Supporting Information for

Long-Range Polymer Chain Dynamics of Pyrene-Labelled Poly(*N*-isopropylacrylamide)s Studied by Fluorescence

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Fluorescence Decay Analysis – The Birks Scheme.[5,10] The Birks scheme assumes that an excited pyrene located at one end of a pyrene end-labelled monodisperse chain can either fluoresce with a lifetime τ_M or form an excimer with a rate constant k_{cy}. Once formed, the excimer can fluoresce with a lifetime τ_E or dissociate with a rate constant k_{-cy}. Samples of polymers end-labelled with pyrene usually contain a finite fraction of monolabelled chains where the pyrene label is incapable of forming excimer. The various pyrene species encountered can be accounted for by fitting the fluorescence decays acquired for the pyrene monomer (*Py**) and excimer (*E**) of the pyrene end-labelled PNIPAM with Equations S.1 and S.2, respectively.[11,42] In Equations S.1 and S.2, the pyrene species Py_{diff}, Py_{free}, and Py_S represent the pyrene monomers that 1) form excimer by diffusion according to the Birks scheme, 2) are covalently attached to monolabelled chains, emit with a lifetime τ_M, and do not form excimer, and 3) emit with a short lifetime τ_S, respectively.

$$[Py^*] = \frac{[Py^*_{diff}]_o}{\sqrt{(X-Y)^2 + 4k_{cy}k_{-cy}}}\left((X-\tau_2^{-1})\times\exp(-t/\tau_1) - (X-\tau_1^{-1})\times\exp(-t/\tau_2)\right)$$

$$+[Py^*_{free}]_o\exp(-t/\tau_M) + [Py^*_S]_o\exp(-t/\tau_S) \qquad \text{(S.1)}$$

$$[E^*] = \frac{k_{cy}[Py^*_{diff}]_o}{\sqrt{(X-Y)^2 + 4k_{cy}k_{-cy}}}\left(-\exp(-t/\tau_1) + \exp(-t/\tau_2)\right) + [Py^*_S]_o\exp(-t/\tau_S) \qquad \text{(S.2)}$$

The parameters X and Y used in Equations S.1 and S.2 equal $k_{cy} + \tau_M^{-1}$ and $k_{-cy} + \tau_E^{-1}$, respectively. The expression of τ_1 and τ_2 is given in Equations S.3 and S.4, respectively.

$$\tau_1^{-1} = \frac{X + Y + \sqrt{(X - Y)^2 + 4k_{cy}k_{-cy}}}{2} \tag{S.3}$$

$$\tau_2^{-1} = \frac{X + Y - \sqrt{(X - Y)^2 + 4k_{cy}k_{-cy}}}{2} \tag{S.4}$$

All excimer decays showed a pronounced spike at the early times which was attributed to the Py_S^* species. The decaytime τ_S was set to equal 2 ns in the analysis. The species Py_S^* has been reported to be the result of poorly stacked pyrene dimers.[24] However, it must be pointed out that Py_S^* is typically observed under conditions where excimer formation by diffusion is disfavored (longer chain and larger solvent viscosity) so that the possibility that Py_S^* be an impurity present in minute amounts or stray light scattering leaking through the detection system cannot be totally ruled out. Finally, analysis of the fluorescence decays with Equations S.1 and S.2 yields the fraction f_{Mfree} which equals $[Py_{free}^*]_o /([Py_{diff}^*]_o + [Py_{free}^*]_o)$ and represents the fraction of pyrenes that are attached onto singly labelled chains and cannot form excimer.

Fluorescence Decay Analysis – The Fluorescence Blob Model. The FBM has been shown to be effective at analyzing the complex fluorescence decays of polymers that have been randomly labelled with pyrene.[7,43-51] Within the FBM framework, five pyrene species are being considered. The pyrene population Py_{diff}^{*} reflects the slow diffusive motion of the structural units bearing a pyrene derivative. These diffusive motions are well-described by the three FBM parameters that are <*n*>, the average number of ground-state pyrene per *blob*, k_{blob}, the rate constant of excimer formation in a *blob* that contains an excited pyrene and a single ground-state pyrene, and the product $k_{\mathrm{e}}\times[blob]$ where k_{e} is the rate constant describing the exchange of pyrene between *blobs* and [*blob*] is the local *blob* concentration inside the polymer coil. When two structural units bearing a pyrene pendant encounter, the excited pyrene monomer Py_{diff}^{*} becomes the pyrene monomer Py_{k2}^{*} which undergoes a rapid rearrangement with the nearby ground-state pyrene to form an excimer with a rate constant k_2. The excimer *E0** fluoresces with a lifetime τ_{E0}. The random labelling of the polymer results in a population Py_{free}^{*} of pyrenes that are isolated along the backbone and cannot form excimer. They emit with the lifetime τ_{M} of the pyrene monomer. The random labelling of the polymer generates some pyrene clusters where direct excitation of poorly stacked pyrene dimers results in long-lived pyrene dimers *EL** that emit with a lifetime τ_{EL}. Based on the above, Equations S.5 and S.6 were derived and they have been found to fit the pyrene monomer and excimer satisfyingly.[47]

$$[Py^*]_{(t)} = [Py_{diff}^{*}]_{(t)} + [Py_{k2}^{*}]_{(t)} + [Py_{free}^{*}]_{(t)} = [Py_{diff}^{*}]_{o} \exp\left(-\left(A_2 + \frac{1}{\tau_M}\right)t - A_3\left(1-\exp(-A_4 t)\right)\right)$$

