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Chain exchange kinetics between linear ABA-type triblock copolymer micelles

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Chain exchange kinetics between triblock block copolymers of ABA-type with end block being soluble in solvent is investigated using dissipative particle dynamics simulations for the first time. In such micelles, the polymer conformation is believed to play an important role. Our simulations find that a majority of polymer chains take loop (bend) conformations within the micelle, and unimer expulsion is the dominant mechanism for exchange. The chain exchange follows a first-order kinetic process, for which the characteristic time τ increases with both core and corona block lengths, showing a qualitative agreement with the literature. While the strong effect of core block length is due to an increase in activation energy, the marginal effect of corona block length is attributable to the re-insertion of an escaping chain into the same micelle. Re-insertion is favored because of greater resistance for a chain to escape a thicker corona.

1. Introduction

Amphiphilic block copolymers, known to self-assemble into micelles in selective solvent, is actively investigated over last two decades [1,2]. In recent years, with the ability to synthesize block copolymers of complex architectures due to advancement in polymerization techniques, numerous applications/advantages have been reported regarding manipulation to achieve desired properties [3–5]. It has been reported that chain architecture can affect the self-assembling properties [6,7]. Available architectures at present include linear, cyclic [8], star [5], tadpole [9], and comblike polymer [10]. Linear triblock copolymer is a simple extension of diblock copolymer and has found various applications [11–13]. For example, Pluronics [14] is commercially available and commonly tested linear triblock copolymer for drug delivery applications [15].

Copolymer chains exchange between micelles and the bulk phase to maintain dynamic equilibrium. The kinetics of chain exchange depends on the properties of the micelle solution such as block lengths, polymer concentration, etc., and the characteristic times are directly related to the micellar stability [16]. Halperin and Alexander [17] proposed two kinetic mechanisms of chain exchange for diblock copolymer micelles using a scaling analysis deduced from Kramer's rate theory: (i) unimer expulsion/insertion and (ii) aggregate fission/fusion. In their model, the exchange behavior was described by a single exponential decay process with unimer expulsion/insertion as the dominant mechanism.

Thanks to improvement in experimental techniques, measurement of equilibrium chain exchange kinetics is possible via reduction of perturbations to equilibrium [18]. Using TR-SANS, prior studies asserted that chain exchange process is dominated by single chain (unimer) expulsion, and micelle fusion/fission mechanism is a rare event [19–23]. Interestingly, single-exponential relaxation was scarcely observed by experiment [24,25]. Instead, many studies reported a logarithmic decay function [19,20] which arises from polydispersity of polymer molecules [20,21]. Chain exchange has been found unanimously to slow down with increasing length of the insoluble block, while the effect of corona block length is generally assumed to be negligible. Recently, Zinn et al. [25] observed that the chain exchange rate decreases with increasing corona block length in dilute micellar solution, and attributed it to reduced diffusion rate of copolymer chains through the micellar corona. In semi-dilute micellar solutions, the kinetics retarded more significantly due to an osmotic penalty from overlapping corona chains [21,26]. All these observations were made for linear diblock copolymers.

For triblock copolymer, the micelle behavior and chain exchange could be affected by chain conformation. Loop and bridge are commonly used to describe a triblock copolymer conformation in self-assembly [27–30]. In an end-block (A) selective solvent, an

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ABA type triblock copolymer involved in a micelle can be in (i) loop conformation where the B block bends; or (ii) bridge conformation where the B block straightens across the core of the structure. The presence of different conformations may lead to complex relaxation behavior in triblock micelle solution [31]. Compared to diblock copolymer, exploration on chain exchange kinetics of linear triblock copolymer in micellar solution remains limited [32–35]. Prior to using TR-SANS method, a few studies expressed support for two relaxation processes in triblock copolymer micelles: unimer expulsion/insertion and aggregate fission/fusion [32,33]. Lund et al. [35] has observed strong logarithmic relaxation in triblock copolymer micelles formed in organic solvents using TR-SANS experiments, and found the relaxation process to be slower as compared to their diblock counterpart having similar static micellar properties (aggregation number). They attributed this behaviour to the complexity arising from chain conformation of triblock copolymers. Lu et al. [34] observed faster chain exchange for triblock copolymer than for the corresponding diblock chains having a similar core forming block length. In addition, they also examined BAB copolymer and found much slower kinetics due to separate extractions of the two B blocks from the micelle core.

Computer simulation appears appropriate to investigate chain exchange kinetics in micellar solution because it can avoid the complexity from chain block length polydispersity and directly examine the chain conformations within micelles. Available computational studies applied Monte Carlo, dissipative particle dynamics (DPD), and stochastic dynamic simulations [7,36–40] to investigate chain insertion, expulsion and mixing. All the simulation results thus far showed that the chain exchange follows 1st order kinetics dominated by the chain expulsion mechanism. Interestingly, micelle fission/fusion and small aggregate fragmentation/merging are also found to take place at a similar time scale for short diblock chains [39]. The present study aims to investigate the equilibrium chain exchange kinetics for micellar solutions of triblock copolymer (ABA-type) to advance the fundamental understanding of the mechanisms in relation to the chain conformation. We employ dissipative particle dynamics (DPD) simulation, which was previously used to study kinetics [39–42], thermodynamics [43–46] and dynamics [47] of polymeric micelles. Emphasis is placed on the effect of block lengths on chain exchange of triblock copolymer in comparison with diblock counterpart. We also investigate the conformational behavior of triblock copolymer within micelles and its influence on the chain exchange process.

