Supporting Information

for

Tadpole and Mixed Linear/Tadpole Micelles of Diblock Copolymers: Thermodynamics and Chain Exchange Kinetics

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Chain Expulsion Function

To examine the chain expulsion process, we compute the chain expulsion $E(t)$ function.[1] At time $t = 0$ chains in all aggregates were labeled. A chain is considered escaped and is unlabeled if it leaves the micelle and remains as a unimer for four consecutive time steps. The time evolution of the number of labeled chains $N(t)$ is tracked and the ratio of $N(t)$ to the initial number of labeled chains $N(0)$ is calculated:

$$E(t) = \left\langle \frac{N(t)}{N(0)} \right\rangle \tag{S1}$$

where averaging occurs over different initial states. The chain expulsion function $E(t)$ can be calculated for a specific range of micelle aggregation numbers as is shown in Figure S1. As is seen in both cases of tadpole and linear diblock copolymer micelles expulsion from smaller micelles is somewhat quicker, the difference in rate of chain escape is rather minor, on the order of $10 - 15\%$.
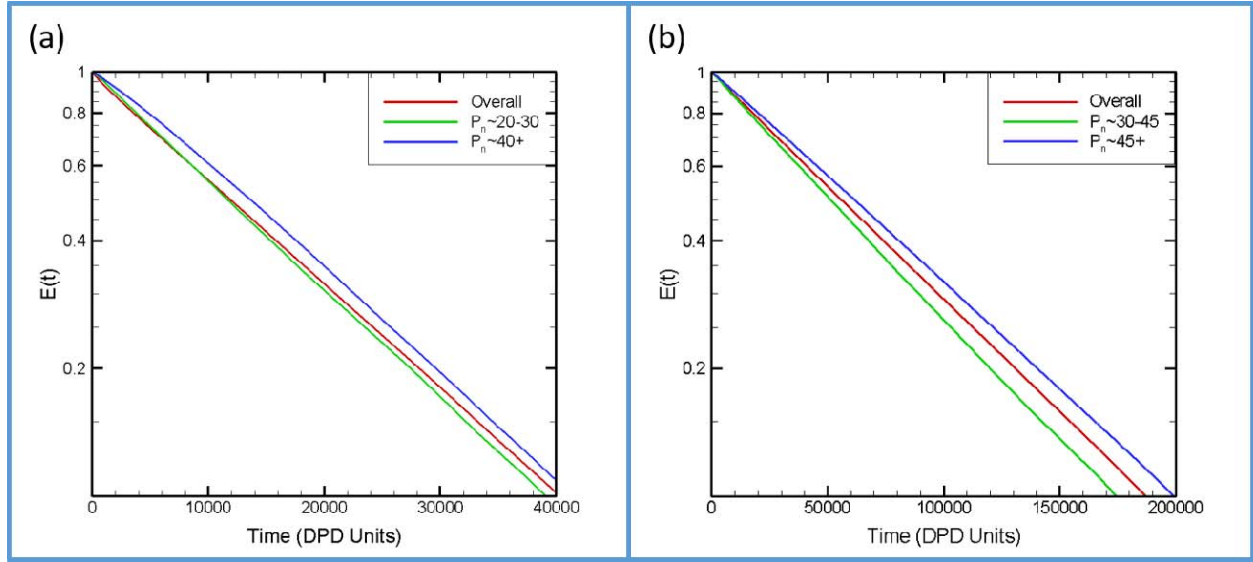
Figure S1: Chain expulsion function for (a) tadpole copolymer (T) micelles (b) linear copolymer micelles (L) of different aggregation numbers

Contrast function for mixed micelles:

The contrast functions $C(t)$ obtained for mixed micelles LT20 and LT60 are compared in Figure S2 to analytical fits using a linear combination of two exponential decay functions with pre-exponential factors corresponding to mixed micelle average composition and time constants extracted from a single exponential fit of corresponding contrast functions in pure tadpole and linear diblock copolymer micelles:

