Supporting Information

Reactants were dissolved in 1,4-dioxane, placed in 50 ml ampoules and degassed thoroughly via a freeze, pump, thaw procedure. They were polymerised at 60°C for 24 hours before being precipitated multiple times into diethyl ether, then freeze dried from water to yield a white solid. ^{1}H NMR of PAA in D_20 (2.35 (m CH) m (1.75 CH_2)). ^{1}H of PAM in D_2O (2.31 (m CH) 1.99 (m CH_2) 1.6 (m CH_3)). Fluorescence measurements were carried out in dilute solutions of ultrapure water in 1 cm quartz cuvettes and anisotropy measurements were carried out on an Edinburgh 199 Fluorescence Spectrometer. Data was analysed over a 200 ns timescale in channels of 0.4 ns per channel, a range chosen for its sensitivity at low PAM concentrations.

Table SM1. Experimental conditions of data shown in Fig. 2.
Sample concentration 0.3 mg ml-1 and carried out at 25°C.
SD represents the standard deviation of the measurement of τ_c.

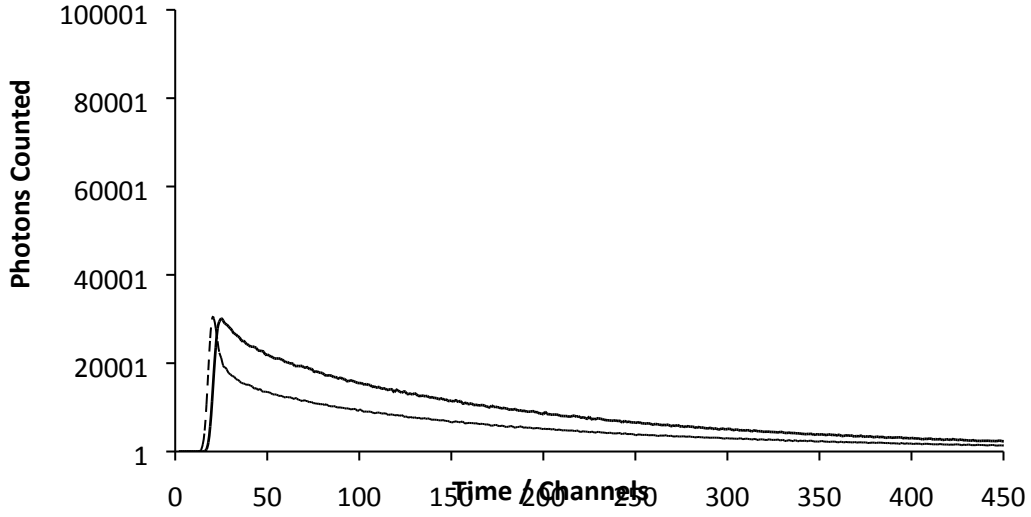
Polymer	pH	τ_c / nS	SD / ns	r_o	A	ChiSq
PAA*	1.65	5.68	0.11	0.12	0.000	1.25
PAA*	2.20	5.58	0.14	0.17	0.002	1.09
PAA*	2.33	4.66	0.15	0.17	0.002	1.09
PAA*	2.64	5.17	0.89	0.13	0.002	1.13
PAA*	2.83	4.42	0.17	0.27	0.002	1.15
PAA*	3.07	4.09	0.15	0.17	0.002	1.08
PAA*	3.13	3.93	0.17	0.15	0.003	1.25
PAA*	3.23	4.48	1.02	0.18	0.003	0.91
PAA*	3.75	3.16	0.19	0.25	0.002	1.22
PAA*	4.28	3.76	0.21	0.12	0.001	1.00
PAA*	4.36	3.61	0.47	0.14	0.002	1.09
PAA*	4.37	3.63	0.40	0.18	0.002	1.04
PAA*	6.01	2.74	0.19	0.13	0.003	1.12
PAA*	6.60	2.62	0.15	0.18	0.002	1.31
PAA*	6.80	2.66	0.15	0.22	0.002	1.14
PAA*	8.10	2.36	0.21	0.19	0.002	0.99
PAA*	9.58	2.35	0.17	0.15	0.003	1.23
PAA*	9.64	1.74	0.21	0.19	0.003	0.95
PAA*	1.60	5.64	0.49	3.84	0.001	1.01
PAM*	6.10	1.88	0.51	0.12	0.005	1.20
PAM*	1.60	1.62	0.16	0.15	0.003	1.13
PAM*	7.40	1.94	0.46	6.44	0.001	1.09
PAM*	7.64	1.21	0.30	0.16	0.003	0.87
PAM*	10.73	1.50	0.26	0.10	0.002	1.08
PAM*	3.00	1.63	0.32	0.12	0.002	1.05
PAM*	6.61	1.48	0.36	9.04	0.002	1.09
PAM*	9.33	1.55	0.27	0.19	0.003	0.97
PAM*	5.83	1.66	0.25	0.18	0.002	1.03

