Supporting Information

for

A Pyrenyl Derivative with a Four Atom-Linker that Can Probe the Local Polarity of Pyrene-Labeled Macromolecules

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Outline of Supporting Information

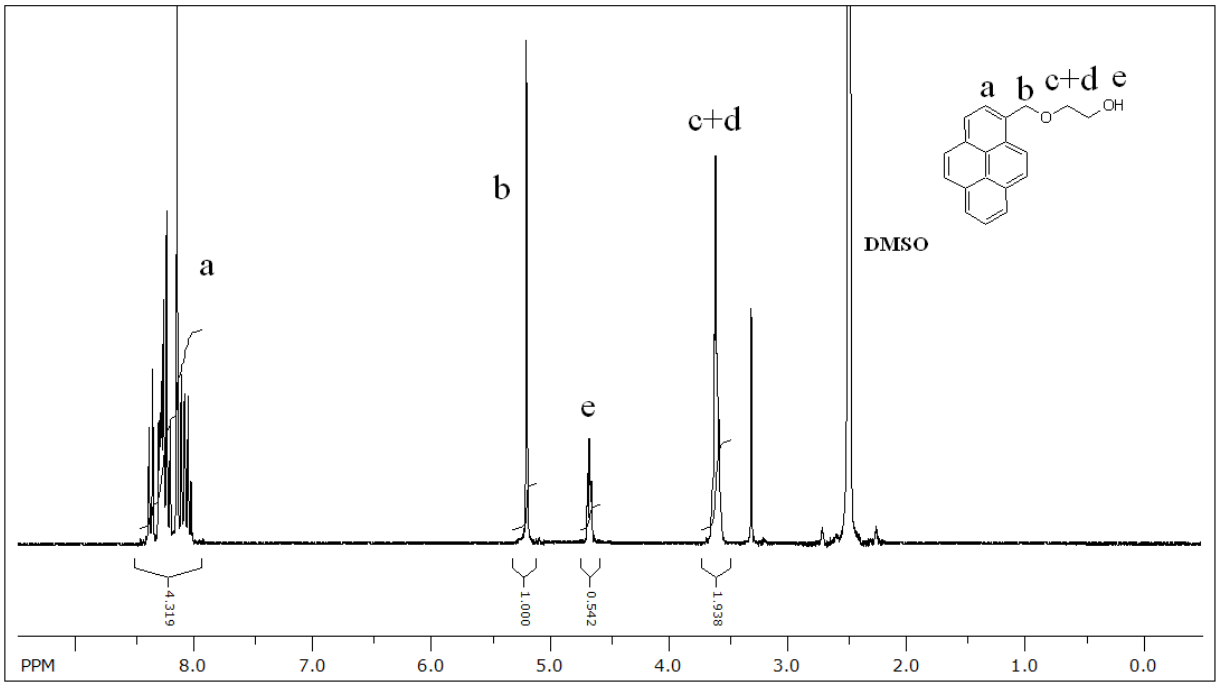


Figure S1. ^{1}H NMR spectrum of PyMeEGOH in DMSO-d_6.

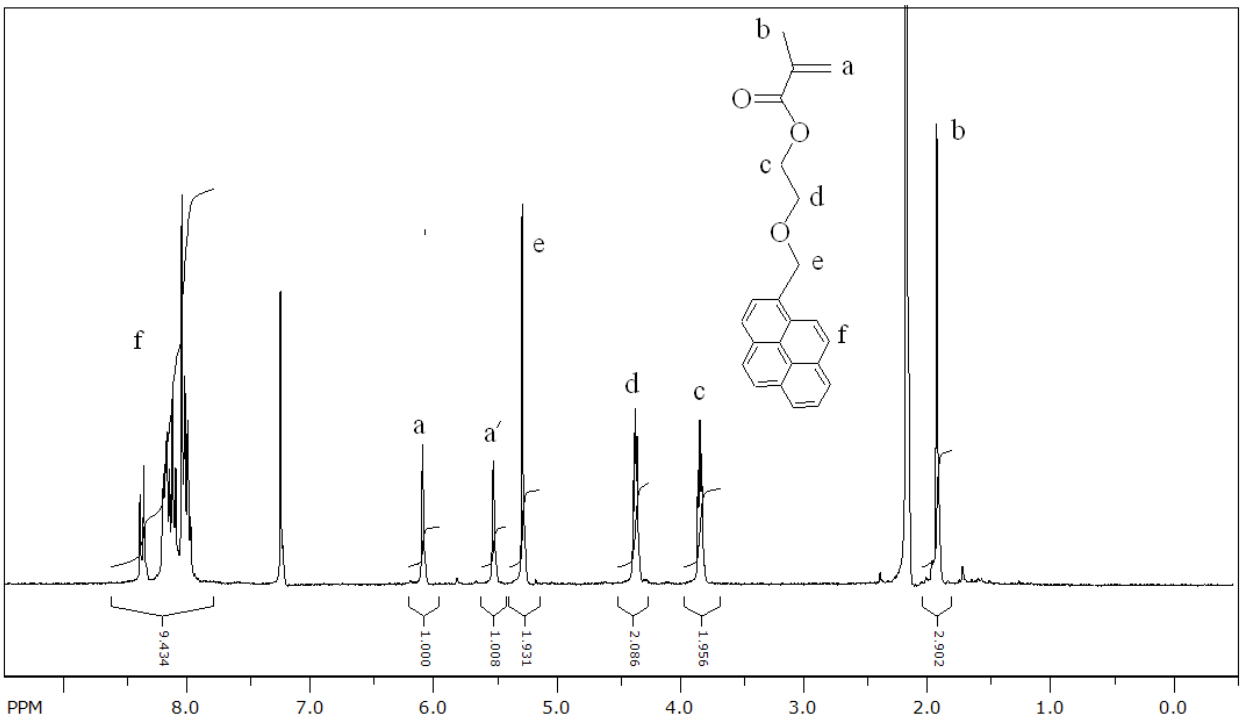


Figure S2. ^{1}H NMR spectrum of PyMeEG-MA in $CDCl_3$.