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

$$-[Py^*_{diff}]_o e^{-A_3}\sum_{i=0}^{\infty}\frac{A_3^i}{i!}\frac{A_2+iA_4}{A_2+iA_4-k_2}\exp\left(-\left(A_2+iA_4+\frac{1}{\tau_M}\right)t\right)$$

$$+[Py^*_{free}]_o\exp\left(-\frac{t}{\tau_M}\right)\Bigg] \qquad \text{(S.5)}$$

$$[E^*]_{(t)}=[E0^*]_{(t)}+[E0^*]_{(t)}+[EL^*]_{(t)}=k_2\left(\left([Py^*_{k2}]_o+[Py^*_{diff}]_o e^{-A_3}\sum_{i=0}^{\infty}\frac{A_3^i}{i!}\frac{A_2+iA_4}{A_2+iA_4-k_2}\right)\right.$$

$$\times\frac{\exp\left(-\frac{t}{\tau_{E0}}\right)-\exp\left(-\left(k_2+\frac{1}{\tau_M}\right)t\right)}{k_2+\frac{1}{\tau_M}-\frac{1}{\tau_{E0}}}$$

$$\left.+[Py^*_{diff}]_o e^{-A_3}\sum_{i=0}^{\infty}\frac{A_3^i}{i!}\frac{A_2+iA_4}{A_2+iA_4-k_2}\frac{\exp\left(-\left(A_2+iA_4+\frac{1}{\tau_M}\right)t\right)-\exp\left(-\frac{t}{\tau_{E0}}\right)}{A_2+iA_4+\frac{1}{\tau_M}-\frac{1}{\tau_{E0}}}\right)$$

$$+[E0^*]_o\times\exp\left(-\frac{t}{\tau_{E0}}\right)+[EL^*]_o\times\exp\left(-\frac{t}{\tau_{EL}}\right) \qquad \text{(S.6)}$$

The expression of the parameters A_2, A_3, and A_4 used in Equations S.5 and S.6 is given in Equations S.7 – S.9 as a function of <n>, k_{blob}, and $k_e[blob]$.

$$A_2 = <n> \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \quad (S.7)$$

$$A_3 = <n> \frac{(k_{blob})^2}{(k_{blob} + k_e [blob])^2} \quad (S.8)$$

$$A_4 = k_{blob} + k_e [blob] \quad (S.9)$$

Fitting the monomer and excimer decays using Equations S.5 and S.6 yields the parameters $<n>$, k_{blob}, and $k_e[blob]$. Fitting the monomer decays using Equation S.5 also yields the fractions f_{Mdiff}, f_{Mk2}, and f_{Mfree} which represent the molar fractions of the Py_{diff}^*, $Py_{k_2}^*$, and Py_{free}^* species contributing to the monomer decays, respectively. In a similar manner, fitting the excimer decays with Equation S.6 yields the fractions f_{Ediff}, f_{Ek2}, f_{EE0}, and f_{EEL} which represent the molar fractions of the Py_{diff}^*, $Py_{k_2}^*$, *E0**, and *EL** species contributing to the excimer decays, respectively. 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 of each pyrene species present in solution f_{diff}, f_{k2}, f_{free}, f_{E0}, and f_{EL}.[47]

The fraction f_{Mfree} together with $<n>$ and the pyrene content λ_{Py} (see Table 1) can be used to determine N_{blob}, the average number of structural units per *blob* given in Equation S.10.

$$N_{blob} = \frac{<n>}{\frac{\lambda_{Py}}{(1-f_{Mfree})} \times (x \times M_1 + (1-x) \times M_2)} \qquad (S.10)$$

In Equation S.10, M_1 and M_2 represent the molar mass of the pyrene labelled (326 g·mol^{-1}) and unlabelled (113 g·mol^{-1}) NIPAM monomer. x is the fraction of NIPAM monomers that are labelled with pyrene.

Summary and definitions of parameters used in the Birks Scheme

	Rate Constants and Lifetimes
k_{cy}	Rate constant for end-to-end cyclization
k_{-cy}	Rate constant for excimer dissociation
τ_M	Lifetime of pyrene monomer
τ_E	Lifetime of pyrene excimer
τ_S	Lifetime of short-lived pyrene species

	Pyrene Species
Py^*_{diff}	Excited pyrene forming excimer by diffusion
Py^*_{free}	Excited pyrene unable to form an excimer
Py^*_S	Short-lived excited pyrene species
E^*	Pyrene excimer

	Molar Fractions of Pyrene Species
f_{Mdiff}	$[Py^*_{diff}]_o / \left([Py^*_{diff}]_o + [Py^*_{free}]_o\right)$
f_{Mfree}	$[Py^*_{free}]_o / \left([Py^*_{diff}]_o + [Py^*_{free}]_o\right)$