Table SM2 - Experimental conditions of data shown in Fig. 3.
Sample concentration 0.3 mg ml-1 and carried out at pH 4.5

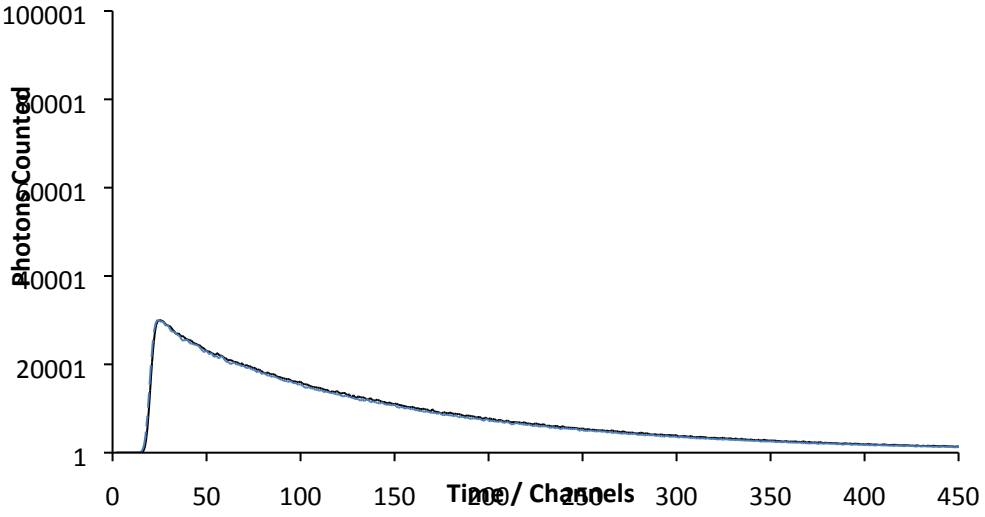
Polymer	Temp	τ_c / nS	SD / nS	r_o	A	ChiSq
PAA*	10	4.16	0.57	0.13	0.002	1.63
PAA*	18	2.70	0.66	0.13	0.002	1.23
PAA*	18	2.65	0.25	0.14	0.002	1.17
PAA*	21	2.37	0.46	0.17	0.002	1.08
PAA*	29	2.00	0.28	0.12	0.002	1.13
PAA*	33	2.01	0.34	0.16	0.002	1.07
PAA*	38	1.72	0.42	0.17	0.002	1.00
PAA*	46	1.15	0.18	0.26	0.002	1.00
PAA*	55	1.09	0.22	0.20	0.002	0.93
PAA*	25	2.36	0.55	0.14	0.002	1.09
PAM*	8	3.24	0.39	0.15	0.002	1.27
PAM*	10	3.55	0.42	0.12	0.001	1.21
PAM*	15	2.72	0.51	0.12	0.005	1.04
PAM*	16	2.20	0.31	0.14	0.008	1.05
PAM*	20	1.99	0.18	0.15	0.010	1.03
PAM*	30	1.41	0.22	0.14	0.008	1.12
PAM*	35	1.52	0.14	0.14	0.005	0.93
PAM*	36	1.26	0.11	0.19	0.000	1.04
PAM*	40	1.10	0.14	0.10	0.007	1.13
PAM*	40	1.22	0.11	0.14	0.005	1.05
PAM*	45	1.18	0.16	0.14	0.006	1.03
PAM*	50	1.11	0.22	0.13	0.003	1.04
PAM*	55	1.02	0.14	0.13	0.003	1.02
PAM*	58	0.88	0.14	0.09	0.008	0.97
PAM*	25	1.66	0.25	0.18	0.002	1.03

Fig SM 1 – Low pH Fluorescent decay of PAA-ACE alone (solid line) and mixed with PAM (dashed line) in solution (0.5 mg ml^{-1}) at pH 3 (a) and pH 6 (b).
1 channel = 0.4 nanoseconds.

a)