LT20: $$C = 0.2 \exp\left(-{t}/{17500}\right) + 0.8\exp\left(-{t}/{102000}\right) \qquad (S2)$$

LT60 $$C = 0.6 \exp\left(-{t}/{17500}\right) + A_2\exp\left(-{t}/{102000}\right) \qquad (S3)$$

As is seen, using this linear combination of two exponential decays (eqs. S2 and S3) does not provide a satisfactory fit for the contract functions for mixed micelles.
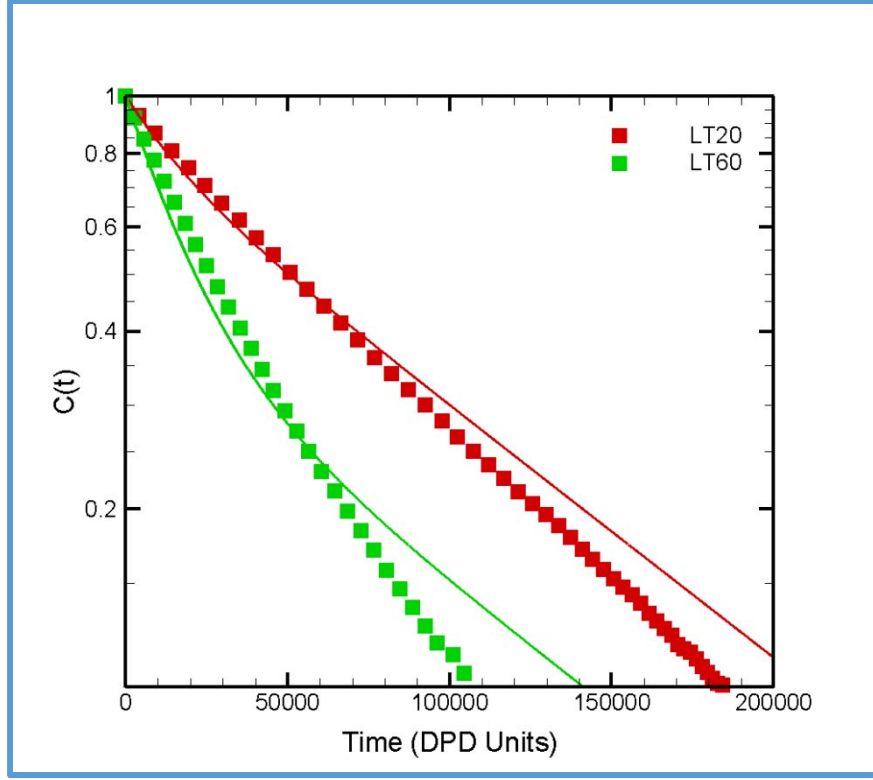
Figure S2: Contrast functions of the mixed micellar systems LT20 (red) and LT60 (green) obtained from simulations (symbols) and the analytical expression (lines) based on the linear combination of two exponential decays given in eqs. S2 and S3.

Even through the bi-exponential fit based on eqs. S2 and S3 has not provided a satisfactory result for mixed micelles, the overall idea of a linear combination of two exponential functions seems logical taking into account the presence of two different species, tadpole and linear diblock copolymer which have different kinetic properties. Thus, we attempted three different bi-exponential fits using general function: $C = A_1 \exp\left(- t/\tau_1\right) + A_2 \exp\left(- t/\tau_2\right)$, where A_1, A_2 are pre-exponential factors related to the fraction of each of components with decay time constants τ_1, τ_2 respectively. In the first case we fixed the pre-exponential factors $A_1 = 0.2$ or 0.8 and $A_2 = 1 - A_1$ for LT20 or LT60 mixed micelles respectively and use τ_1, τ_2 as fitting parameters. In the second case we fixed τ_1 and τ_2 using the decay constant values obtained from single

exponential fit for contrast functions for tadpole and linear chains in mixed micelles (Table 2 of main text) and used A_1 and A_2 as fitting parameters. Finally, we allow all four constants A_1, A_2 and τ_1, τ_2 to be fitting parameters. The results of these fits are presented in Table S1. In all cases a reasonable fit was obtained with the goodness of the fit (χ^2) shown in Table S1.While there are some variations between the fits, in all cases the obtained time constants were significantly different from that obtained from the single exponential fit for pure tadpole micelles and pure linear diblock copolymer micelles, and within 20% of the time constants obtained from single exponential decay fitting of contrast functions for individual components in mixed micelles.

