Supporting Information

Chemicals and Instrumentation. Beside the IBH time-resolved fluorometer which was used to acquire the fluorescence decays and the surface tension experiments which were performed on a DuNouy Tensiometer from the CSC Scientific Company, Inc., all other instruments, polymer samples, and chemicals were the same as those used in an earlier publication.[1]

Analysis of the fluorescence decays. The fluorescence decays of Py-HASE were quantitatively analyzed using the *blob* model which has been described in numerous earlier publications.[1-7] The blob model describes the kinetics of excimer formation inside the polymer coil with three parameters, namely, the average number of pyrene groups in a blob, $<n>$, the rate constant of excimer formation inside a blob, k_{blob}, and the rate at which pyrene groups exchange from blob to blob, $k_{\mathrm{e}}[blob]$, where k_{e} is the exchange rate constant and $[blob]$ is the blob concentration inside the polymer coil. The equation used to fit the monomer decays is shown hereafter.

$$[Py^*]_{(t)} = [Py^*_{diff}]_{(t=0)} \exp\left[-\left(A_2 + \frac{1}{\tau_M} \right) t - A_3 \left(1 - \exp\left(-A_4\, t \right) \right) \right] + [Py^*_{free}]_{(t=0)} \exp\left(-t / \tau_M \right) \qquad (1)$$

The parameters A_2, A_3, and A_4 are given in Equation 2.

$$A_2 = <n> \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \quad A_3 = <n> \frac{k_{blob}^2}{\left(k_{blob} + k_e [blob] \right)^2} \quad A_4 = k_{blob} + k_e [blob] \qquad (2)$$

Fitting the monomer decays with Equation 1 provides the fractions $f_{Mdiff} = [Py^*_{diff}]_{(t=0)} / \left([Py^*_{diff}]_{(t=0)} + [Py^*_{free}]_{(t=0)} \right)$ and $f_{Mfree} = [Py^*_{free}]_{(t=0)} / \left([Py^*_{diff}]_{(t=0)} + [Py^*_{free}]_{(t=0)} \right)$ which

represent the fractions of pyrene monomers which form excimer via diffusion ($[Py^*_{diff}]_{(t=0)}$) and those which are isolated ($[Py^*_{free}]_{(t=0)}$) and do not form an excimer, respectively. The index *M* indicates that these fractions were obtained from the monomer decays.

The excimer decays were fitted with Equation 3.

$$[E^*] = -[Py^*_{diff}]_{(t=0)}\, e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^{\,i}}{i!} \frac{A_2 + i\,A_4}{\frac{1}{\tau_M} - \frac{1}{\tau_{E0}} + A_2 + i\,A_4} \exp\left(-\left(\frac{1}{\tau_M} + A_2 + i\,A_4 \right) t \right)$$
$$+ \left([E0^*]_{(t=0)} + [Py^*_{diff}]_{(t=0)}\, e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^{\,i}}{i!} \frac{A_2 + i\,A_4}{\frac{1}{\tau_M} - \frac{1}{\tau_{E0}} + A_2 + i\,A_4} \right) e^{-t/\tau_{E0}} + [D^*]_{(t=0)}\, e^{-t/\tau_D} \qquad (3)$$

Fits of the excimer decays allows the determination of the fractions

$$f_{Ediff} = [Py^*_{diff}]_{(t=0)} / \left([Py^*_{diff}]_{(t=0)} + [E0^*]_{(t=0)} + [D^*]_{(t=0)} \right),$$

$$f_{EE0} = [E0^*]_{(t=0)} / \left([Py^*_{diff}]_{(t=0)} + [E0^*]_{(t=0)} + [D^*]_{(t=0)} \right),$$

$$\text{and } f_{ED} = [D^*]_{(t=0)} / \left([Py^*_{diff}]_{(t=0)} + [E0^*]_{(t=0)} + [D^*]_{(t=0)} \right),$$

where the meaning of the equilibrium concentrations $[Py^*_{diff}]_{(t=0)}$, $[Py^*_{free}]_{(t=0)}$, $[E0^*]_{(t=0)}$, and $[D^*]_{(t=0)}$ is given hereafter. The fractions obtained from fitting the excimer decays with Equation 3 have the index *E*. In Equations 1 and 3, $[Py^*_{diff}]_{(t=0)}$, $[Py^*_{free}]_{(t=0)}$, $[E0^*]_{(t=0)}$, and $[D^*]_{(t=0)}$ represent the equilibrium concentrations of the pyrenes which form excimer via diffusion, are too isolated to form excimer and fluoresce with their lifetime τ_M, are pre-associated and form an excimer upon direct excitation, and are pre-associated and form a long-lived excimer upon absorption of a photon, respectively. The lifetimes of $E0^*$ and D^* are τ_{E0} and τ_D, respectively. The parameters $\langle n \rangle$, k_{blob}, $k_e[blob]$ were fit globally. The

