

Electronic Supplementary Information For:

Fluorophore Exchange Kinetics in Block Copolymer Micelles with Varying Solvent-Fluorophore and Solvent-Polymer Interactions

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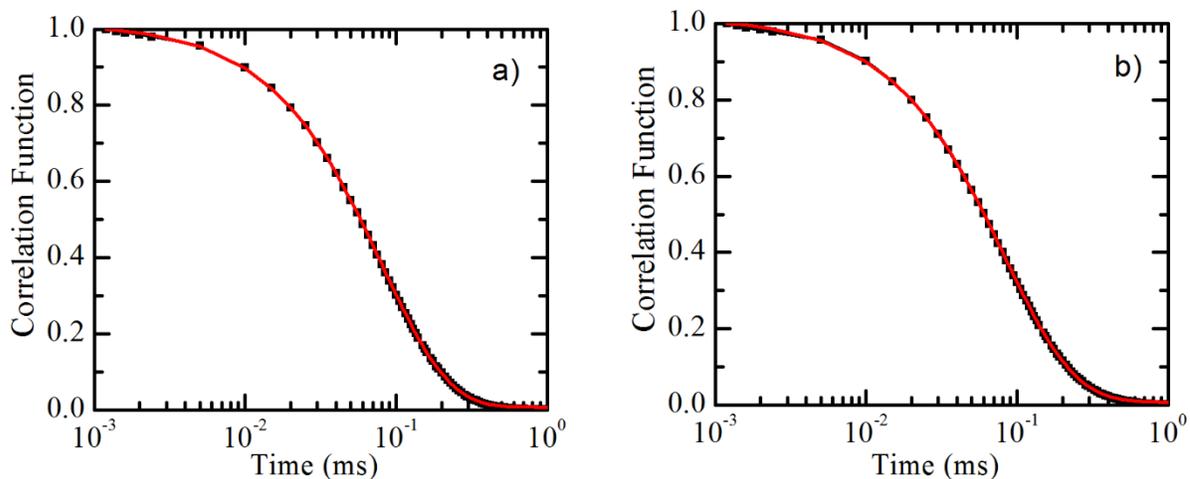


Figure S1: Dynamic light scattering data obtained from PCL-PEO micelles in a solvent mixture containing 5% THF. Data sets a) and b) were obtained from two samples of the same composition that were prepared separately. Solid red curve is a fit to the data using the method of cumulants.

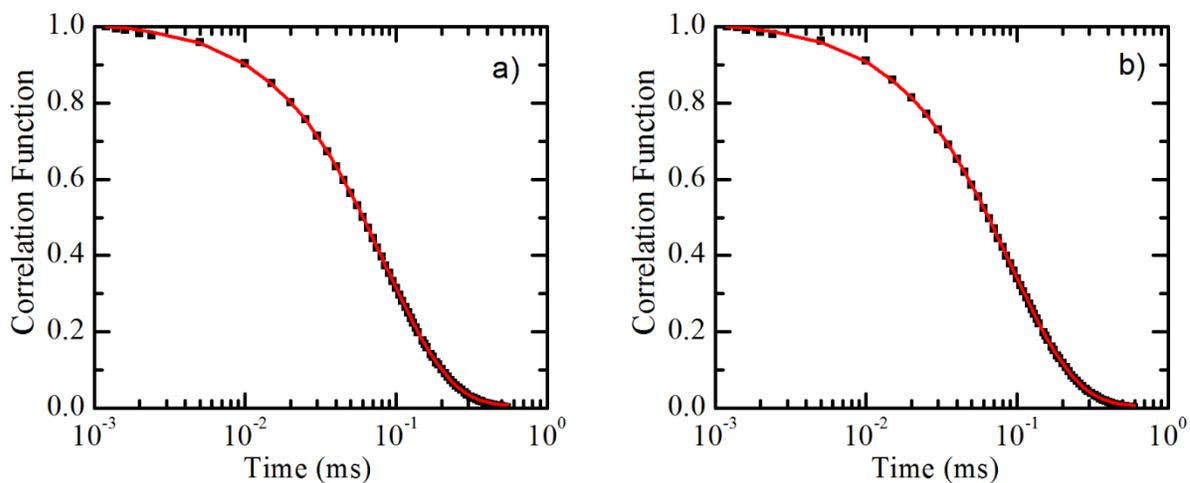


Figure S2: Dynamic light scattering data obtained from PCL-PEO micelles in a solvent mixture containing 10% THF. Data sets a) and b) were obtained from two samples of the same composition that were prepared separately. Solid red curve is a fit to the data using the method of cumulants.