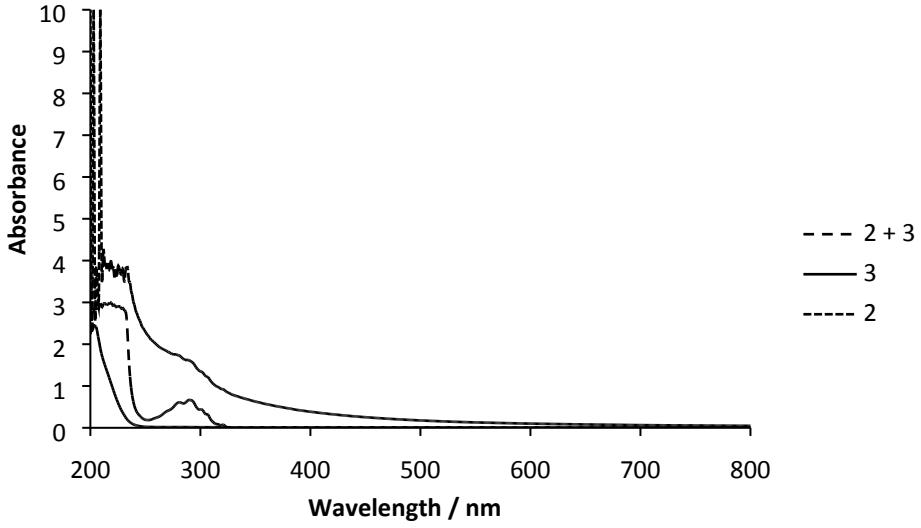


b)



The calculated lifetimes of PAA-ACE and PAA-ACE + PAM mixtures at pH 6 are identical. At pH 3 the fluorescence decay is identical between the two systems with the exception of the scattered light peak (caused by aggregated particles clouding solution) visible for the first twenty channels following the peak.

Fig SM2 – UV absorbance of polymer samples at 0.1 mg ml-1 of polymer 2 (PAA), polymer 3 (PAM) and a mixture of the two, all carried out at pH 2.



Mixing of polymer 2 and 3 leads to a broadening of the ACE absorbance observed at 295 nm however no new peaks are observed in this region.

Table SM3 - Experimental conditions of data shown in Fig. 7, fitted analysis using Eq. 2 and Eq. 3

	τ_c / nS	SD / nS	r_o	A	ChiSq
Eq. 2	12.3	1.68	0.05	0.005	1.35
Eq. 3	127.9	2.83	0.08	0.000	1.12

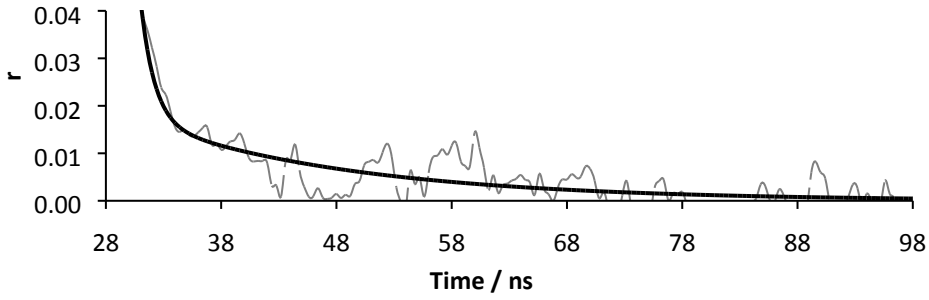
Table SM4 - Experimental conditions of data shown in Fig. 9

Sample	pH	τc / nS	Sd / nS	ChiSq
PAA* + PAM	0.64	214	8.77	1.04
PAA* + PAM	0.96	196	8.29	1.04
PAA* + PAM	1.20	183	4.26	1.17
PAA* + PAM	1.70	179	2.83	1.12
PAA* + PAM	2.16	181	9.70	1.24
PAA* + PAM	2.30	119	10.65	1.31
PAA* + PAM	2.52	120	4.52	1.22
PAA* + PAM	2.95	16.1	0.64	1.47
PAA* + PAM	3.19	20.56	1.26	0.95
PAA* + PAM	3.64	19.77	1.43	0.98
PAA* + PAM	5.00	13.56	0.83	1.03
PAA* + PAM	6.15	3.19	0.22	1.18
PAA* + PAM	7.21	2.75	0.17	1.03
PAA* + PAM	8.92	2.84	0.07	1.44

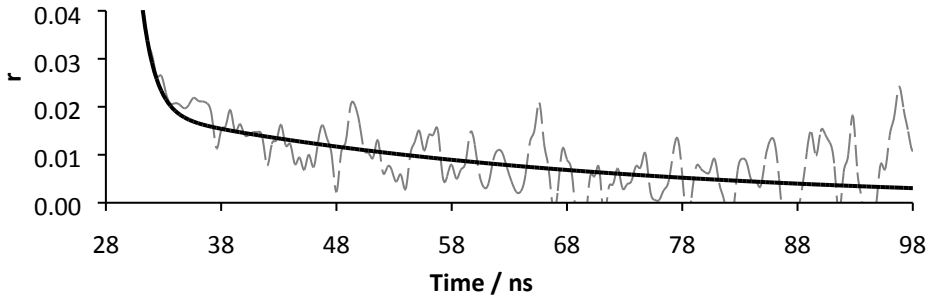
Fitting using equation 2 does not clearly differentiate polymers engaged in an IPC whereas Eq. 3 gives a distinct rise in observed τ_c, however this comes at a significant cost to the SD and ChiSq. PAA* shows very high ChiSq because when there is no complexation therefore fixing A to zero is not appropriate and better fits could be obtained if A is left variable, however for PAA* + PAM mixtures ChiSq is lowered to below 1.5