Summary and definitions of parameters used in the Fluorescence Blob Model

	Parameters describing the diffusive encounters between two pyrene units
k_{blob}	Rate constant describing the process bringing to polymer units bearing a pyrene moiety in contact
$k_e \times [blob]$	Rate constant describing the exchange of polymer units bearing a pyrene moiety from one *blob* to another
$<n>$	Average number of polymer unit bearing a pyrene moiety per *blob*
k_2	Rate constant describing the rapid rearrangement between two pyrene units after having been brought into contact
τ_M	Lifetime of pyrene monomer
τ_E	Lifetime of pyrene excimer
τ_{EL}	Lifetime of long-lived pyrene dimers

	Pyrene Species
Py^*_{diff}	Excited pyrene being brought into range for forming an excimer with a rate constant k_2
Py^*_{free}	Excited pyrene unable to form an excimer
Py^*_{k2}	Excited pyrene forming excimer after a rapid rearrangement of the chain with a rate constant k_2
$E0^*$	Pyrene excimer formed by diffusion
EL^*	Long-lived pyrene dimer

	Molar fractions of pyrene species obtained in the monomer fluorescence decays
f_{Mdiff}	$[Py^{*}_{diff}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o\right)$
f_{Mfree}	$[Py^{*}_{free}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o\right)$
f_{Mk2}	$[Py^{*}_{k2}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o\right)$

	Molar fractions of pyrene species obtained in the excimer fluorescence decays
f_{Ediff}	$[Py^{*}_{diff}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{Ek2}	$[Py^{*}_{k2}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{EE0}	$[E0^{*}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{EEL}	$[EL^{*}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$

	Overall molar fractions of pyrene species
f_{diff}	$[Py^{*}_{diff}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{free}	$[Py^{*}_{free}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{k2}	$[Py^{*}_{k2}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{E0}	$[E0^{*}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$
f_{EL}	$[EL^{*}]_o / \left([Py^{*}_{diff}]_o + [Py^{*}_{free}]_o + [Py^{*}_{k2}]_o + [E0^{*}]_o + [EL^{*}]_o\right)$

Table S.1A: Decay times and pre-exponential factors retrieved from the Birks Scheme analysis of the monomer decays of the Py_2-PNIPAM-6K sample.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_M (ns)	A_M	τ_s (ns)	A_s	χ^2
Acetonitrile	41	0.26	78	0.63	190	0.10	2	0.02	1.10
2-Butanone	35	0.08	72	0.72	105	0.04	2	0.16	1.07
Tetrahydrofuran	43	0.07	140	0.81	190	0.10	2	0.02	1.06
Methanol	47	0.07	108	0.64	220	0.08	2	0.20	1.09
80%	49	0.06	135	0.78	220	0.12	2	0.05	1.12
60%	48	0.04	152	0.74	220	0.10	2	0.12	1.10
Ethanol	47	0.05	142	0.66	220	0.10	2	0.19	1.05
30%	46	0.04	175	0.80	220	0.14	2	0.02	1.14
Hexanol	36	0.04	191	0.76	220	0.17	2	0.02	1.12

Table S.1B: Decay times and pre-exponential factors retrieved from the Birks Scheme analysis of the excimer decays of the Py_2-PNIPAM-6K sample.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_E (ns)	τ_s (ns)	A_s	k_{cy} (μs^{-1})	k_{-cy} (μs^{-1})	χ^2
Acetonitrile	41	–2.82	78	2.94	54	2	0.05	11	2.6	1.10
2-Butanone	35	–2.60	72	2.76	43	2	0.39	5.9	3.3	1.07
Tetrahydrofuran	43	–0.57	140	0.61	63	2	0.18	3.2	6.0	1.06
Methanol	47	–0.82	108	0.86	56	2	0.08	5.9	2.2	1.09
80%	49	–0.66	135	0.72	59	2	0.06	3.8	2.9	1.12
60%	48	–0.59	152	0.66	61	2	0.14	2.8	3.7	1.10
Ethanol	47	–0.59	142	0.65	60	2	0.14	3.4	3.6	1.05
30%	46	–0.44	175	0.52	66	2	0.16	1.9	6.0	1.14
Hexanol	36	–0.30	191	0.42	77	2	0.25	1.9	14	1.12

Table S.2A: Decay times and pre-exponential factors retrieved from the Birks Scheme analysis of the monomer decays of the Py_2-PNIPAM-8K sample.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_M (ns)	A_M	τ_s (ns)	A_s	χ^2
Acetonitrile	43	0.16	89	0.67	190	0.06	2	0.12	1.02
2-Butanone	37	0.09	77	0.80	105	0.04	2	0.08	1.06
Tetrahydrofuran	44	0.04	152	0.77	190	0.10	2	0.09	1.04
Methanol	49	0.05	126	0.72	220	0.08	2	0.15	1.15
80%	50	0.05	151	0.82	220	0.13	2	0.01	1.11
60%	49	0.04	171	0.84	220	0.12	2	0.00	1.15
Ethanol	48	0.05	159	0.82	220	0.10	2	0.04	1.10
30%	47	0.03	187	0.77	220	0.07	2	0.12	1.10
Hexanol	41	0.04	199	0.70	220	0.20	2	0.06	1.08

