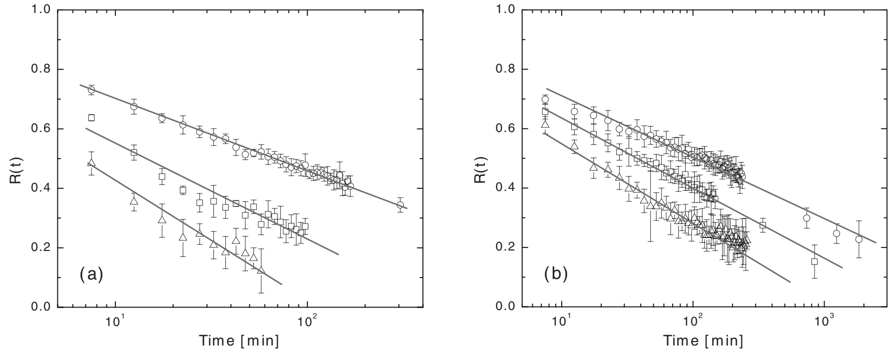

FIG. 2. Decay of reduced SANS intensity as a function of time for (a) dPS-PEP-1/hPS-PEP-1 at 100 °C (circle), 110 °C (square), and 115 °C (triangle) and (b) dPS-PEP-2/hPS-PEP-2 at 135 °C (circle), 140 °C (square), and 145 °C (triangle). These results are linear over the measurement range.

mer melts the longest (Rouse) relaxation time is given by $\tau_{\mathrm{Rouse}} = (N^2b^2\zeta)/(6\pi^2kT)$, where k, T, b, and ζ are the Boltzmann constant, temperature, statistical segment length, and the monomeric friction factor, respectively [21]; the PS blocks considered in this Letter are at most weakly entangled and thus are governed by Rouse dynamics.

Extraction of a core block carries a thermodynamic penalty proportional to the product χN due to the creation of enthalpically unfavorable segment-solvent contacts. This hinders movement of a core chain beyond the core boundary by the factor $\exp(-\alpha\chi N)$, where χ is the Flory-Huggins interaction parameter and α is an unknown $O(1)$ prefactor [22–24], leading to the following time correlation function for the escape of PS blocks from the micelle cores,

$$K(t, N) = \exp\left[-t\frac{6\pi^2kT}{N^2b^2\zeta}\exp(-\alpha\chi N)\right]. \qquad (1)$$

This relation is analogous to the standard Kramers-Arrhenius expression for traversing the transition state. Since $K(t, N)$ is a stiff function of chain length N (a double exponential) we expect polydispersity (i.e., a distribution of core block chain lengths) to play an important role in the exchange dynamics. Thus even a small distribution in N will significantly broaden $K(t, N)$. Based on the molecular weight distribution produced during the polymerization of the block copolymers, we have modified $K(t, N)$ using a Schulz-Zimm distribution function of core block chain lengths,

$$P(N_i) = \frac{z^{z+1}}{\Gamma(z+1)}\frac{N_i^{z-1}}{N_n^z}\exp\left(-\frac{zN_i}{N_n}\right), \qquad (2)$$

where $z = [(N_w/N_n) - 1]^{-1}$ (N_w and N_n are the weight and number average chain lengths) and Γ is the gamma function, resulting in the final relaxation function,

$$R(t) = \int_0^\infty P(N)K(t, N)dN. \qquad (3)$$

Equations (1)–(3) have been used to model the TR-SANS data appearing in Fig. 3. Only two parameters have been adjusted to optimize these fits, the polydispersity index N_w/N_n and the combination parameter $\alpha\chi$. The monomeric friction factor $\zeta(T)$ was estimated based on published rheological data for polystyrene [25], and the statistical segment length $b = 0.67$ nm was taken from the literature [26]. Table II summarizes the parameters associated with fitting $R(t)$ to the two branches shown in Fig. 3. Figure 4 illustrates the sensitivity of this model to modest variations in core block polydispersity. Increasing N_w/N_n from 1.0 to 1.04 leads to significant changes in the structure of $R(t)$, transforming the relaxation function from an exponential decay to one that is approximately logarithmic in form. For both systems optimal fitting requires relatively narrow polydispersity indices (Table II), in close agree-