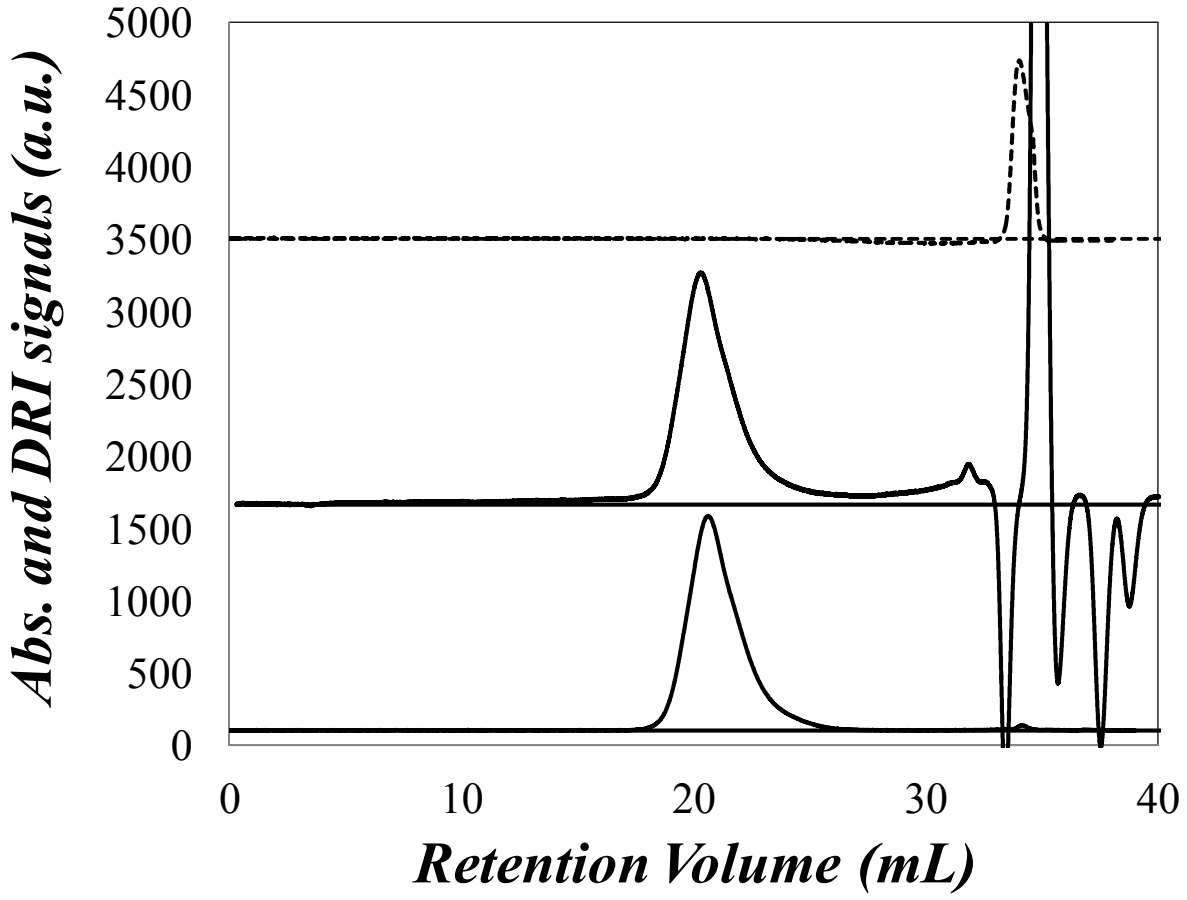
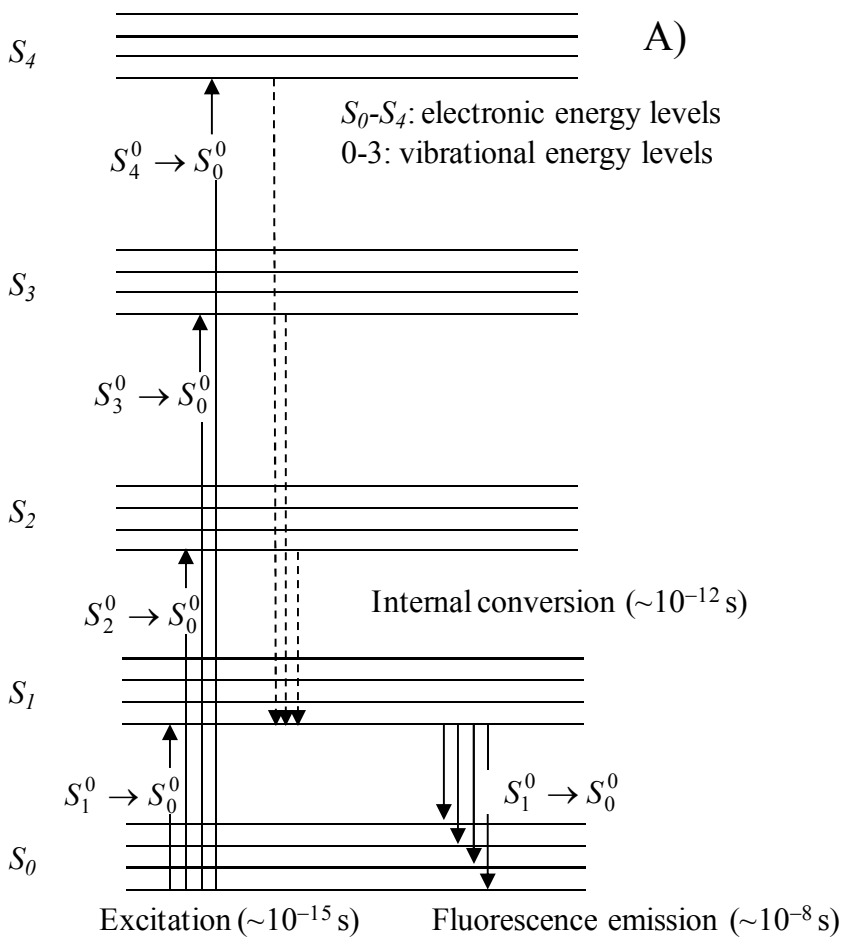
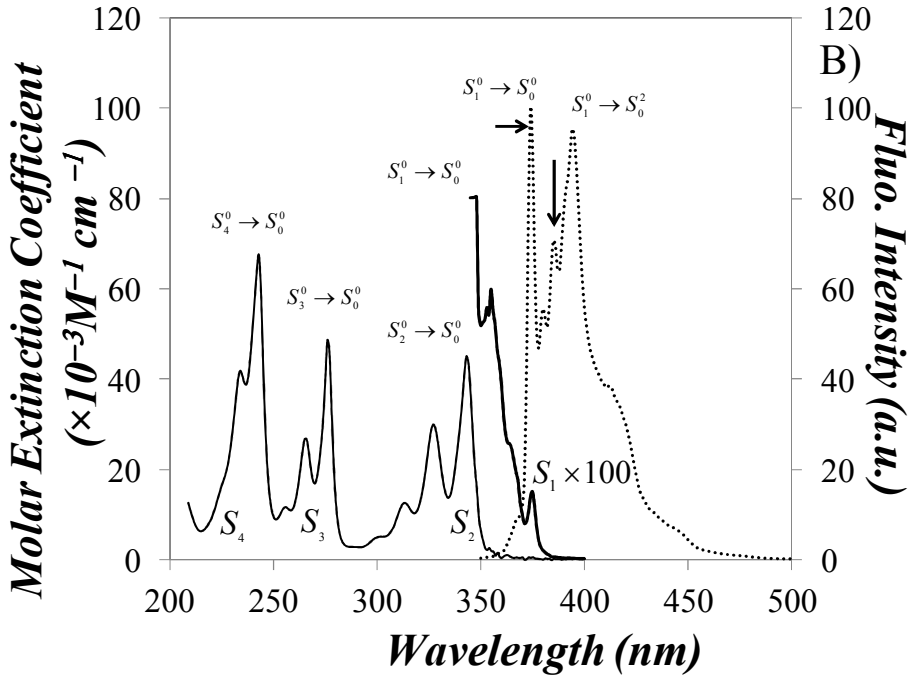


Figure S3. GPC traces of (top) 2-(1-pyrenemethoxy ethyl) methacrylate acquired with a UV-Vis absorption detector and PyMeEG(3.8)-PBMA acquired with (middle) a DRI detector and (bottom) a UV-Vis absorption detector set at λ=344 nm. Elution solvent: THF

Photophysical properties of PyButOH and PyMeEGOH

The absorption spectra of PyButOH and PyMeEGOH in THF along with their fluorescence spectra are shown in Figures S4B and S4C. Figure S4A shows the Jablonski diagram depicting the different transitions observed in the absorption and fluorescence spectra. As can be seen in Figures S4B and S4C, the symmetry forbidden 0-0 transition of the pyrene labels is strongly reduced in the absorption and emission spectra of the PyMeEGOH samples. The molar absorption coefficient (ε) of 1-PyButOH and 1-PyMeEGOH at 344 nm were found to equal 42,000 and 45,000 $M^{-1}.cm^{-1}$ in THF, respectively.





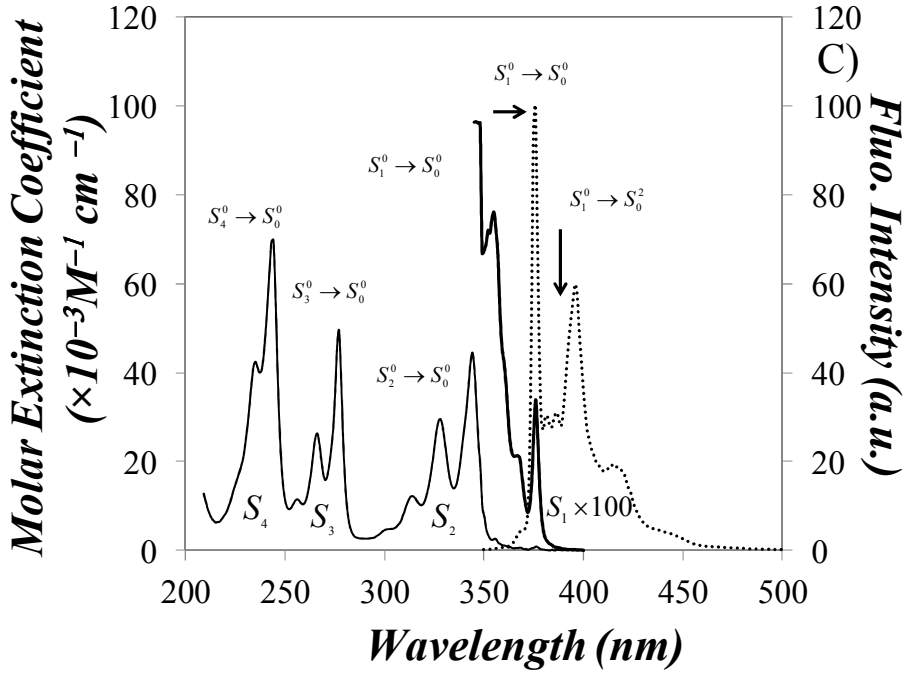


Figure S4. A) Jablonsky diagram and the corresponding transitions of a chromophore. Absorption (solid line) and fluorescence emission (dashed line) spectra of B) PyMeEGOH and C) PyButOH in THF respectively. [*Py*] = 2.5×10^{-6} M and λ_{ex} = 334 nm for the emission spectra.