Table S.2B: Decay times and pre-exponential factors retrieved from the Birks Scheme analysis of the excimer decays of the Py_2-PNIPAM-8K sample.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_E (ns)	τ_s (ns)	A_s	k_{cy} (μs^{-1})	k_{-cy} (μs^{-1})	χ^2
Acetonitrile	43	–0.90	89	0.93	54	2	0.06	8.1	2.6	1.02
2-Butanone	37	–2.44	77	2.59	45	2	0.58	4.9	3.5	1.06
Tetrahydrofuran	44	–0.55	152	0.58	61	2	0.27	2.1	5.5	1.04
Methanol	49	–0.69	126	0.73	58	2	0.13	4.2	2.4	1.15
80%	50	–0.63	151	0.68	62	2	0.14	2.8	3.3	1.11
60%	49	–0.55	171	0.60	66	2	0.23	1.9	4.6	1.15
Ethanol	48	–0.51	159	0.56	64	2	0.17	2.6	4.3	1.10
30%	47	–0.45	187	0.52	72	2	0.34	1.4	6.8	1.10
Hexanol	41	–0.20	199	0.28	93	2	0.41	1.5	12.4	1.08

Table S.3A: Decay times and pre-exponential factors retrieved from the Birks Scheme analysis of the monomer decays of the Py_2-PNIPAM-14K sample.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_M (ns)	A_M	τ_s (ns)	A_s	χ^2
Acetonitrile	44	0.06	124	0.67	190	0.13	2	0.14	1.08
Tetrahydrofuran	40	0.03	172	0.61	190	0.26	2	0.11	1.01
Methanol	47	0.04	167	0.77	220	0.19	2	0.00	1.11
80%	45	0.03	185	0.65	220	0.20	2	0.12	1.08
60%	41	0.03	195	0.56	220	0.29	2	0.12	1.04
Ethanol	42	0.03	190	0.61	220	0.24	2	0.13	1.11
30%	36	0.02	200	0.49	220	0.34	2	0.14	1.15
Hexanol[a]	--	--	--	--	--	--	--	--	--

[a]Decays could not be fit using the Birks Scheme

Table S.3B: Decay times and pre-exponential factors retrieved from the Birks Scheme analysis of the excimer decays of the Py_2-PNIPAM-14K sample.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_E (ns)	τ_s (ns)	A_s	k_{cy} (μs^{-1})	k_{-cy} (μs^{-1})	χ^2
Acetonitrile	44	–0.63	124	0.69	57	2	0.13	3.9	4.0	1.08
Tetrahydrofuran	40	–0.44	172	0.52	78	2	0.55	1.4	11.3	1.01
Methanol	47	–0.49	167	0.59	64	2	0.21	2.2	5.1	1.11
80%	45	–0.41	185	0.51	71	2	0.34	1.6	7.5	1.08
60%	41	–0.34	195	0.47	87	2	0.37	1.7	11.6	1.04
Ethanol	42	–0.35	190	0.48	74	2	0.31	1.5	9.4	1.11
30%	36	–0.20	200	0.30	84	2	0.49	1.4	15.2	1.15
Hexanol[a]	--	--	--	--	--	--	--	--	--	--

[a]Decays could not be fit using the Birks Scheme

Table S.4: Pre-exponential factors and decay times obtained by fitting the monomer fluorescence decays of the Py_2-PNIPAM-25K sample with a sum of two exponentials.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	$<\tau>$ (ns)	χ^2
Acetonitrile	76	0.136	174	0.864	160	1.09
Methanol	82	0.097	209	0.903	197	1.09
80%	76	0.077	216	0.923	206	1.14
60%	89	0.082	217	0.918	206	0.97
Ethanol	81	0.083	215	0.917	204	1.08
30%	86	0.070	217	0.930	208	1.06
Hexanol	49	0.056	212	0.944	203	1.23

Table S.5: Pre-exponential factors and decay times obtained by fitting the monomer fluorescence decays of the Py_2-PNIPAM-45K sample with a sum of two exponentials.

Solvent	τ_1 (ns)	A_1	τ_2 (ns)	A_2	$<\tau>$ (ns)	χ^2
Acetonitrile	58	0.060	185	0.94	177	1.05
Methanol	87	0.057	220	0.94	212	1.22
80%	100	0.063	222	0.94	214	1.13
60%	71	0.043	219	0.96	213	1.06
Ethanol	105	0.060	219	0.94	212	1.20
30%	88	0.049	219	0.95	213	0.99
Hexanol	69	0.035	216	0.97	210	1.08

Table S.6A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in acetonitrile.