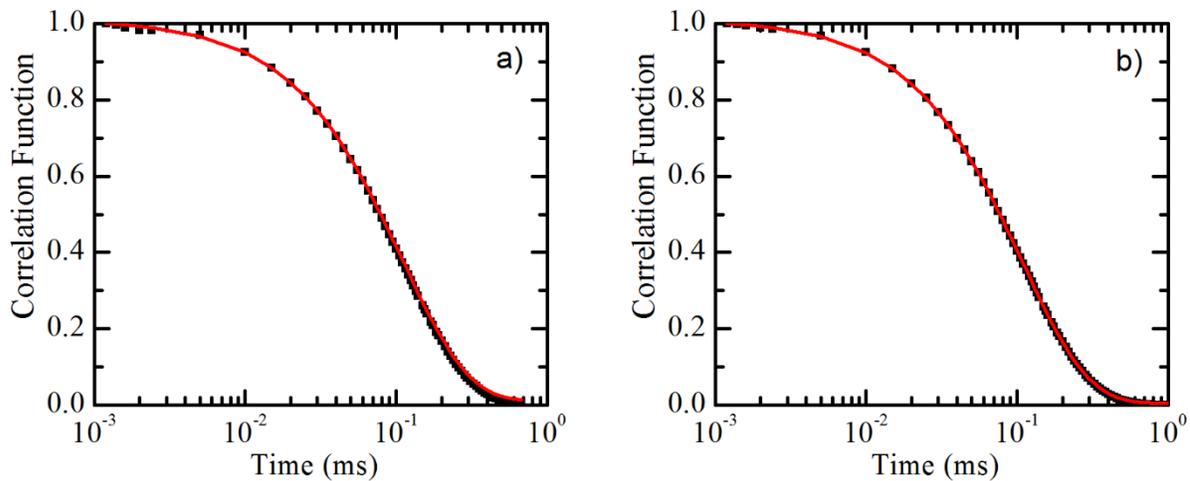


Figure S3: Dynamic light scattering data obtained from PCL-PEO micelles in a solvent mixture containing 20% THF. Data sets a) and b) were obtained from two samples of the same composition that were prepared separately. Solid red curve is a fit to the data using the method of cumulants.