The ε_{375} value of 1-PyButOH and 1-PyMeEGOH at 375 nm for the 0-0 transition equaled 263 and 151 $M^{-1}.cm^{-1}$. The much larger ε_{375} value obtained for PyButOH suggests that the 0-0 transition is more allowed than for PyMeEGOH, a consequence of the oxygen atom in the position β to pyrene which restores the wavefunction of pyrene.

Fluorescence Blob Model (FBM) and its parameters

The monomer and excimer fluorescence decays of the randomly labeled PBMA samples of PyBut-PBMA and PyMeEG-PBMA were fitted globally according to Equations S1 and S2 derived for the FBM. The different parameters that are used in the FBM have been listed in Table S1.

Table S1. List of parameters used for the FBM analysis of fluorescence decays.

Type of pyrene species	
Py^*_{diff}	Pyrene labels attached onto the structural units of the polymer that diffuse toward each other in solution.
Py^*_{free}	Pyrenes that are isolated and do not form excimer.
Py^*_{k2}	Pyrenes that have been brought in close proximity by diffusive backbone motions and form excimer rapidly with a rate constant k_2.
$E0^*$	Pyrene excimer resulting from well-stacked pyrenes.
EL^*	Long-lived excited pyrene dimers resulting from poorly stacked pyrenes.
Lifetime of pyrene species	
τ_{E0}	Fluorescence lifetime of pyrene excimer.
τ_{EL}	Fluorescence lifetime of the long-lived dimers.
τ_M	Fluorescence lifetime of excited pyrene monomer.
Molar Fraction of pyrene species contributing to the monomer decays	
f_{Mdiff}	Molar fraction of the Py^*_{diff} species.
f_{Mk2}	Molar fraction of the Py^*_{k2} species.
f_{Mfree}	Molar fraction of the Py^*_{free} species.
Molar Fraction of pyrene species contributing to the excimer decays	
f_{Ediff}	Molar fraction of the Py^*_{diff} species.
f_{Ek2}	Molar fraction of the Py^*_{k2} species.

f_{EE0}	Molar fraction of the *E*0* species.
f_{EEL}	Molar fraction of the *EL** species.
Overall molar fraction of the pyrene species	
f_{diff}	Molar fraction of the Py^*_{diff} species in the solution.
f_{k2}	Molar fraction of the Py^*_{k2} species in the solution.
f_{free}	Molar fraction of the Py^*_{free} species in the solution.
f_{E0}	Molar fraction of the *E*0* species excimer in the solution.
f_{EL}	Molar fraction of the *EL** species in the solution.
Fluorescence Blob Model parameters	
k_{blob}	Rate constant describing the encounters between one excited Py^*_{diff} monomer and one ground-state pyrene monomer located in the same *blob* as they diffuse toward each other to form a species Py^*_{k2}.
$k_e \times [blob]$	Rate constant of pyrene exchange between *blobs* times the local concentration of *blobs* inside the polymer coil.
N_{blob}	Average number of structural units per *blob* whose expression is given in Eq. S4.
$\langle n \rangle$	Average number of pyrenes per *blob*.
k_2	Rate constant for the rapid rearrangement of the pyrene labels to form an excimer.

Based on the kinetic scheme shown in Figure S5, pyrene excimer formation occurs in a sequential manner. First the structural units bearing a pyrene label Py^*_{diff} diffuse toward each other with a rate constant k_{blob}. Upon contact, the structural units Py^*_{diff} turn into the Py^*_{k2} species. The pyrene labels rearrange on a fast time scale with a rate constant k_2 to form an excimer. Excimers can be the result of two well-stacked pyrenes (*E*0*) or two improperly stacked pyrenes (*EL**) that emit with a lifetime τ_{EL} which is larger than that of the excimer τ_{E0}. The excimer species *E*0* and *EL** can be generated by diffusive encounters between an excited

and a ground-state-pyrene or direct excitation of a pyrene aggregate. Pyrene labels that cannot form excimer are referred to as Py^*_{free} and they emit with the monomer natural lifetime τ_M.

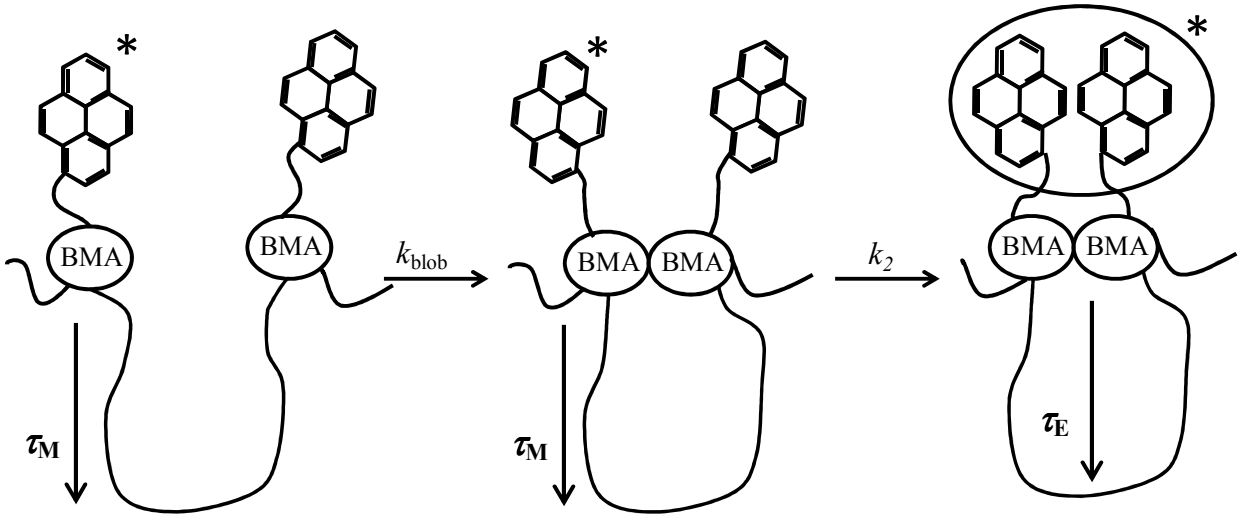


Figure S5: Scheme representing the kinetics of excimer formation for the pyrene-labeled PBMAs.

The diffusive motion of the pyrene-labeled structural units in the polymer coil can be described by the FBM parameters $<n>$, k_{blob}, and $k_e \times [blob]$. By fitting the monomer decays, the molar fractions f_{Mdiff}, f_{Mk2}, and f_{Mfree} representing the pyrene species Py^*_{diff}, Py^*_{k2}, and Py^*_{free} that contribute to the monomer decays can be calculated. In a similar manner, the excimer decay analysis yields the fractions f_{Ediff}, f_{Ek2}, f_{EE0}, and f_{EEL} which represent the molar fractions of the respective pyrene species Py^*_{diff}, Py^*_{k2}, $E0^*$, and EL^* that contribute to the excimer decay. The fractions f_{Mdiff}, f_{Mk2}, f_{Mfree}, f_{Ediff}, f_{Ek2}, f_{EE0}, and f_{EEL} can then be combined to determine the overall molar fractions f_{diff}, f_{k2}, f_{free}, f_{E0}, and f_{EL} of each pyrene species present in solution. Equations S1

and S2 employ the parameters described above and in Table S1 to fit the monomer and excimer decays globally.

$$
\begin{aligned}
[Py^*]_{(t)} = [Py^*_{diff}]_{(t)} + [Py^*_{k2}]_{(t)} + [Py^*_{free}]_{(t)} = [Py^*_{diff}]_o \exp\left(-\left(A_2 + \frac{1}{\tau_M}\right)t - A_3\left(1-\exp(-A_4 t)\right)\right) \\
+\left([Py^*_{k2}]_o + [Py^*_{diff}]_o e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^i}{i!} \frac{A_2 + iA_4}{A_2 + iA_4 - k_2}\right) \exp\left(-\left(k_2 + \frac{1}{\tau_M}\right)t\right) \\
-[Py^*_{diff}]_o e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^i}{i!} \frac{A_2 + iA_4}{A_2 + iA_4 - k_2} \exp\left(-\left(A_2 + iA_4 + \frac{1}{\tau_M}\right)t\right) \\
+[Py^*_{free}]_o \exp\left(-\frac{t}{\tau_M}\right)\Bigg]
\end{aligned}
\tag{S1}
$$

$$
\begin{aligned}
[E^*]_{(t)} = [E0^*]_{(t)} + [EL^*]_{(t)} = k_2 \Bigg(\Bigg([Py^*_{k2}]_o + [Py^*_{diff}]_o e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^i}{i!} \frac{A_2 + iA_4}{A_2 + iA_4 - k_2} \Bigg) \\
\times \frac{\exp\left(-\frac{t}{\tau_{E0}}\right) - \exp\left(-\left(k_2 + \frac{1}{\tau_M}\right)t\right)}{k_2 + \frac{1}{\tau_M} - \frac{1}{\tau_{E0}}} \\
+[Py^*_{diff}]_o e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3^i}{i!} \frac{A_2 + iA_4}{A_2 + iA_4 - k_2} \frac{\exp\left(-\left(A_2 + iA_4 + \frac{1}{\tau_M}\right)t\right) - \exp\left(-\frac{t}{\tau_{E0}}\right)}{A_2 + iA_4 + \frac{1}{\tau_M} - \frac{1}{\tau_{E0}}} \Bigg) \\
+ [E0^*]_o \times \exp\left(-\frac{t}{\tau_{E0}}\right) + [EL^*]_o \times \exp\left(-\frac{t}{\tau_{EL}}\right)
\end{aligned}
\tag{S2}
$$