Sample	$k_e[blob]$ (µs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	6.7	1.4	1.4	0.60	0.26	0.25	190	0.15	1.14
Py-PNIPAM-3%	7.5	1.5	1.9	0.60	0.26	0.34	190	0.05	1.08
Py-PNIPAM-4%	7.5	1.6	2.1	0.62	0.26	0.36	190	0.02	1.19
Py-PNIPAM-5%	6.6	1.5	2.7	0.53	0.26	0.46	190	0.01	1.23
Py-PNIPAM-6%	6.3	1.6	3.1	0.47	0.26	0.53	190	0.01	1.18

Table S.6B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in acetonitrile.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.56	51	0.00	81	0.20	0.26	0.23	1.14
Py-PNIPAM-3%	0.50	52	0.03	75	0.19	0.26	0.28	1.08
Py-PNIPAM-4%	0.49	52	0.00	70	0.23	0.26	0.28	1.19
Py-PNIPAM-5%	0.43	50	0.00	72	0.20	0.26	0.37	1.23
Py-PNIPAM-6%	0.36	50	0.00	70	0.24	0.26	0.40	1.15

Table S.6C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in acetonitrile.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.50	0.12	0.00	0.21	0.17
Py-PNIPAM-3%	0.48	0.04	0.03	0.27	0.18
Py-PNIPAM-4%	0.48	0.01	0.00	0.28	0.22
Py-PNIPAM-5%	0.42	0.01	0.00	0.37	0.20
Py-PNIPAM-6%	0.36	0.01	0.00	0.40	0.23

Table S.7A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in 2-butanone.

Sample	$k_e[blob]$ (μs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	9.9	1.9	0.6	0.69	0.17	0.22	105	0.08	1.14
Py-PNIPAM-3%	9.0	1.7	1.0	0.67	0.17	0.29	105	0.04	1.07
Py-PNIPAM-4%	8.9	1.7	1.2	0.69	0.17	0.28	105	0.03	1.2
Py-PNIPAM-5%	4.9	1.1	1.9	0.57	0.17	0.42	105	0.01	1.2
Py-PNIPAM-6%	6.0	1.1	2.3	0.53	0.17	0.46	105	0.01	1.2

Table S.7B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in 2-butanone.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.65	49	0.03	71	0.11	0.17	0.21	1.14
Py-PNIPAM-3%	0.59	44	0.00	63	0.16	0.17	0.25	1.07
Py-PNIPAM-4%	0.56	43	0.01	62	0.19	0.17	0.23	1.16
Py-PNIPAM-5%	0.51	44	0.00	63	0.11	0.17	0.37	1.2
Py-PNIPAM-6%	0.47	43	0.00	63	0.13	0.17	0.41	1.15

Table S.7C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in 2-butanone.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.60	0.07	0.03	0.19	0.10
Py-PNIPAM-3%	0.57	0.03	0.00	0.25	0.15
Py-PNIPAM-4%	0.55	0.02	0.01	0.22	0.19
Py-PNIPAM-5%	0.51	0.01	0.00	0.37	0.11
Py-PNIPAM-6%	0.46	0.01	0.00	0.40	0.13

Table S.8A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in ethyl acetate.

Sample	$k_e[blob]$ (μs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	5.0	1.1	0.9	0.58	0.15	0.24	200	0.18	1.14
Py-PNIPAM-3%	5.6	1.1	1.3	0.61	0.15	0.31	200	0.07	1.12
Py-PNIPAM-4%	6.7	1.4	1.3	0.63	0.15	0.32	200	0.04	1.23
Py-PNIPAM-5%	4.2	0.9	2.0	0.53	0.15	0.45	200	0.01	1.10
Py-PNIPAM-6%	4.1	01.0	2.3	0.48	0.15	0.51	200	0.01	1.19

Table S.8B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in ethyl acetate.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.59	47	0.00	103	0.16	0.15	0.24	1.14
Py-PNIPAM-3%	0.54	49	0.00	93	0.18	0.15	0.28	1.12
Py-PNIPAM-4%	0.50	50	0.01	86	0.23	0.15	0.26	1.23
Py-PNIPAM-5%	0.46	51	0.00	82	0.15	0.15	0.39	1.10
Py-PNIPAM-6%	0.41	51	0.00	83	0.16	0.15	0.43	1.19

Table S.8C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in ethyl acetate.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.50	0.16	0.00	0.21	0.14
Py-PNIPAM-3%	0.51	0.06	0.00	0.26	0.17
Py-PNIPAM-4%	0.49	0.03	0.01	0.25	0.22
Py-PNIPAM-5%	0.45	0.01	0.00	0.39	0.15
Py-PNIPAM-6%	0.40	0.01	0.00	0.43	0.16

Table S.9A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in tetrahydrofuran.