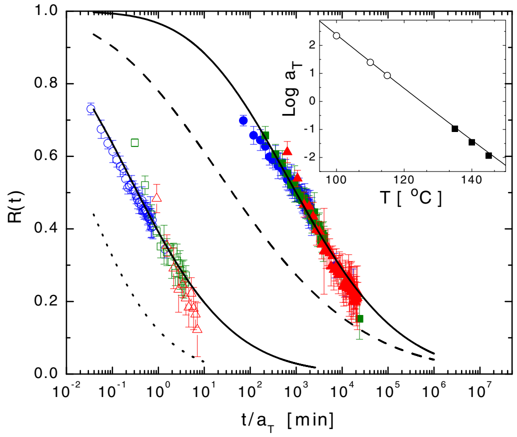

FIG. 3 (color online). Time-temperature superposed TR-SANS results with $T_{\mathrm{ref}} = 125$ °C. a_T shift factors conform to a single equation as shown in the inset. Master curves for chain exchange kinetics for PS-PEP-1 [originally measured at 100 °C (○), 110 °C (□), and 115 °C (△)] and PS-PEP-2 [originally measured at 135 °C (●), 140 °C (■), and 145 °C (▲)]. Solid curves are best fit to Eq. (3) with $\alpha\chi = 0.041$ (circles) and 0.042 (squares). Dotted and dashed curves were calculated with $\alpha\chi = 0.03$ and 0.06 and $N = 255$ and $N_w/N_n = 1.08$.

TABLE II. Fitting results[a] at $T = 125$ °C.

	N_n (input)	N_w/N_n[b] (fit)	$\alpha\chi$[b] (fit)
PS-PEP-1	255	1.08	0.041
PS-PEP-2	412	1.04	0.042

[a] $\zeta = 1.71 \times 10^{-8}$ (N · s · m^{-1}).
[b] Standard deviation is less than 1%.

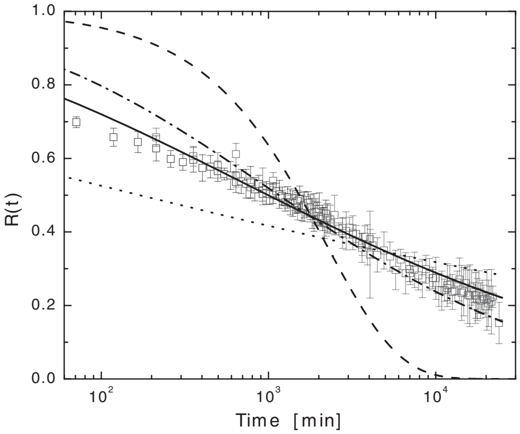

FIG. 4. Sensitivity of calculated $R(t)$ to variations in core block polydispersity. Data are superimposed PS-PEP-2 ($T_{\rm ref} = 125\,^\circ$C) results from Fig. 3. Polydispersity of core block length: 1 (dash), 1.02 (dash-dotted), 1.04 (solid), and 1.20 (dot).

ment with the experimental values listed in Table I. (Here we note that a tenfold change in ζ leads to less than a 17% variation in the fitted value of $\alpha\chi$).

The second fitting parameter $\alpha\chi$ influences $R(t)$ very differently as shown in Fig. 3 for the PS-PEP-1 system. Varying this parameter between 0.03 and 0.06 shifts $R(t)$ by roughly 5 orders of magnitude along the time axis. Significantly, both systems yield nearly identical values, $\alpha\chi = 0.041$ and 0.042 for PS-PEP-1 and PS-PEP-2, respectively (Table II). Independent measurements of the PS-PEP segment-segment interaction parameter yield $\chi \approx 0.07$ [27], which gives $\alpha \approx 0.6$, consistent with theoretical expectation.

These results establish the mechanism and rate-limiting step that controls the molecular exchange dynamics of block copolymer-based amphiphilic dispersions. The effects of temperature and core block molecular weight have been isolated and quantified. While the data analysis and overall logarithmic form of the time correlation function $R(t)$ are consistent with previous reports, we have shown that departure from a simple exponential decay is primarily a consequence of hypersensitivity of the exchange process to variations in the core block length N, i.e., polydispersity, contrary to the conclusion drawn by Lund *et al.* [12,13]. The model we employ is functionally similar to theirs. However, a key factor that distinguishes our work from that of Lund *et al.* is the investigation of diblock copolymers with different values of N, which directly exposes the hypersensitivity of $R(t)$ to this parameter after accounting for the effects of temperature (see Fig. 3). By studying separate compounds we also were able to independently verify the fitting parameter $\alpha\chi$ as shown in Table II.

Hypersensitivity of micelle exchange dynamics to block copolymer chain length explains the rapid onset of nonergodicity in block copolymer dispersions with increasing molecular weight [28,29], which carries significant technological consequences. Moreover, our conclusions should be applicable to many types of amphiphilic block copolymer dispersions, independent of shape, including wormlike cylindrical micelles and bilayer vesicles, and structures formed using tailored combinations of different molecular weight compounds.

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*Corresponding author.
lodge@umn.edu
†Corresponding author.
bates@cems.umn.edu

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