parameters, which were not fit globally, were $[Py^*_{diff}]_{(t=0)}$, $[Py^*_{free}]_{(t=0)}$, $[E0^*]_{(t=0)}$, $[D^*]_{(t=0)}$, τ_{E0}, and τ_D. The monomer lifetime, τ_M, was fixed in the global analysis to equal 165 ns. It was determined from fitting the fluorescence decay of a poly(ethylene oxide) capped at one end with pyrene in 0.01 M Na_2CO_3 buffer with (162 ns) and without surfactant (165 ns). All χ^2 were between 0.96 and 1.18 and the distribution of the residuals and the autocorrelation function of the residuals were randomly distributed around zero. The parameters retrieved from the global analysis of the fluorescence decays are listed in the following Tables 1 and 2. The χ^2 is obtained from the global fit of both monomer and excimer decays. According to published procedures,[1,3,5,7] the fractions f_{Mdiff}, f_{Mfree}, f_{Ediff}, f_{EE0}, and f_{ED} were then used to determine the fraction f_{diff}, f_{free}, f_{E0}, and f_D for the pyrene species at equilibrium under the form of Py^*_{diff}, Py^*_{free}, $E0^*$, and D^*, respectively. The f_{diff}, f_{free}, f_{E0}, and f_D values are listed in Table 3. The fraction of aggregated pyrenes (f_{agg}) is obtained by summing f_{E0} and f_D.[1,3,5,7]

The parameters $<n>$, k_{blob}, and k_e[blob] show substantial scattering. Because these parameters describe the formation of excimer via diffusion, it has been our experience that they can be obtained with sufficient accuracy when the pyrene content of the polymer is, at least, larger than 100 μmol/g of polymer.[1-5,7] In this case, the pyrene content of the Py-HASE is too low and equals 35 μmol/g. Thus many pyrene groups are isolated and do not form excimer via diffusion so that f_{Mfree} (= 1 – f_{Mdiff}) is large. Indeed f_{Mfree} is always larger than 0.25 and can be as large as 0.73 as shown in Table 1. Ideally one would like f_{Mfree} to be smaller than 0.05 to obtain a good accuracy on the $<n>$, k_{blob}, and k_e[blob] parameters.[1-5,7] Nevertheless, the scattering observed with $<n>$, k_{blob}, and k_e[blob] is much smaller for the fractions f_{Mdiff}, f_{Mfree}, f_{Ediff}, f_{EE0}, and f_{ED}. Since these values are used to determine the fractions f_{diff}, f_{free}, f_{E0}, and f_D, these later fractions are obtained with reasonable accuracy.

The data retrieved from the global analysis of the fluorescence decays indicate that the lifetime of the excimer (τ_E) equals 50±4 ns, a reasonable value,[1-5,7] whether in the presence or absence of surfactant. The long-lived pyrene dimers emit with a lifetime (τ_D) equal to 126±11 ns which is also reasonable

according to our earlier studies.[2,4,6,7] When the pyrene aggregates melt by association with the surfactant, the concentration of long-lived dimers decreases to undetectable levels for SDS concentrations larger than 2.1 mmol.L^{-1}. Under those conditions, the lifetime of the long-lived dimers was either set to equal 126 ns (the average of the τ_D values obtained at lower SDS concentrations), or $[D^*]_{(t=0)}$ was set to equal 0.0 in the analysis.

References

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Table 1: Parameters retrieved from the analysis of the fluorescence decays of the monomer with Equation 1. The lifetime of the monomer (τ_M) is fixed to equal 165 ns.