Sample	$k_e[blob]$ (µs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	8.5	1.2	0.8	0.54	0.12	0.21	190	0.25	1.13
Py-PNIPAM-3%	5.1	0.9	1.2	0.66	0.12	0.27	190	0.06	1.06
Py-PNIPAM-4%	7.7	1.5	1.0	0.70	0.12	0.24	190	0.06	1.16
Py-PNIPAM-5%	4.0	0.8	1.9	0.59	0.12	0.39	190	0.01	1.15
Py-PNIPAM-6%	3.9	0.8	1.3	0.56	0.12	0.43	190	0.01	1.15

Table S.9B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in tetrahydrofuran.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.63	55	0.11	172	0.02	0.12	0.24	1.13
Py-PNIPAM-3%	0.63	52	0.05	108	0.07	0.12	0.26	1.06
Py-PNIPAM-4%	0.60	54	0.14	100	0.06	0.12	0.21	1.16
Py-PNIPAM-5%	0.53	52	0.00	87	0.11	0.12	0.35	1.15
Py-PNIPAM-6%	0.50	50	0.00	86	0.11	0.12	0.39	1.15

Table S.9C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in tetrahydrofuran.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.49	0.23	0.08	0.19	0.02
Py-PNIPAM-3%	0.59	0.06	0.04	0.24	0.06
Py-PNIPAM-4%	0.57	0.05	0.13	0.20	0.05
Py-PNIPAM-5%	0.53	0.01	0.00	0.35	0.11
Py-PNIPAM-6%	0.50	0.01	0.00	0.38	0.11

Table S.10A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in methanol.

Sample	$k_e[blob]$ (μs^{-1}·M)	k_{blob} (×10^{7} s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	7.4	1.3	1.2	0.56	0.21	0.22	210	0.22	1.16
Py-PNIPAM-3%	5.5	1.2	1.5	0.65	0.21	0.29	210	0.06	1.13
Py-PNIPAM-4%	5.7	1.2	1.8	0.64	0.21	0.33	210	0.03	1.25
Py-PNIPAM-5%	5.8	1.2	2.2	0.55	0.21	0.44	210	0.01	1.19
Py-PNIPAM-6%	5.8	1.2	2.7	0.49	0.21	0.50	210	0.01	1.09

Table S.10B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in methanol.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.58	57	0.13	116	0.07	0.21	0.23	1.16
Py-PNIPAM-3%	0.53	52	0.00	83	0.24	0.21	0.24	1.13
Py-PNIPAM-4%	0.50	52	0.00	79	0.25	0.21	0.26	1.25
Py-PNIPAM-5%	0.43	54	0.00	72	0.23	0.21	0.34	1.19
Py-PNIPAM-6%	0.37	53	0.04	72	0.23	0.21	0.37	1.09

Table S.10C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in methanol.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.47	0.18	0.10	0.18	0.06
Py-PNIPAM-3%	0.50	0.04	0.00	0.22	0.23
Py-PNIPAM-4%	0.49	0.02	0.00	0.25	0.24
Py-PNIPAM-5%	0.42	0.01	0.00	0.34	0.23
Py-PNIPAM-6%	0.35	0.00	0.04	0.38	0.24

Table S.11A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in 80% methanol in hexanol.

Sample	$k_e[blob]$ (µs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	5.5	1.0	1.2	0.54	0.17	0.21	210	0.25	1.18
Py-PNIPAM-3%	4.9	1.0	1.4	0.65	0.17	0.28	210	0.07	1.09
Py-PNIPAM-4%	5.6	1.2	1.4	0.66	0.17	0.30	210	0.04	1.08
Py-PNIPAM-5%	4.4	1.0	2.0	0.59	0.17	0.40	210	0.01	1.14
Py-PNIPAM-6%	4.1	0.9	2.5	0.53	0.17	0.46	210	0.01	1.21

Table S.11B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in 80% methanol in hexanol.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.60	52	0.03	117	0.13	0.17	0.24	1.18
Py-PNIPAM-3%	0.58	51	0.00	96	0.17	0.17	0.25	1.09
Py-PNIPAM-4%	0.55	52	0.00	87	0.21	0.17	0.25	1.08
Py-PNIPAM-5%	0.49	54	0.03	83	0.14	0.17	0.33	1.14
Py-PNIPAM-6%	0.43	53	0.01	76	0.18	0.17	0.38	1.21

Table S.11C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in 80% methanol in hexanol.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.47	0.22	0.02	0.19	0.10
Py-PNIPAM-3%	0.54	0.06	0.00	0.24	0.16
Py-PNIPAM-4%	0.53	0.03	0.00	0.24	0.20
Py-PNIPAM-5%	0.49	0.01	0.03	0.33	0.14
Py-PNIPAM-6%	0.43	0.01	0.01	0.38	0.18

Table S.12A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in 60% methanol in hexanol.

Sample	$k_e[blob]$ (μs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	4.9	0.80	1.0	0.52	0.11	0.22	210	0.26	1.05
Py-PNIPAM-3%	2.9	0.67	1.4	0.66	0.11	0.28	210	0.06	1.12
Py-PNIPAM-4%	3.5	0.68	1.5	0.64	0.11	0.31	210	0.05	1.01
Py-PNIPAM-5%	3.7	0.65	2.0	0.58	0.11	0.39	210	0.02	1.08
Py-PNIPAM-6%	3.2	0.66	2.4	0.54	0.11	0.45	210	0.01	1.06

Table S.12B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in 60% methanol in hexanol.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.58	57	0.13	154	0.05	0.11	0.24	1.05
Py-PNIPAM-3%	0.59	47	0.00	103	0.15	0.11	0.25	1.12
Py-PNIPAM-4%	0.55	55	0.13	111	0.05	0.11	0.27	1.01
Py-PNIPAM-5%	0.50	54	0.11	101	0.05	0.11	0.34	1.08
Py-PNIPAM-6%	0.43	51	0.02	81	0.19	0.11	0.36	1.06

Table S.12C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in 60% methanol in hexanol.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.45	0.22	0.10	0.19	0.04
Py-PNIPAM-3%	0.56	0.05	0.01	0.24	0.14
Py-PNIPAM-4%	0.53	0.04	0.12	0.26	0.05
Py-PNIPAM-5%	0.49	0.02	0.11	0.33	0.05
Py-PNIPAM-6%	0.43	0.01	0.02	0.36	0.19

Table S.13A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in ethanol.