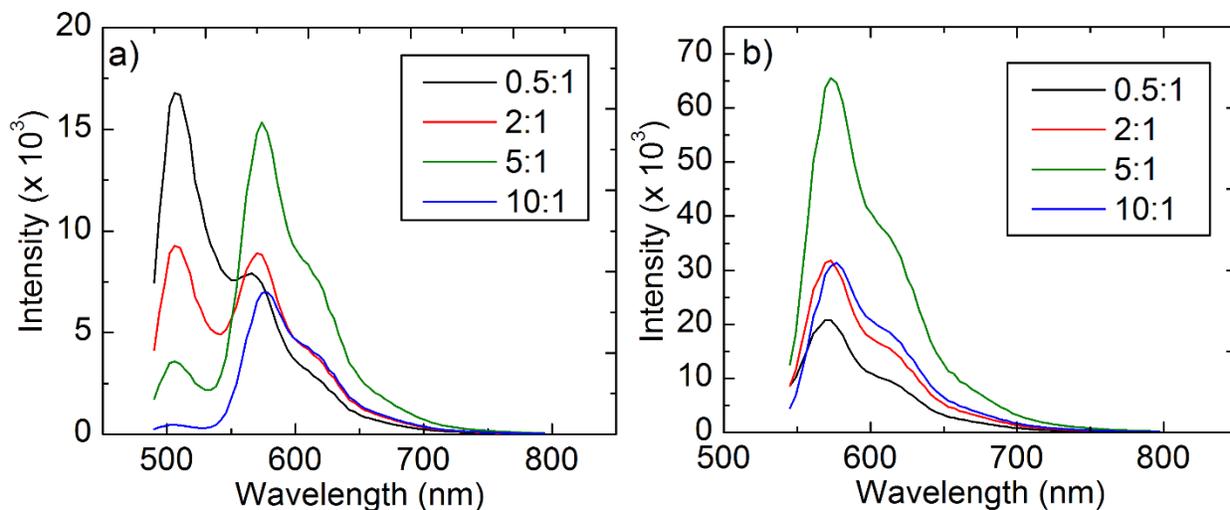


Figure S4: Fluorescence spectra measured at a) 450 nm and b) 505 nm of pre-mixed micelles in water. The legend indicates the molar ratio of DiI : DiO used in the micelle preparation. Fluorescence spectroscopy experiments were conducted using a Tecan M200 Pro microplate reader in fluorescence mode. The excitation bandwidth was < 5 nm (for wavelength $\lambda \leq 315$ nm) and < 9 nm (for $\lambda > 315$ nm). The emission bandwidth was < 20 nm. The PEO-PCL diblock copolymer used in this experiment had the following characteristics: $M_{n, \text{PEO}} = 2$ kg/mol, $M_{n, \text{PCL}} = 3$ kg/mol, 60 wt% PCL. The micelles were prepared through dialysis in Millipore water (1 wt% polymer, 8 $\mu\text{mol/L}$ DiO).

Table S1: Calculations described in the main text. Here, the total volume of the PEO-PCL block copolymer was used to calculate the aggregation number (i.e. N_{agg} = hydrodynamic volume of the micelle / PEO-PCL chain volume).

% THF	R_h (nm)	V_h (nm ³)	N_{agg}	$\rho_{solvent}$ (g/mL)	g polymer / L solvent	# chains / L solvent	# micelles / L solvent	# DiI molecules / micelle	# DiO molecules / micelle
5	6.6	1204	140	0.994	9.92	1.01E+21	7.26E+18	1.6	0.3
5	6.8	1317	153	0.994	9.92	1.01E+21	6.64E+18	1.8	0.4
10	6.1	951	110	0.989	9.87	1.01E+21	9.14E+18	1.3	0.3
10	6.5	1150	133	0.989	9.87	1.01E+21	7.56E+18	1.5	0.3
20	6.5	1150	133	0.978	9.76	9.96E+20	7.47E+18	1.6	0.3
20	6.4	1098	127	0.978	9.76	9.96E+20	7.83E+18	1.5	0.3

R_h = hydrodynamic radius measured from DLS

V_h = hydrodynamic volume (assuming a sphere)

N_{agg} = aggregation number

Table S2: Calculations described in the main text. Here, only the PCL block was used to calculate the aggregation number (i.e. N_{agg} = hydrodynamic volume of the micelle / PCL block volume).

% THF	R_h (nm)	V_h (nm ³)	N_{agg}	$\rho_{solvent}$ (g/mL)	g polymer / L solvent	# chains / L solvent	# micelles / L solvent	# DiI molecules / micelle	# DiO molecules / micelle
5	6.6	1204	207	0.994	9.92	1.01E+21	4.90E+18	2.4	0.5
5	6.8	1317	226	0.994	9.92	1.01E+21	4.48E+18	2.6	0.5
10	6.1	951	163	0.989	9.87	1.01E+21	6.17E+18	1.9	0.4
10	6.5	1150	197	0.989	9.87	1.01E+21	5.10E+18	2.3	0.5
20	6.5	1150	197	0.978	9.76	9.96E+20	5.04E+18	2.3	0.5
20	6.4	1098	188	0.978	9.76	9.96E+20	5.29E+18	2.2	0.4

Relevant parameters for calculations:

$M_{w,PEO}$ = 1.9 kg/mol

$M_{w,PCL}$ = 4.0 kg/mol

ρ_{PEO} = 1.125 g/cm³

ρ_{PCL} = 1.14 g/cm³

$V_{block,PEO}$ = 2804 Å³

$V_{block,PCL}$ = 5827 Å³

CMC = 0.002 wt%

Polymer concentration in micelles = 1 wt%

DiI concentration = 19.3 µmol/L

DiO concentration = 3.9 µmol/L

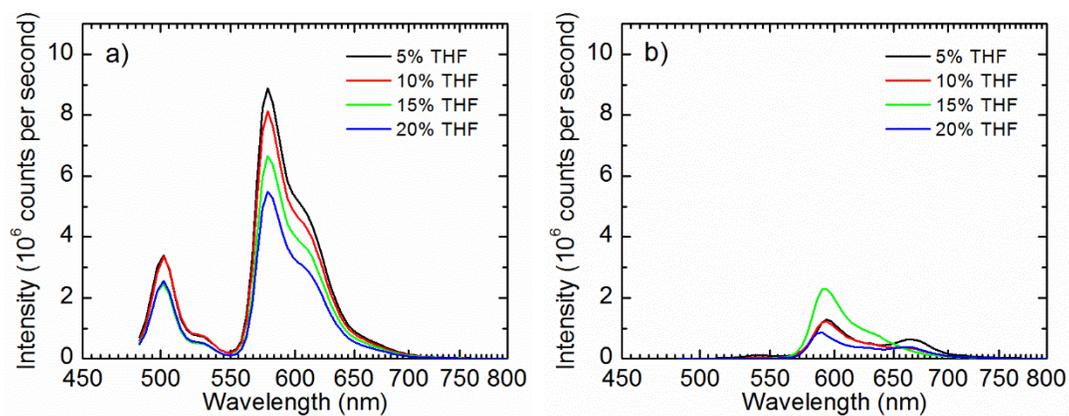


Figure S5: Fluorescence emission spectra (at an excitation wavelength of 450 nm) are shown for a) water/THF mixtures without polymer micelles and b) premixed micelle solutions (in which both DiI and DiO were encapsulated within the micelles at the very beginning of the micelle preparation). The fluorophore concentrations in the solutions were the same as that described in the main text: 19.3 and 3.9 $\mu\text{mol/L}$ for DiI and DiO, respectively (5:1 molar ratio of DiI:DiO).

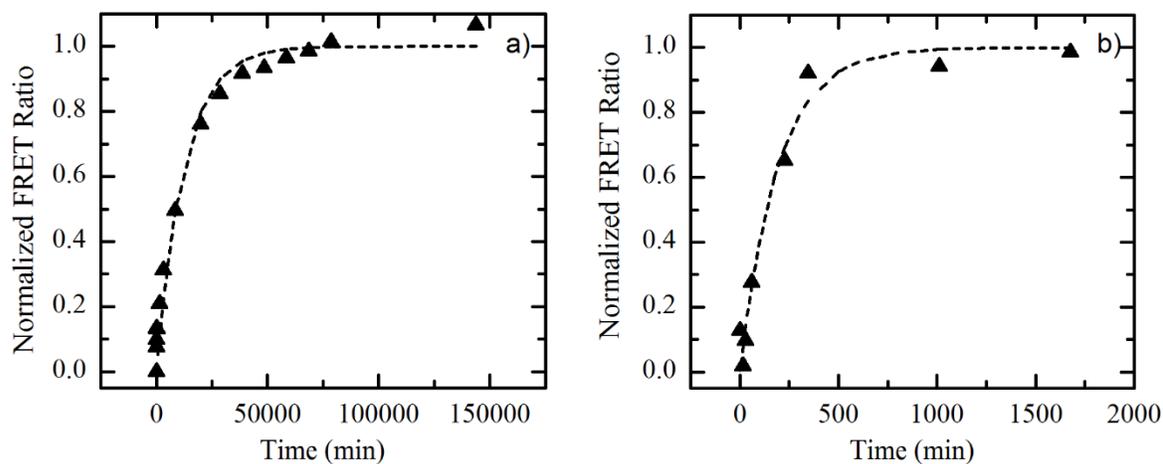


Figure S6: Normalized FRET ratio as a function of time for post-mixed micelle solutions containing a) 5 vol% THF and b) 10 vol% THF. Dashed curves represent the fit to the data obtained on post-mixed micelles (equation 3; described in main text) with the resulting time constants: a) 1.2×10^4 min (5% THF) and b) 1.9×10^2 min (10% THF). The normalized FRET ratio is defined as $[FR(t) - FR_o] / [FR_\infty - FR_o]$ where $FR(t)$, FR_o , and FR_∞ are the FRET ratio measured at time t , initial ($t=0$) FRET ratio, and long time ($t \rightarrow \infty$) FRET ratio, respectively.

Table S3: Parameters extracted from the fit of equation 3 to the data in Figures 6 and S5

Vol% THF	FR_o	FR_∞	τ (min)	R^2
5	0.45	0.64	1.2×10^4	0.995
10	0.49	0.65	1.9×10^2	0.986