[SDS] mmol.L^{-1}	f_{Mdiff}	k_{blob} 10^7 ns^{-1}	<*n*>	$k_e[blob]$ 10^6 ns^{-1}	f_{Mfree}	χ^2
0.00	0.43	1.6	0.6	4.1	0.57	1.13
0.13	0.40	2.3	0.6	6.1	0.60	1.06
0.21	0.30	4.0	0.6	11.3	0.70	1.11
0.51	0.27	5.8	0.7	14.3	0.73	1.14
1.0	0.35	4.8	0.7	7.5	0.65	1.17
1.2	0.36	5.8	0.7	8.0	0.64	0.97
1.5	0.31	6.4	1.0	11.1	0.69	1.19
1.8	0.34	3.8	1.0	5.6	0.66	1.11
2.1	0.38	3.6	1.1	3.8	0.62	1.11
2.5	0.43	2.9	1.6	4.1	0.57	1.16
3.0	0.50	1.5	2.6	4.2	0.50	1.11
3.9	0.68	1.1	2.4	8.0	0.32	1.16
4.0	0.71	1.0	2.2	10.2	0.29	1.11
4.3	0.74	1.1	1.7	12.5	0.26	1.18
4.5	0.75	0.9	2.0	8.8	0.25	1.06
5.0	0.75	0.8	2.0	5.8	0.25	1.14
6.0	0.69	1.0	1.6	11.7	0.31	1.07
7.0	0.70	0.8	1.9	5.8	0.30	1.12
8.0	0.70	0.8	1.8	5.2	0.30	1.11
10	0.68	0.8	1.9	4.9	0.32	1.08
20	0.67	0.8	1.6	6.6	0.33	1.09
50	0.57	0.7	1.8	5.9	0.43	1.04

Table 2: Parameters retrieved from the analysis of the fluorescence decays of the excimer with Equation 3. The lifetime of the monomer (τ_M) is fixed to equal 165 ns.

[SDS] mmol.L^{-1}	f_{Ediff}	f_{EE0}	f_{ED}	τ_E ns	τ_D ns	χ^2
0.00	0.21	0.65	0.14	45	108	1.13
0.13	0.17	0.70	0.13	47	112	1.06
0.21	0.07	0.82	0.11	51	133	1.11
0.51	0.10	0.79	0.11	50	131	1.14
1.0	0.11	0.78	0.10	50	129	1.17
1.2	0.14	0.76	0.09	50	130	0.97
1.5	0.38	0.59	0.03	47	140	1.19
1.8	0.52	0.47	0.02	44	126	1.11
2.1	0.59	0.40	0.01	46	126	1.11
2.5	0.66	0.34	0.01	45	126	1.16
3.0	0.74	0.25	0.01	46	126	1.11
3.9	0.82	0.18	0.00	48	N.A.*	1.16
4.0	0.84	0.15	0.01	47	126	1.11
4.3	0.87	0.13	0.00	46	N.A.*	1.18
4.5	0.86	0.14	0.00	49	N.A.*	1.06
5.0	0.87	0.13	0.00	52	126	1.14
6.0	0.88	0.12	0.00	48	N.A.*	1.07
7.0	0.87	0.13	0.00	53	N.A.*	1.12
8.0	0.87	0.13	0.00	58	N.A.*	1.11
10	0.88	0.12	0.00	57	126	1.08
20	0.90	0.10	0.00	53	N.A.*	1.09
50	0.89	0.11	0.00	57	N.A.*	1.04

* The concentration $[D^*]_{(t=0)}$ in Equation 3 was set to equal 0.0 in the analysis of the excimer decays.

Table 3: Fractions f_{diff}, f_{free}, f_{E0}, and f_D obtained as a function of SDS concentration according to a procedure established in earlier publications.[1,3,5,7]

[SDS] mmol.L^{-1}	f_{Ediff}	f_{free}	f_{E0}	f_D
0.00	0.16	0.22	0.51	0.11
0.13	0.14	0.20	0.56	0.10
0.21	0.06	0.15	0.70	0.09
0.51	0.08	0.22	0.61	0.09
1.0	0.09	0.17	0.65	0.09
1.2	0.11	0.20	0.61	0.07
1.5	0.23	0.39	0.36	0.02
1.8	0.26	0.50	0.23	0.01
2.1	0.30	0.48	0.21	0.01
2.5	0.35	0.47	0.18	0.00
3.0	0.43	0.42	0.14	0.00
3.9	0.59	0.28	0.13	0.00
4.0	0.63	0.25	0.11	0.00
4.3	0.67	0.23	0.10	0.00
4.5	0.66	0.23	0.11	0.00
5.0	0.67	0.23	0.10	0.00
6.0	0.64	0.28	0.08	0.00
7.0	0.64	0.27	0.09	0.00
8.0	0.63	0.27	0.10	0.00
10	0.62	0.30	0.08	0.00
20	0.62	0.31	0.07	0.00
50	0.53	0.40	0.07	0.00