Sample	$k_e[blob]$ (μs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	4.4	0.92	0.9	0.60	0.15	0.21	210	0.19	1.12
Py-PNIPAM-3%	4.3	0.90	1.2	0.64	0.15	0.28	210	0.09	1.10
Py-PNIPAM-4%	4.1	0.94	1.3	0.66	0.15	0.30	210	0.04	1.23
Py-PNIPAM-5%	3.8	0.91	1.7	0.61	0.15	0.38	210	0.01	1.10
Py-PNIPAM-6%	5.1	1.00	1.9	0.55	0.15	0.43	210	0.01	1.05

Table S.13B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in ethanol.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.61	52	0.10	118	0.09	0.15	0.21	1.12
Py-PNIPAM-3%	0.56	51	0.08	106	0.13	0.15	0.24	1.10
Py-PNIPAM-4%	0.52	52	0.04	94	0.17	0.15	0.25	1.23
Py-PNIPAM-5%	0.50	51	0.00	87	0.19	0.15	0.31	1.10
Py-PNIPAM-6%	0.34	51	0.01	80	0.22	0.15	0.34	1.05

Table S.13C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in ethanol.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.51	0.16	0.08	0.17	0.07
Py-PNIPAM-3%	0.52	0.07	0.07	0.22	0.12
Py-PNIPAM-4%	0.53	0.03	0.04	0.25	0.17
Py-PNIPAM-5%	0.49	0.01	0.00	0.30	0.19
Py-PNIPAM-6%	0.40	0.01	0.01	0.40	0.26

Table S.14A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in 30% methanol in hexanol.

Sample	$k_e[blob]$ (µs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	4.7	0.69	0.9	0.43	0.086	0.20	210	0.37	1.06
Py-PNIPAM-3%	3.2	0.66	1.0	0.61	0.086	0.26	210	0.13	1.04
Py-PNIPAM-4%	3.3	0.68	1.1	0.66	0.086	0.28	210	0.06	0.98
Py-PNIPAM-5%	2.5	0.58	1.5	0.64	0.086	0.34	210	0.02	1.15
Py-PNIPAM-6%	2.5	0.55	1.7	0.60	0.086	0.38	210	0.02	1.02

Table S.14B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in 30% methanol in hexanol.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.58	55	0.12	169	0.04	0.086	0.26	1.06
Py-PNIPAM-3%	0.59	52	0.08	128	0.07	0.086	0.26	1.04
Py-PNIPAM-4%	0.59	50	0.05	113	0.11	0.086	0.25	0.98
Py-PNIPAM-5%	0.56	52	0.06	103	0.09	0.86	0.30	1.15
Py-PNIPAM-6%	0.52	54	0.11	118	0.03	0.086	0.36	1.02

Table S.14C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in 30% methanol in hexanol.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.39	0.34	0.08	0.17	0.03
Py-PNIPAM-3%	0.53	0.11	0.07	0.23	0.06
Py-PNIPAM-4%	0.56	0.05	0.05	0.24	0.10
Py-PNIPAM-5%	0.55	0.02	0.06	0.30	0.08
Py-PNIPAM-6%	0.51	0.02	0.11	0.33	0.03

Table S.15A: Parameters retrieved from the FBM analysis of the monomer decays of the Py-PNIPAM-X% samples in hexanol.

Sample	$k_e[blob]$ (µs^{-1}·M)	k_{blob} (×10^7 s^{-1})	$<n>$	f_{Mdiff}	k_2 (ns^{-1})	$f_{M_{k_2}}$	τ_M (ns)	$f_{M_{free}}$	χ^2
Py-PNIPAM-2%	2.8	0.76	0.77	0.39	0.072	0.16	210	0.45	0.99
Py-PNIPAM-3%	2.7	0.73	0.76	0.59	0.072	0.21	210	0.20	1.07
Py-PNIPAM-4%	3.2	0.78	0.77	0.63	0.072	0.21	210	0.15	1.02
Py-PNIPAM-5%	2.5	0.60	1.00	0.66	0.072	0.28	210	0.07	1.24
Py-PNIPAM-6%	2.5	0.62	1.15	0.65	0.072	0.32	210	0.03	1.06

Table S.15B: Parameters retrieved from the FBM analysis of the excimer decays of the Py-PNIPAM-X% samples in hexanol.