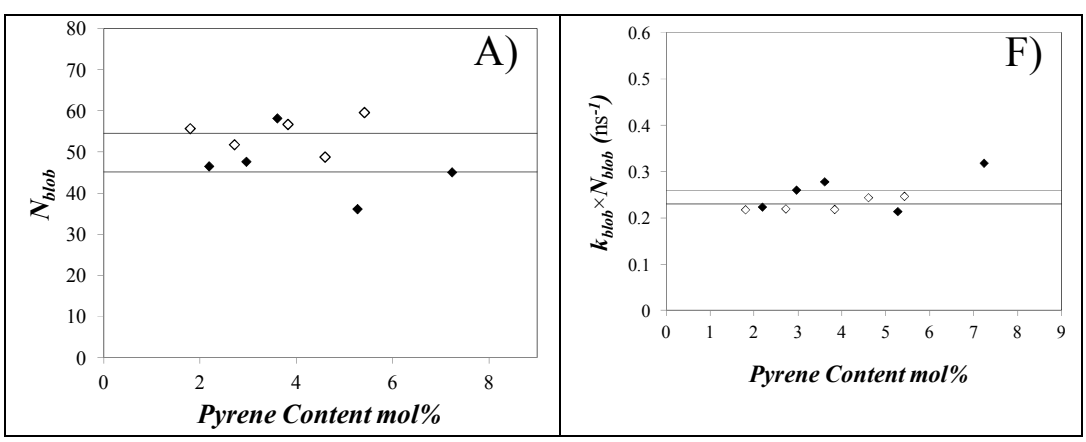
The expression of the parameters A_2, A_3, and A_4 used in Equations S1 and S2 have been provided in Equation S3 as a function of $<n>$, k_{blob}, and $k_e \times [blob]$ which have been already discussed in Table S1.

$$A_2 = <n> \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \qquad A_3 = <n> \left(\frac{k_{blob}}{k_{blob} + k_e [blob]} \right)^2 \qquad A_4 = k_{blob} + k_e [blob] \quad \text{(S3)}$$

The parameters f_{Mfree} and $<n>$ obtained from the FBM decay analysis and the pyrene content λ_{Py} can be combined into Equation S4 to yield N_{blob}, the number of structural units found in a *blob*.

$$N_{blob} = \frac{1 - f_{Mfree}}{\lambda_{Py}} \frac{\langle n \rangle}{\left[M_{Py}(x) + M_{BMA}(1-x) \right]} \quad \text{(S4)}$$

In Equation S4, M_{BMA} is the molar mass of the BMA monomer (M_{BMA}=142 g/mol) and M_{py} is the molar mass of the pyrene labeled monomer, M_{Py} being equal to 344 g/mol or 342 g/mol for PyMeEGMA or PyButMA, respectively. Plots of N_{blob} and $k_{blob} \times N_{blob}$ are presented as a function of pyrene content in Figures S6A-E and F-J, respectively.



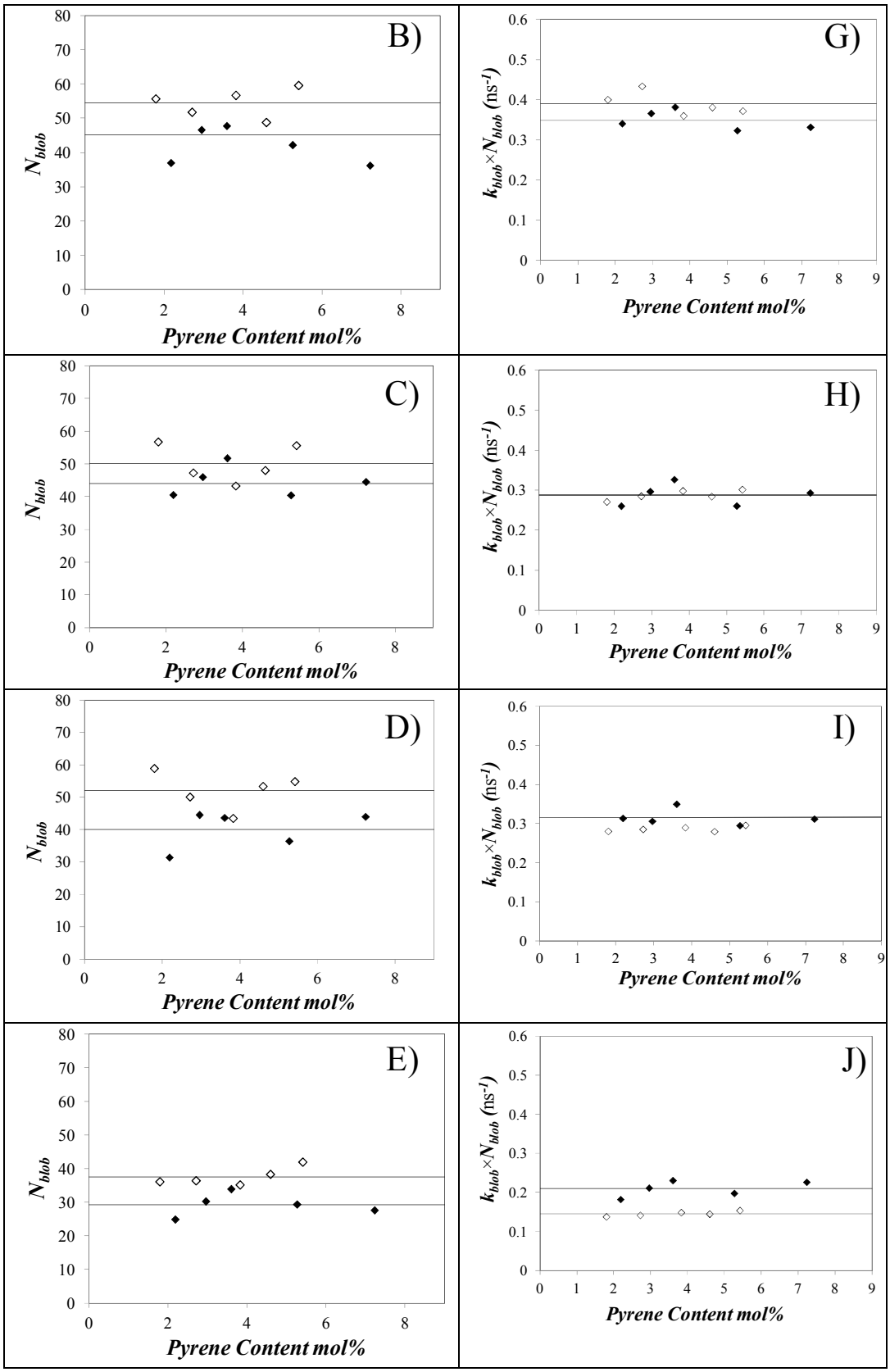

B)
G)
C)
H)
D)
I)
E)
J)
N_{blob}
$k_{blob} \times N_{blob}$ (ns^{-1})
Pyrene Content mol%

Figure S6. Plots of N_{blob} (A-E) and $k_{blob} \times N_{blob}$ (F-J) as a function of pyrene content for (◇) PyMeEG-PBMA and (◆) PyBut-PBMA in different solvents: A and F) DMF, B and G) DCM, C and H) THF, D and I) toluene, and E and F) cyclohexane. $[Py] = 2.5 \times 10^{-6}$ M, $\lambda_{ex} = 344$ nm.