Table S1. Time constants obtained from single exponential function fits for contrast functions for pure micelles (T, L, Lw) and fitting parameters for double exponential function fits for overall contrast function of mixed micelles (parameters shown in bold were fixed) together with chi-square goodness of the fit

		τ_{Faster}		τ_{Slower}		χ^2
	single exponential fit	Double exponential fit*		Double exponential fit *		
		τ_1	A_1	τ_2	A_2	
T	17500	-	-	-		4.9×10^{-5}
L	102000	-		-		3.7×10^{-5}
LT20		34000	**0.2**	90000	**0.8**	1.5×10^{-5}
		44300	0.24	91500	0.74	1.9×10^{-6}
		41000	0.15	**86800**	0.83	4.1×10^{-6}

LT60		26400	**0.6**	71500	**0.4**	$\mathbf{5.8 \times 10^{-6}}$
		29400	0.69	83100	0.3	$\mathbf{1.7 \times 10^{-6}}$
		29500	0.56	**63300**	0.41	$\mathbf{2.2 \times 10^{-5}}$
Lw	13200	-	-	-	-	$\mathbf{1.4 \times 10^{-4}}$
LLw20		25600	**0.2**	95600	**0.8**	$\mathbf{1.3 \times 10^{-5}}$
		32200	0.24	98300	0.75	$\mathbf{1.1 \times 10^{-5}}$
		26500	0.21	**95900**	0.79	$\mathbf{1.3 \times 10^{-5}}$

* Linear combination is fitted using double exponential function of the form

$$C = A_1 \exp\left(-\,{}^{t}/_{\tau_1}\right) + A_2 \exp\left(-\,{}^{t}/_{\tau_2}\right)$$

CMC and Number of Contacts with Solvent

To better understand the chain exchange kinetics in mixed micelles, we investigated the CMC of individual components in mixed micelles and compared them to that in pure micellar systems. We calculated the number of tadpoles or chains in unimers and in small aggregates ($2 \leq P \leq 10$) for pure and mixed micelles. As is seen the number of unimer tadpoles or chains decreases in mixed micelles following the overall tadpole/chain concentration. However, the representation of tadpoles in small aggregates is less and chains is more than dictated by the overall concentration of the components. For less hydrophobic chains L_w both unimer amount and number of chains in mixed aggregates is less than dictated by the overall number of L_w chains in the system. This is consistent with slower chain exchange of L_w or tadpole chains observed in mixed micelles.

Table S2. Number of tadpole T, linear diblock copolymers L and less hydrophobic diblock copolymers L_w in unimers and small aggregates (2≤P≤10) in equilibrium with pure T, L and L_w micelles and mixed micelles LT20, LT60 and LL_w20.

Micelle-polymer type	Number of unimers	Number of chain in aggregates $2 \leq P \leq 10$
T	10.3 ± 3.2	19.2 ± 6.8
LT60-T	6.3 ± 2.3	6.7 ± 2.5
LT20-T	2.5 ± 1.5	1.4 ± 0.3
L	4.5 ± 1.9	1.9 ± 1.5
LT20-L	2.9 ± 1.6	3.5 ± 1.8
LT60-L	1.6 ± 1.3	2.7 ± 1.4
LL_w20-L	3.5 ± 2	2.2 ± 1.1
LL_w20-L_w	3.4 ± 1.9	1.4 ± 0.3
L_w	16.3 ± 3.9	21.5 ± 6.4

Further, we also calculated the number of contacts per chain between hydrophobic block of tadpoles or linear chains with the solvent beads when the polymer chains reside in solution as unimers, dimers and trimers. It is observed that the number of contacts is reduced when chains/tadpoles reside in small aggregates or in micelles.