1.1. Simulation methodology

Dissipative particle dynamics (DPD) method was first introduced by Hoogerbrugge and Koelman [48] to simulate complex fluid systems at coarse-grained level, and has been well-tested to study the thermodynamics and kinetics of block copolymer self-assembly [39,41,49,50]. Beads are used in DPD simulation, each representing a group of atoms. The force acting on a bead is the sum of three pairwise additive forces, namely conservative ($\overrightarrow{F_{ij}^C}$), dissipative ($\overrightarrow{F_{ij}^D}$) and random forces ($\overrightarrow{F_{ij}^R}$):

$$\overrightarrow{F_i} = \sum_{j\neq i} \overrightarrow{F_{ij}^C} + \overrightarrow{F_{ij}^D} + \overrightarrow{F_{ij}^R} \qquad (1)$$

Table 1
Coefficients of conservative force a_{ij}.

	A	B	Water
A	25		
B	48.9	25	
Water	25.9	38.4	25

These forces act only when the separation distance between two beads is within the cut-off value $r_c = 1$. For all the DPD simulations in this study, block copolymers are modeled as bead-spring chains denoted by AαBβAα, where α and β are the numbers of hydrophilic beads (A) and hydrophobic beads (B) in each chain, respectively. Neighbouring beads in a polymer chain are linked by harmonic bonds, $\overrightarrow{F_{ij}^S} = K(r_{ij})\widehat{r_{ij}}$, where r_{ij} is the separation distance between two beads and $K = 4$ is the spring constant used to produce a spring force similar to that by a "weak spring" in the work of Schlijper et al. [51] The reason to use weak springs is because it allows for simulation of copolymer with long blocks within a feasible computational time [40]. Solvent is modeled as individual beads. All beads had the same mass equal to unity and temperature $k_BT = 1$ are used. A simulation cubic box with side length $40r_c$ is chosen after trials shown in Fig. S1 and is used for all the simulations unless otherwise mentioned. The box is filled with the required number of block copolymers and corresponding number of water beads to achieve the fixed polymer concentration $\varphi = 0.05$ with a total bead density equal to 3. We adopt the values for the coefficient of conservative force a_{ij} from the literature as shown in Table 1 [44], which resembles those for Pluronic-type copolymer in aqueous solutions.

The random force coefficient σ_{ij} is set to 3. We use $\Delta t = 0.04$ such that the normalized temperature does not exceed 1.03. Simulations are initiated with a homogeneous solution of copolymers and allowing the free-chains self-assemble to form micelles during simulation. A time duration of around 3.2×10^5 is required for equilibration, and trajectories are obtained thereafter by storing configurations every 4.0 time units for the next time period of 1.4×10^6. To distinguish between unimers and aggregates in the system, we use the distance criterion: chains are considered to belong to the same cluster if any of their hydrophobic beads are separated within the cut-off distance ($r_c = 1.0$) from several testing runs of the particular systems. The simulations are carried out in LAMMPS [52] by adopting a NVT ensemble in HPC clusters of National University of Singapore.

Apart from triblock copolymers, we also study a few diblock copolymer systems for comparison purpose, for which a cubic box with side length $30r_c$ is used. Table 2 lists all the systems investigated in the present study. Note that in our earlier work on short diblock copolymer, multiple relaxation rates are observed due to the presence of a substantial fraction of small aggregates [40]. To avoid the complexity of multiple rates, we have herein chosen only the systems possessing a sufficient portion of large aggregates, which is reflected by a clear peak after the initial decay (from small aggregates) in the plot of probability distribution of aggregation

Table 2
Average micelle aggregation number ($\boldsymbol{P_n}$), radii of gyration for micelles ($\boldsymbol{R_{gm}}$) and their cores ($\boldsymbol{R_{gc}}$).

System	$\boldsymbol{P_n}$	$\boldsymbol{R_{gm}}$ (DPD Units)	$\boldsymbol{R_{gc}}$ (DPD Units)	$\frac{\boldsymbol{R_{gm}-R_{gc}}}{\boldsymbol{R_{gc}}}$
A8B16A8	18±2	3.24±0.06	2.38±0.06	0.27
A8B17A8	22±2	3.39±0.09	2.54±0.07	0.33
A10B16A10	16±1	3.33±0.06	2.27±0.06	0.47
A10B17A10	19±1	3.48±0.05	2.42±0.06	0.44
A10B18A10	20±2	3.49±0.05	2.44±0.04	0.43
A15B17A15	15±1	3.46±0.13	2.04±0.11	0.7
A10B9	36±3	3.32±0.11	2.33±0.12	0.42
A10B10	43±3	3.6±0.16	2.6±0.16	0.38
A12B10	39±3	3.8±0.07	2.6±0.08	0.46
A15B10	34±2	3.8±0.11	2.4±0.1	0.58