Adjusting the lifetime of the PyMeEG-PBMA samples by fluorescence dynamic quenching

In order to investigate the effect that the lifetime (τ_M) of PyMeEG-OH used to prepare the PyMeEG-PBMA samples has on N_{blob} and the product $k_{blob}\times N_{blob}$, τ_M was adjusted by adding nitromethane, an efficient quencher of pyrene to a dilute solution of PyMeEG(0.3)-PBMA in THF. This sample had a very low pyrene content of 15.8 μmol/g equivalent to 0.3 mol% pyrene-labeled monomer. A Stern Volmer (SV) plot was built where the fluorescence decays of PyMeEG(0.3)-PBMA were fitted with a sum of exponentials after the solution had been spiked with a known amount of nitromethane. The exponential with the longest decay time had a pre-exponential weight of 80% and this decay time was attributed to τ_M since most pyrene labels were unable to form an excimer and decayed with their natural lifetime. τ_M decreased with each addition of nitromethane and a linear SV plot was obtained in Figure S4 where the ratio τ_M^o/τ_M was plotted as a function of nitromethane concentration. The intercept of the plot equaled unity and the slope equaled the product $k_q\times\tau_M^o$ where k_q is the quenching rate constant and τ_M^o is the lifetime of the pyrene label in the absence of quencher. Since τ_M^o in THF equaled 270 ns for PyMeEG(0.3)-PBMA, k_q took a value of 1.12×10^9 $M^{-1}.s^{-1}$. The value of k_q and τ_M^o were then applied to determine the amount of nitromethane that needed to be added to a solution of PyMeEG-PBMA solution in THF to achieve a given τ_M value.

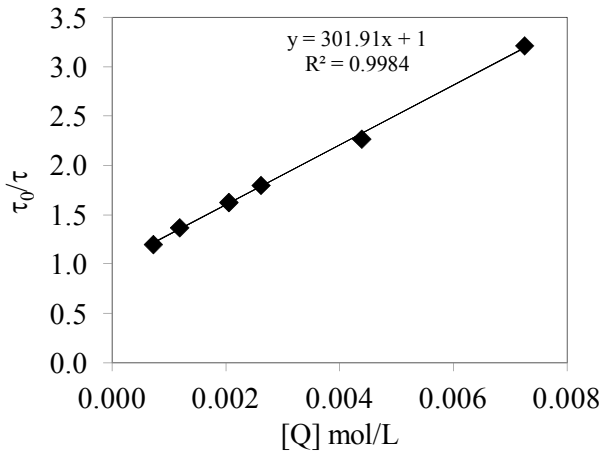


Figure S7. Plot of τ_M^o/τ_M versus nitromethane concentration [Q] for a PyMeEG(0.2)-PBMA solution in THF.

The different natural lifetimes τ_M of PyBut-PBMA and PyMeEG-PBMA do not affect the FBM parameters. Since the PyMeEGOH derivative with its larger lifetime could probe a larger *blob* volume (V_{blob}) inside the polymer coil resulting in a larger $<N_{blob}>$ value, quenching experiments were carried out to investigate the effect of lifetime on $<N_{blob}>$. Nitromethane, a well-known quencher of pyrene, was added to the PyMeEG-PBMA solutions in THF to decrease τ_M.[2] Using the sample PyMeEG(0.3)-PBMA which was labeled with a very small amount of pyrene, quenching of this sample with nitromethane yielded a bimolecular quenching rate constant k_q equal to 1.12×10^9 $M^{-1}.s^{-1}$ (see Figure S7 in SI). Knowing k_q, the nitromethane concentration required to obtain a desired lifetime τ_M for the pyrene label was found from the relationship shown in Equation 2 where τ_M^o = 270 ns represents the natural lifetime of PyMeEG(0.3)-PBMA in THF without nitromethane.

$$[Q] = \frac{1}{k_q} \times \left(\frac{\tau_M^o}{\tau_M} - 1 \right) \quad (2)$$

The pyrene monomer and excimer fluorescence decays of the PyMeEG-PBMA series were acquired with a nitromethane concentration of 0.0, 1.2, 2.6, 5.6, and 14.0 mmol.L^{-1} to reduce the natural lifetime of the PyMeEG derivative attached onto PBMA from 270 ns without nitromethane to 200, 150, 100, and 50 ns, respectively. For each nitromethane concentration, the FBM analysis was applied to the decays of the five PyMeEG-PBMA constructs to yield the parameters $<N_{blob}>$ and the product $<k_{blob} \times N_{blob}>$ as a function of τ_M. A plot of $<N_{blob}>$ as a function of τ_M is shown in Figure S8A. As τ_M decreased, so did $<N_{blob}>$ as the volume probed by the shorter-lived PyMeEG derivative decreased. However, $<N_{blob}>$ in Figure S8A did not change much when τ_M decreased from 270 to 150 ns, a range of τ_M values representative of those used to fit the decays obtained for solutions of the two Py-PBMA constructs in five different solvents.

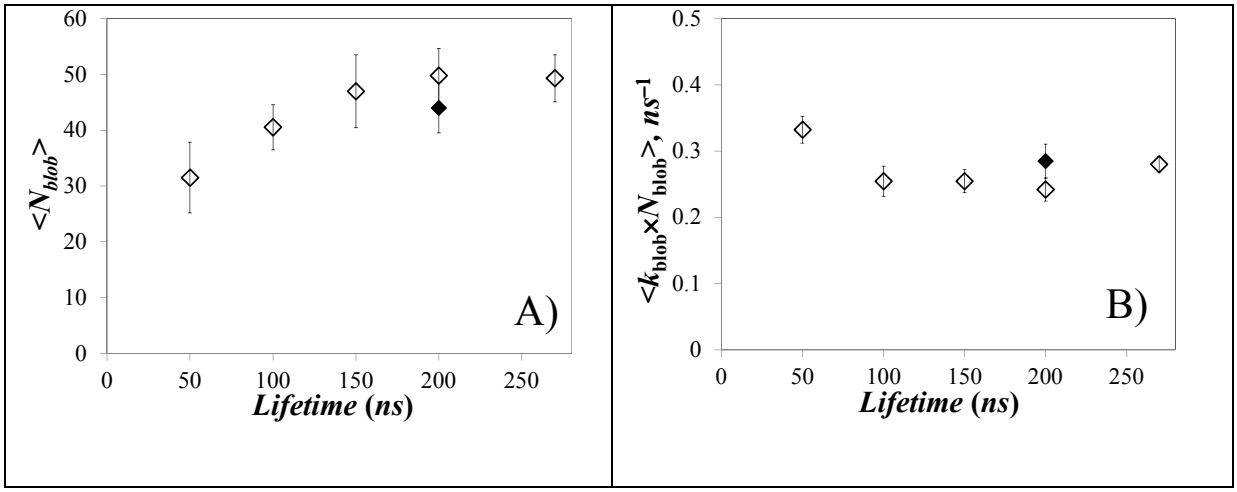


Figure S8. Plots of A) $<N_{blob}>$ and B) $<k_{blob} \times N_{blob}>$ as a function of pyrene lifetime for the Py-PBMA samples in THF. (◆) PyBut-PBMA, (◇) PyMeEG-PBMA. The lifetime of the PyMeEG-PBMA samples was adjusted by addition of nitromethane.

Only with a τ_M value of 50 ns was a significant decrease in $<N_{blob}>$ observed. The $<N_{blob}>$ value determined for the PyBut-PBMA series was also given in Figure S8A. The $<N_{blob}>$ values obtained for the two constructs at a same lifetime τ_M=200 ns were comparable in THF within experimental error. Figure S8A also suggested that despite the variations in τ_M resulting from the solvent used to prepare the Py-PBMA solutions, the different τ_M values obtained in these solvents were not expected to affect the $<N_{blob}>$ values much.

Similarly, the product $<k_{blob}\times N_{blob}>$ did not depend much on τ_M in Figure S8B. Only for a τ_M value of 50 ns did the product $<k_{blob}\times N_{blob}>$ show an uptick which was due to the fact that $<k_{blob}\times N_{blob}>$ scales as $N_{blob}^{1-3\nu}$ where ν equals 0.6 PBMA in a good solvent like THF. As explained in the main text of this study, the decrease in N_{blob} with decreasing τ_M results in the increase in the product $<k_{blob}\times N_{blob}>$ for small τ_M values, as shown in Figure S8B.