Table S3. The average number of contacts per chain between hydrophobic blocks of tadpole or linear chain and solvent in unimers, dimers, trimers and micelles

Number of contacts per chain	Unimer	Dimer	Trimer	Micelle
Linear Chains (L)	43.3 ± 5.7	35.4 ± 4.3	31.1 ± 3.9	11.9 ± 0.5
Tadpole Chains (T)	42.6 ± 1.7	33.6 ± 3.1	29.7 ± 3.3	13.1 ± 0.5

Contribution of different kinetic events in mixed micelles

To understand the origin of the inter-dependence of tadpole and linear chain exchange kinetics in mixed micelles, we analyzed native chain expulsion. To this end, all chains present at time $t = 0$ in a micelle are selected and their time evolution is followed until about 50% of chains left the micelle. A chain is considered to escape the micelle if it resides outside the micelle for four consecutive time steps. The kinetic mechanism by which a copolymer chain escaped the micelle is classified as unimer expulsion or aggregate escape ($P_n \geq 2$). The frequency of the kinetic events and contribution of each event (i.e. the frequency of the event weighted by the number of chains escaped) are evaluated by grouping the corresponding events and averaging over different micelles [with an aggregation numbers in the range $20 \leq P_n \leq 40$ for pure tadpoles and $30 \leq P_n \leq 50$ for linear and mixed micelles] and different initial states. While unimer exchange is heavily dominant in all cases ($\geq 70\%$), we also observed aggregate escape events, especially in tadpole-dominated micelles, as is seen in Figure S3. Among the non-unimer escape events in mixed micelles $\sim 10 - 20\%$ are attributed to escape of mixed tadpole/linear chain small aggregates. These contributed to about 10% of chains (3% of linear chains and 7% of tadpoles) in LT20 and about 20% of chains (12% of linear chains and 8% of tadpoles) in LT60 escaped via mixed aggregate escape. Such mixed aggregate escape occurs slower than pure tadpole aggregate escape, but quicker than linear chain escape therefore slowing down the average rate of tadpole escape and increasing chain escape

in qualitative agreement with the observed contrast function (Figure 4). Mixed small aggregate escape from mixed micelles of linear chains of different hydrophobicity LL_w20 contributed only 3.7%.
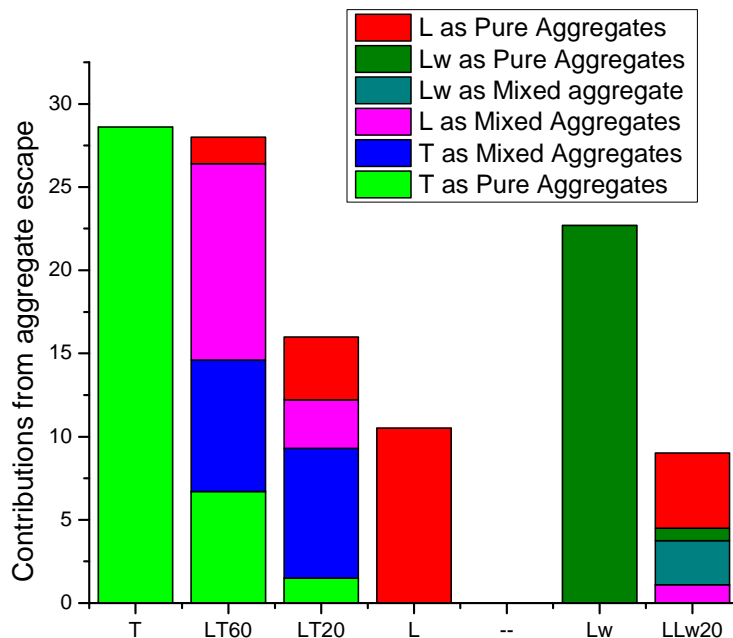

Figure S3. Contribution of aggregate escape mechanism in tadpole (T), linear (L), less hydrophobic linear (L_w) chains and mixed (LT20, LT60, LL_w20) micelles. Contribution of escaped aggregates containing tadpoles only (green bars), linear chains only (red bars), less hydrophobic linear chains only (dark green bars) as well as linear chains (magenta bars) and tadpoles (blue bars) or less hydrophobic linear chains (cyan bars) escaped as part of mixed tadpole/linear or linear/linear aggregates are shown.