Sample	$f_{E_{diff}}$	τ_{E0} (ns)	f_{EE0}	τ_{EL} (ns)	f_{EL}	k_2 (ns^{-1})	$f_{E_{k_2}}$	χ^2
Py-PNIPAM-2%	0.60	52	0.11	169	0.04	0.072	0.25	0.99
Py-PNIPAM-3%	0.64	51	0.08	145	0.05	0.072	0.23	1.07
Py-PNIPAM-4%	0.64	50	0.07	127	0.07	0.072	0.21	1.02
Py-PNIPAM-5%	0.63	53	0.05	127	0.05	0.072	0.26	1.24
Py-PNIPAM-6%	0.59	53	0.07	118	0.06	0.072	0.29	1.06

Table S.15C: Overall fractions of pyrene species obtained from the FBM analysis of the monomer and excimer decays for the Py-PNIPAM-X% samples in hexanol.

Sample	f_{diff}	f_{free}	f_{E0}	f_S	f_{EL}
Py-PNIPAM-2%	0.35	0.41	0.06	0.15	0.02
Py-PNIPAM-3%	0.52	0.18	0.07	0.19	0.04
Py-PNIPAM-4%	0.55	0.13	0.06	0.19	0.06
Py-PNIPAM-5%	0.59	0.06	0.05	0.25	0.05
Py-PNIPAM-6%	0.57	0.03	0.07	0.28	0.06

Table S.16: Errors on the exponents given in Figure 5.

Parameter	Scales as
k_{cy}	$\eta^{-0.76\pm0.09}\times N^{-1.0\pm0.1}$
$k_{-\mathrm{cy}}$	$\eta^{0.82\pm0.05}\times N^{1.3\pm0.1}$
τ_{E}	$\eta^{0.14\pm0.03}\times N^{0.23\pm0.05}$
f_{Mfree}	$\eta^{0.5\pm0.1}\times N^{2.2\pm0.4}$

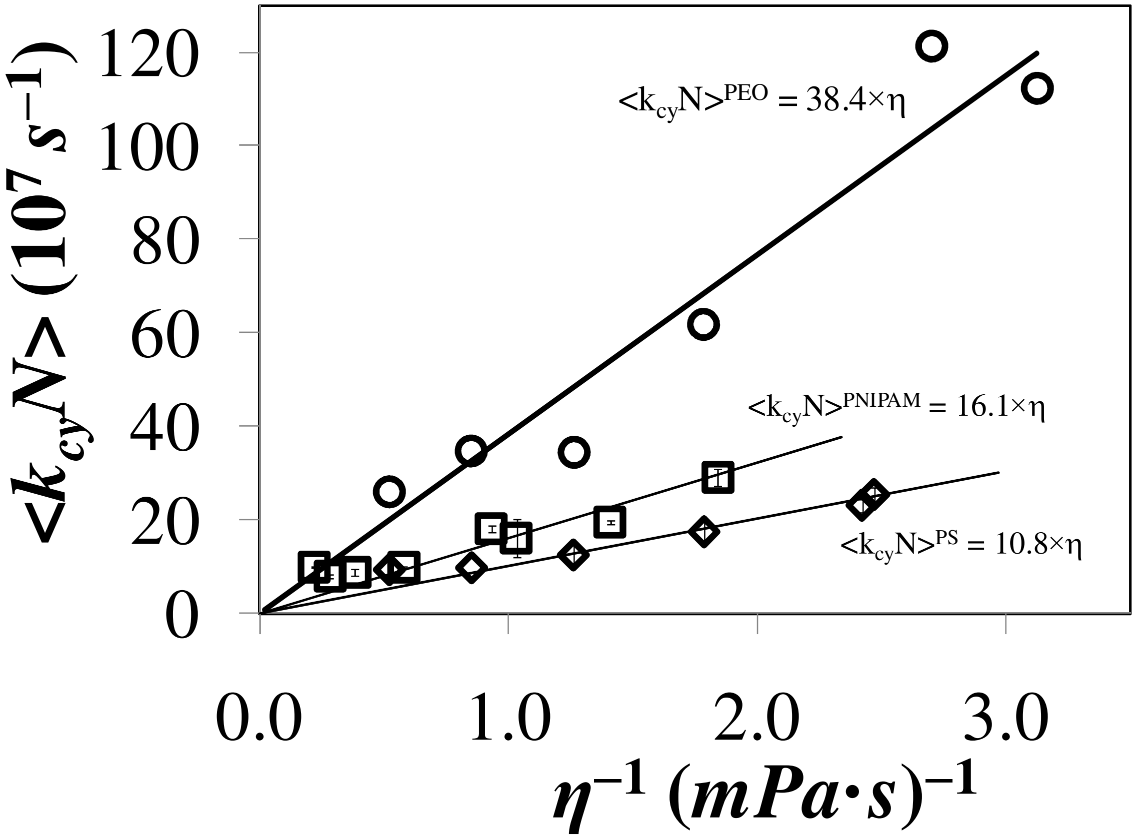

Figure S1: Plots of <k_{cy}×N> versus the inverse of viscosity for poly(ethylene oxide) (from ref. 42 in main text; ○), poly(*N*-isopropylacrylamide) (□), and polystyrene (from ref. # 11 in main text; ◇).