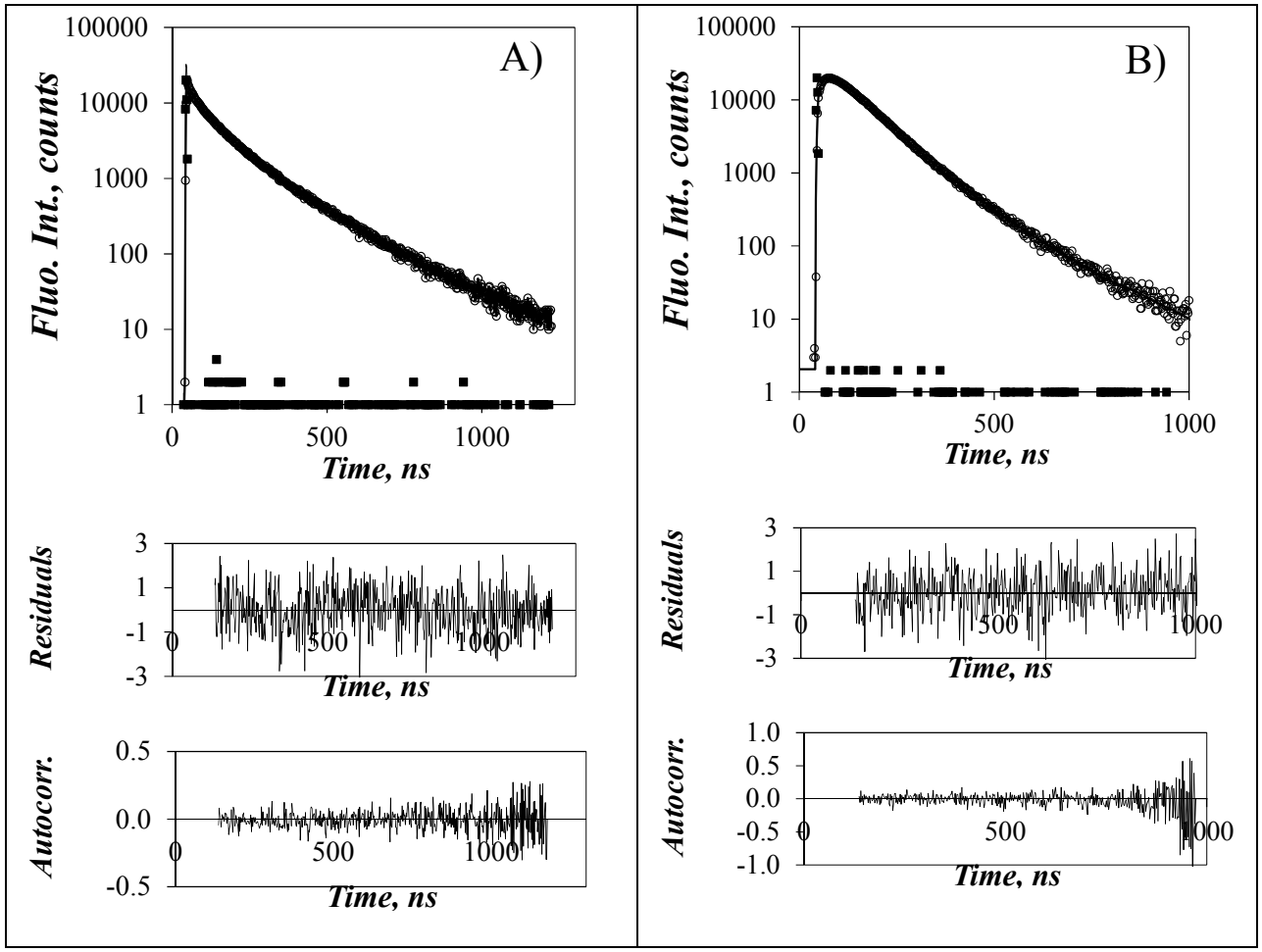


Figure S9. Fit of the fluorescence decays of the pyrene A) monomer (λ_{em} = 375 nm) and B) excimer (λ_{em} = 510 nm) of PyMeEG(3.8)-PBMA in THF according to the FBM. [*Py*] = 2.5×10^{-6} M, λ_{ex} = 344 nm, χ^2 = 1.05.

Table S2. Intrinsic viscosities of poly(butyl methacrylate) (M_n = 337,000, PDI = 1.48) in different organic solvents.

Solvent	**Intrinsic viscosity** (mL.g^{-1})	**Error**
THF	50.12	±0.93
Toluene	50.93	±0.85
DCM	56.50	±1.15
DMF	25.90	±0.44
Cyclohexane	20.44	±0.34

Table S3. Parameters retrieved from the FBM analysis of the monomer decays of the PyMeEG-PBMA samples.

Sample	Mol%	k_{blob} ($10^7 s^{-1}$)	<n>	$k_e[blob]$ ($10^7 s^{-1}$)	f_{Mdiff}	k_2 (ns^{-1})	f_{k2}	τ_M (ns)	f_{Mfree}	χ^2
Py-PEGMA	1.8	0.48	1.2	0.19	0.75	0.1	0.12	270	0.12	1.1
	2.7	0.60	1.4	0.31	0.75	0.1	0.19	270	0.06	1.1
(THF)	3.8	0.65	1.7	0.34	0.71	0.1	0.25	270	0.04	1.0
	4.6	0.59	2.2	0.37	0.67	0.1	0.31	270	0.02	1.1
	5.4	0.54	3.0	0.25	0.62	0.1	0.38	270	0.00	1.1
Py-PEGMA	1.8	0.39	1.2	0.31	0.73	0.08	0.13	228	0.14	1.2
	2.7	0.43	1.4	0.28	0.81	0.08	0.17	228	0.03	1.1
(DMF)	3.8	0.39	2.2	0.35	0.70	0.08	0.28	228	0.02	1.1
	4.6	0.50	2.3	0.48	0.69	0.08	0.29	228	0.01	1.3
	5.4	0.42	3.3	0.40	0.64	0.08	0.35	228	0.01	1.1
Py-PEGMA	1.8	0.38	0.7	0.19	0.8	0.06	0.10	288	0.07	1.3
	2.7	0.39	1.1	0.28	0.7	0.06	0.17	288	0.10	1.2
(CycloHexane)	3.8	0.42	1.4	0.24	0.7	0.06	0.26	288	0.03	1.0
	4.6	0.38	1.8	0.23	0.7	0.06	0.30	288	0.00	1.0
	5.4	0.37	2.3	0.19	0.6	0.06	0.37	288	0.01	1.0
Py-PEGMA	1.8	0.48	1.2	0.22	0.75	0.1	0.12	246	0.13	1.3
	2.7	0.57	1.5	0.37	0.74	0.1	0.18	246	0.08	1.2
(Toluene)	3.8	0.67	1.7	0.42	0.69	0.1	0.27	246	0.04	1.1
	4.6	0.53	2.5	0.24	0.66	0.1	0.31	246	0.03	1.1
	5.4	0.54	3.0	0.23	0.62	0.1	0.37	246	0.00	1.1
Py-PEGMA	1.8	0.87	0.9	0.39	0.74	0.12	0.14	155	0.12	1.0
	2.7	0.89	1.4	0.50	0.71	0.12	0.21	155	0.08	1.1
(DCM)	3.8	0.69	2.0	0.29	0.72	0.12	0.26	155	0.02	1.0
	4.6	0.75	2.4	0.45	0.68	0.12	0.30	155	0.01	1.1
	5.4	0.66	3.1	0.30	0.61	0.12	0.38	155	0.01	1.0

Table S4. Parameters retrieved from the FBM analysis of the excimer decays of the PyMeEG-PBMA samples.

Sample	Mol%	f_{Ediff}	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EEL}	k_2 (ns^{-1})	f_E	χ^2
Py-PEGMA	1.8	0.79	47	0.03	157	0.05	0.1	0.13	1.1
	2.7	0.73	53	0.05	146	0.03	0.1	0.19	1.1
(THF)	3.8	0.66	53	0.08	121	0.02	0.1	0.24	1.0
	4.6	0.59	52	0.11	108	0.02	0.1	0.28	1.1
Py-PEGMA	5.4	0.53	48	0.00	82	0.15	0.1	0.32	1.1
	1.8	0.78	47	0.02	144	0.06	0.08	0.14	1.2
	2.7	0.76	46	0.02	126	0.06	0.08	0.16	1.1
Py-PEGMA	3.8	0.64	53	0.09	148	0.01	0.08	0.26	1.1
	4.6	0.60	51	0.12	106	0.02	0.08	0.25	1.3
(DMF)	5.4	0.55	48	0.13	119	0.02	0.08	0.30	1.1
	1.8	0.82	46	0.06	194	0.02	0.06	0.10	1.3
	2.7	0.70	52	0.12	177	0.02	0.06	0.16	1.2
Py-PEGMA	3.8	0.58	52	0.14	143	0.06	0.06	0.22	1.0
	4.6	0.54	51	0.16	121	0.07	0.06	0.23	1.0
(Cyclohexane	5.4	0.49	53	0.20	119	0.06	0.08	0.24	1.0
	1.8	0.80	41	0.02	132	0.06	0.1	0.13	1.3
	2.7	0.73	48	0.08	142	0.01	0.1	0.18	1.2
Py-PEGMA	3.8	0.63	50	0.11	108	0.01	0.1	0.25	1.1
	4.6	0.58	45	0.07	90	0.08	0.1	0.27	1.1
(Toluene)	5.4	0.52	45	0.04	78	0.14	0.1	0.31	1.1
Py-PEGMA	1.8	0.76	53	0.02	100	0.08	0.12	0.14	1.0
	2.7	0.69	53	0.10	146	0.01	0.12	0.20	1.1
(DCM)	3.8	0.64	46	0.07	89	0.05	0.12	0.23	1.0
	4.6	0.57	45	0.01	70	0.16	0.12	0.25	1.1
	5.4	0.50	46	0.00	67	0.18	0.12	0.31	1.0

Table S5. Overall molar fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the PyMeEG-PBMA samples.