Unimer escape in mixed micelles

To test whether chain escape as unimers reflects the tendency observed for the contrast functions shown in Figure 6 we analyzed the cumulative escape of native chains as unimers from different aggregates. We tracked and summed up with respect to time the average number of chains escaped as unimers from all micelles $N_{unimer}(t)$. The calculation was performed until about 50% of all chains escaped. To compare tadpole and linear unimer escape from mixed micelles $N_{unimer}(t)$ was normalized by the total number of unimers available $N_{unimer-escape}$, leading to

$$F(t) = \frac{N_{unimer}(t)}{N_{unimer-escape}} \qquad (4)$$

Figure S4 shows the relative fraction of tadpole unimers and linear chain unimers $1 - F(t)$ remained in mixed LT20 micelles. The analysis of the data reveals that the unimer escape rate of tadpoles is slower than in pure tadpole micelles and varies with composition, speeding up with increased fraction of tadpole block copolymers in mixed micelles. However unimers of linear diblock copolymers escape from mixed micelles in a rather similar manner to that in pure linear diblock copolymer micelles. The observed differences between the chain exchange contrast function $C(t)$ (Figure 6) and unimer escape $1 - F(t)$ (Figure S4) are attributed to small aggregate exchange and chain re-entrance to the same micelle, which contribute only to C(t).
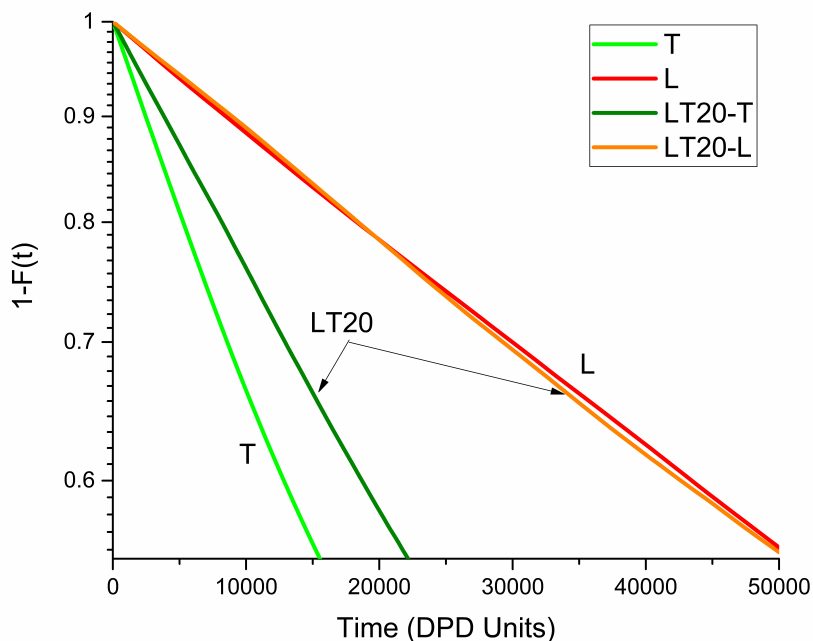

Figure S4: Native chain unimer expulsion 1-F(t) in pure tadpole (T) or linear (L) diblock copolymer micelles, native tadpole unimer (LT20-T) and native linear copolymers unimer (LT20-L) expulsion in mixed (LT 20) micelles.

References:

1.   Li, Z.; Dormidontova, E. E. Equilibrium chain exchange kinetics in block copolymer micelle solutions by dissipative particle dynamics simulations. *Soft Matter* **2011,** *7* (9), 4179-4188.