Sample	Mol%	f_{k2}	f_{free}	f_{E0}	f_{diff}	f_{E1}
Py-PEGMA	1.8	0.12	0.11	0.03	0.70	0.04
	2.7	0.18	0.06	0.05	0.69	0.03
(THF)	3.8	0.23	0.04	0.07	0.64	0.02
	4.6	0.28	0.01	0.10	0.59	0.02
Py-PEGMA	5.4	0.32	0.00	0.00	0.52	0.15
	1.8	0.12	0.13	0.02	0.68	0.05
	2.7	0.15	0.03	0.02	0.74	0.06
Py-PEGMA	3.8	0.26	0.02	0.09	0.63	0.01
	4.6	0.25	0.01	0.12	0.60	0.02
(DMF)	5.4	0.30	0.01	0.13	0.55	0.02
	1.8	0.09	0.07	0.09	0.77	0.02
	2.7	0.15	0.09	0.15	0.64	0.02
Py-PEGMA	3.8	0.21	0.02	0.21	0.57	0.06
	4.6	0.23	0.00	0.23	0.54	0.07
(Cyclohexan	5.4	0.28	0.01	0.28	0.47	0.06
	1.8	0.11	0.12	0.02	0.70	0.05
	2.7	0.17	0.07	0.08	0.68	0.01
Py-PEGMA	3.8	0.24	0.04	0.11	0.61	0.01
	4.6	0.26	0.03	0.07	0.56	0.08
(Toluene)	5.4	0.31	0.00	0.04	0.51	0.14
Py-PEGMA	1.8	0.13	0.11	0.01	0.68	0.07
	2.7	0.19	0.07	0.09	0.64	0.01
(DCM)	3.8	0.23	0.02	0.07	0.63	0.05
	4.6	0.25	0.01	0.01	0.57	0.16
	5.4	0.31	0.00	0.00	0.50	0.18

Table S6. Parameters retrieved from the FBM analysis of the monomer decays of the PyBut-PBMA samples.

Sample	Mol%	k_{blob} ($10^7 s^{-1}$)	<n>	$k_e[blob]$ ($10^7 s^{-1}$)	f_{Mdiff}	k_2 (ns^{-1})	f_{k2}	τ_M (ns)	f_{Mfree}	χ^2
Py-PC4MA	2.2	0.67	0.8	0.63	0.50	0.12	0.06	195	0.44	1.1
	2.9	0.64	1.0	0.51	0.73	0.12	0.12	195	0.15	1.2
(THF)	3.6	0.65	1.5	0.61	0.72	0.12	0.17	195	0.11	1.0
	5.2	0.63	2.0	0.46	0.70	0.12	0.23	195	0.07	1.1
	7.2	0.65	2.2	0.47	0.72	0.12	0.27	195	0.01	1.1
Py-PC4MA	2.2	0.55	1.0	0.77	0.67	0.09	0.11	160	0.23	1.2
	2.9	0.56	1.5	0.52	0.74	0.09	0.19	160	0.07	1.2
(DMF)	3.6	0.58	2.1	1.24	0.62	0.09	0.21	160	0.17	1.2
	5.2	0.55	2.3	0.66	0.68	0.09	0.24	160	0.03	1.0
	7.2	0.88	2.4	0.98	0.70	0.09	0.38	160	0.01	1.2
Py-PC4MA	2.2	0.73	0.63	0.57	0.77	0.12	0.10	224	0.13	1.0
	2.9	0.70	0.96	0.53	0.80	0.12	0.14	224	0.06	1.1
(Cyclohexane)	3.6	0.68	1.35	0.54	0.72	0.12	0.19	224	0.09	1.2
	5.2	0.67	1.56	0.46	0.77	0.12	0.22	224	0.01	1.3
	7.2	0.82	2.05	0.59	0.71	0.12	0.27	224	0.03	1.3
Py-PC4MA	2.2	1.00	0.9	0.68	0.68	0.12	0.12	180	0.20	1.1
	2.9	0.69	1.5	0.70	0.72	0.12	0.19	180	0.09	1.2
(Toluene)	3.6	0.82	1.7	0.68	0.70	0.12	0.22	180	0.08	1.2
	5.2	0.81	2.0	0.60	0.76	0.12	0.22	180	0.02	1.2
	7.2	0.71	3.2	0.44	0.60	0.12	0.39	180	0.01	1.1
Py-PC4MA	2.2	0.80	1.1	0.65	0.68	0.12	0.13	110	0.18	1.1
	2.9	0.72	1.6	0.43	0.74	0.12	0.21	110	0.05	1.0
(DCM)	3.6	0.60	2.4	0.22	0.66	0.12	0.29	110	0.06	1.0
	5.2	0.66	2.6	0.24	0.68	0.12	0.32	110	0.00	1.1
	7.2	0.53	4.6	0.17	0.52	0.12	0.47	110	0.01	1.3

Table S7. Parameters retrieved from the FBM analysis of the excimer decays of the PyBut-PBMA samples.

Sample	Mol %	f_{Ediff}	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EEL}	k_2 (ns^{-1})	f_E	χ^2
Py-PC4MA	2.2	0.84	56	0.02	178.9	0.01	0.12	0.13	1.2
	2.9	0.77	54	0.04	156.5	0.02	0.12	0.18	1.0
(THF)	3.6	0.71	52	0.00	100.3	0.06	0.12	0.23	1.1
	5.2	0.69	53	0.00	95.7	0.05	0.12	0.26	1.1
	7.2	0.57	51	0.00	83.8	0.07	0.12	0.36	1.1
	2.2	0.83	53	0.00	139	0.04	0.09	0.13	1.2
	2.9	0.74	54	0.00	103	0.07	0.09	0.19	1.2
Py-PC4MA	3.6	0.69	50	0.00	106	0.07	0.09	0.24	1.2
	5.2	0.66	52	0.09	91	0.07	0.09	0.23	1.0
(DMF)	7.2	0.53	56	0.09	98	0.05	0.09	0.33	1.2
	2.2	0.84	53	0.00	140	0.05	0.12	0.10	1.0
	2.9	0.78	55	0.02	121	0.06	0.12	0.14	1.1
Py-PC4MA	3.6	0.71	53	0.00	110	0.10	0.12	0.19	1.2
	5.2	0.68	53	0.02	104	0.11	0.12	0.19	1.3
(Cyclohexane)	7.2	0.57	50	0.00	91	0.22	0.12	0.21	1.3
	2.2	0.79	60	0.07	284	0.00	0.12	0.14	1.1
	2.9	0.74	53	0.06	185	0.01	0.12	0.19	1.2
Py-PC4MA	3.6	0.69	53	0.08	197	0.00	0.12	0.22	1.2
	5.2	0.66	52	0.13	78	0.02	0.12	0.19	1.2
(Toluene)	7.2	0.52	49	0.00	72	0.14	0.12	0.34	1.0
Py-PC4MA	2.2	0.80	52	0.0	93	0.05	0.12	0.16	1.1
	2.9	0.73	52	0.1	94	0.01	0.12	0.20	1.0
(DCM)	3.6	0.65	51	0.0	78	0.06	0.12	0.29	1.0
	5.2	0.62	49	0.0	77	0.09	0.12	0.29	1.1
	7.2	0.46	50	0.0	70	0.13	0.12	0.42	1.3

Table S8. Overall molar fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the PyBut-PBMA samples

Sample	Mol	f_{k2}	f_{free}	f_{E0}	f_{diff}	f_{E1}
Py-PC4MA	2.2	0.11	0.15	0.02	0.71	0.01
	2.9	0.16	0.11	0.03	0.68	0.02
(THF)	3.6	0.22	0.06	0.00	0.67	0.05
	5.2	0.25	0.01	0.00	0.68	0.05
	7.2	0.36	0.01	0.00	0.56	0.07
	2.2	0.10	0.22	0.00	0.65	0.03
	2.9	0.18	0.06	0.00	0.70	0.06
Py-PC4MA	3.6	0.20	0.16	0.00	0.58	0.06
	5.2	0.27	0.02	0.02	0.63	0.05
(DMF)	7.2	0.30	0.01	0.09	0.55	0.05
	2.2	0.09	0.13	0.00	0.74	0.05
	2.9	0.13	0.05	0.02	0.74	0.06
Py-PC4MA	3.6	0.17	0.08	0.00	0.65	0.09
	5.2	0.19	0.01	0.02	0.68	0.11
(Cyclohexane)	7.2	0.21	0.02	0.00	0.56	0.21
	2.2	0.11	0.19	0.05	0.65	0.00
	2.9	0.18	0.08	0.05	0.68	0.00
Py-PC4MA	3.6	0.21	0.07	0.07	0.64	0.00
	5.2	0.18	0.02	0.13	0.65	0.02
(Toluene)	7.2	0.34	0.01	0.00	0.52	0.14
Py-PC4MA	2.2	0.13	0.18	0.00	0.66	0.04
	2.9	0.19	0.05	0.05	0.70	0.01
(DCM)	3.6	0.27	0.05	0.00	0.62	0.06
	5.2	0.29	0.00	0.00	0.62	0.09
	7.2	0.41	0.01	0.00	0.45	0.13

Table S9. Parameters retrieved from the FBM analysis of the monomer decays of the PyMeEG-PBMA samples when the lifetime was adjusted using nitromethane as quencher in THF.

Sample	Mol%	k_{blob} ($10^7 s^{-1}$)	<n>	$k_e[blob]$ ($10^7 s^{-1}$)	f_{Mdiff}	k_2 (ns^{-1})	f_{k2}	τ_M (ns)	f_{Mfree}	χ^2
Py-PEGMA	1.8	0.48	1.2	0.19	0.75	0.1	0.12	270	0.12	1.1
	2.7	0.60	1.4	0.31	0.75	0.1	0.19	270	0.06	1.1
(THF)	3.8	0.65	1.7	0.34	0.71	0.1	0.25	270	0.04	1.0
	4.6	0.59	2.2	0.37	0.67	0.1	0.31	270	0.02	1.1
τ=270 ns	5.4	0.54	3.0	0.25	0.62	0.1	0.38	270	0.00	1.1
Py-PEGMA	1.8	0.48	1.2	0.32	0.77	0.085	0.14	200	0.09	1.0
	2.7	0.58	1.4	0.40	0.74	0.085	0.20	200	0.05	1.1
(THF)	3.8	0.50	2.0	0.29	0.71	0.085	0.26	200	0.02	1.2
	4.6	0.44	2.7	0.14	0.69	0.085	0.31	200	0.00	1.1
τ=200 ns	5.4	0.45	3.2	0.20	0.64	0.085	0.36	200	0.01	1.1
Py-PEGMA	1.8	0.51	1.2	0.45	0.75	0.085	0.15	150	0.10	1.2
	2.7	0.63	1.3	0.41	0.74	0.085	0.20	150	0.05	1.1
(THF)	3.8	0.57	1.9	0.41	0.72	0.085	0.24	150	0.04	1.1
	4.6	0.46	2.7	0.28	0.67	0.085	0.32	150	0.01	1.2
τ=150 ns	5.4	0.57	2.7	0.38	0.66	0.085	0.33	150	0.01	0.9
Py-PEGMA	1.8	0.66	0.9	0.36	0.76	0.085	0.15	100	0.09	1.1
	2.7	0.52	1.5	0.26	0.70	0.085	0.19	100	0.11	1.1
(THF)	3.8	0.64	1.9	0.79	0.70	0.085	0.26	100	0.03	1.1
	4.6	0.72	1.8	0.40	0.68	0.085	0.31	100	0.02	1.1
τ=100 ns	5.4	0.62	2.4	0.36	0.64	0.085	0.34	100	0.02	1.0
Py-PEGMA	1.8	0.8	1.3	0.1	0.74	0.15	0.11	50	0.43	1.2
(THF)	2.7	1.2	1.0	1.0	0.74	0.15	0.14	50	0.18	1.5
	3.8	1.3	1.0	0.4	0.74	0.15	0.20	50	0.00	1.2
τ=50 ns	4.6	0.9	2.1	0.5	0.63	0.15	0.29	50	0.05	1.1
	5.4	1.2	1.8	1.0	0.62	0.15	0.29	50	0.04	1.2

Table S10. Parameters retrieved from the FBM analysis of the excimer decays of the PyMeEG-PBMA samples when the lifetime was adjusted using nitromethane as quencher in THF.

Sample	Mol%	f_{Ediff}	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EEL}	k_2 (ns^{-1})	f_E	χ^2
Py-PEGMA	1.8	0.79	47	0.03	157	0.05	0.1	0.13	1.1
	2.7	0.73	53	0.05	146	0.03	0.1	0.19	1.1
(THF)	3.8	0.66	53	0.08	121	0.02	0.1	0.24	1.0
	4.6	0.59	52	0.11	108	0.02	0.1	0.28	1.1
τ=270 ns	5.4	0.53	48	0.00	82	0.15	0.1	0.32	1.1
Py-PEGMA	1.8	0.77	44	0.0	100	0.09	0.09	0.1	1.0
	2.7	0.72	48	0.0	96	0.09	0.09	0.2	1.1
(THF)	3.8	0.65	50	0.1	100	0.05	0.09	0.2	1.2
	4.6	0.58	47	0.0	84	0.15	0.09	0.3	1.1
τ=200 ns	5.4	0.51	49	0.1	83	0.13	0.09	0.3	1.1
Py-PEGMA	1.8	0.75	47	0.0	76	0.10	0.09	0.2	1.2
	2.7	0.72	50	0.0	84	0.06	0.09	0.2	1.1
(THF)	3.8	0.65	49	0.1	89	0.08	0.09	0.2	1.1
	4.6	0.58	48	0.1	81	0.09	0.09	0.3	1.2
τ=150 ns	5.4	0.53	46	0.0	76	0.21	0.09	0.3	0.9
Py-PEGMA	1.8	0.75	47	0.0	74	0.08	0.09	0.2	1.1
	2.7	0.72	47	0.0	83	0.08	0.09	0.2	1.1
(THF)	3.8	0.61	47	0.2	187	0.00	0.09	0.2	1.1
	4.6	0.59	52	0.0	71	0.09	0.09	0.3	1.1
τ=100 ns	5.4	0.53	48	0.0	70	0.19	0.09	0.3	1.0
Py-PEGMA	1.8	0.74	52	0.01		0.08	0.15	0.2	1.2
	2.7	0.74	48	0.00		0.08	0.15	0.2	1.3
(THF)	3.8	0.74	47	0.01		0.06	0.15	0.2	1.2
	4.6	0.63	46	0.09		0.01	0.15	0.3	1.1
τ=50 ns	5.4	0.62	44	0.01		0.11	0.15	0.3	1.2

Table S11. Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the PyMeEG-PBMA samples when the lifetime was adjusted using nitromethane as quencher in THF.

Sample	Mol%	f_{k2}	f_{free}	f_{E0}	f_{diff}	f_{El}
Py-PEGMA	1.8	0.12	0.11	0.03	0.70	0.04
	2.7	0.18	0.06	0.05	0.69	0.03
(THF)	3.8	0.23	0.04	0.07	0.64	0.02
	4.6	0.28	0.01	0.10	0.59	0.02
τ=270 ns	5.4	0.32	0.00	0.00	0.52	0.15
Py-PEGMA	1.8	0.12	0.09	0.00	0.71	0.08
	2.7	0.18	0.05	0.00	0.68	0.08
(THF)	3.8	0.24	0.02	0.05	0.64	0.05
	4.6	0.26	0.00	0.00	0.58	0.15
τ=200 ns	5.4	0.29	0.01	0.07	0.51	0.13
Py-PEGMA	1.8	0.14	0.09	0.00	0.68	0.09
	2.7	0.18	0.05	0.03	0.68	0.06
(THF)	3.8	0.21	0.03	0.06	0.63	0.07
	4.6	0.27	0.01	0.06	0.57	0.09
τ=150 ns	5.4	0.26	0.01	0.00	0.53	0.20
Py-PEGMA	1.8	0.14	0.08	0.02	0.69	0.07
	2.7	0.18	0.10	0.00	0.65	0.07
(THF)	3.8	0.22	0.03	0.15	0.60	0.00
	4.6	0.27	0.01	0.04	0.59	0.09
τ=100 ns	5.4	0.27	0.02	0.00	0.52	0.19
100Py-PEGMA	1.8	0.10	0.40	0.01	0.44	0.05
	2.7	0.13	0.16	0.00	0.64	0.07
(THF)	3.8	0.19	0.00	0.01	0.74	0.06
	4.6	0.26	0.05	0.09	0.60	0.01
τ=50 ns	5.4	0.26	0.04	0.01	0.60	0.10

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