Fig SM3 – Raw anisotropic decay of polymer 2 (200 ppm) with varying polymer 3 concentration at pH 2. Fitted correlation times using Eq. 3 are shown in Fig. 10

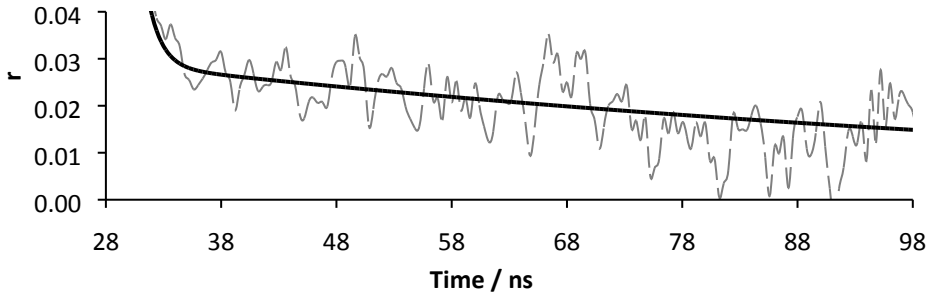
a) 0 ppm



b) 2 ppm



c) 31 ppm



d) 105 ppm

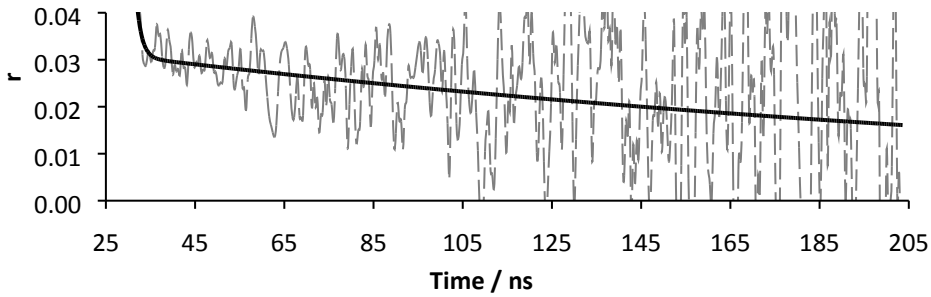
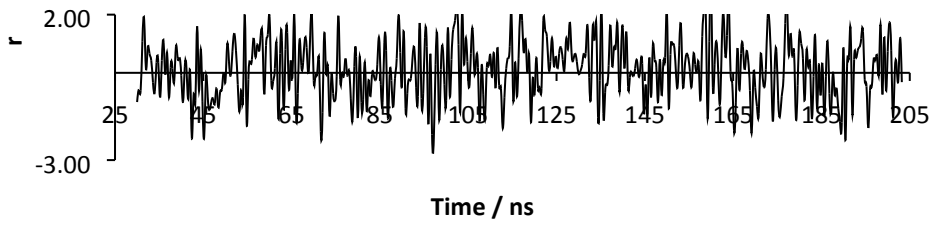
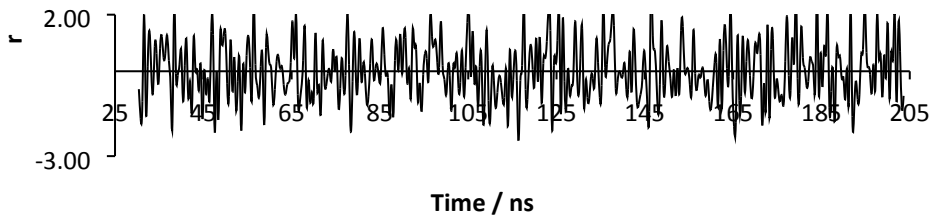


Fig SM4 – Residuals of Fitted Correlation Times shown in Fig. 10 (raw anisotropic decay SM2 fitted using Eq. 3) Varying concentrations of poly(acrylamide): a) 0 ppm , b) 2 ppm, c) 21 ppm, d) 105 ppm

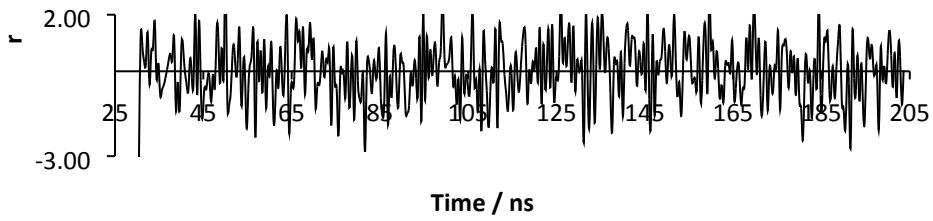
a)



b)



c)



d)

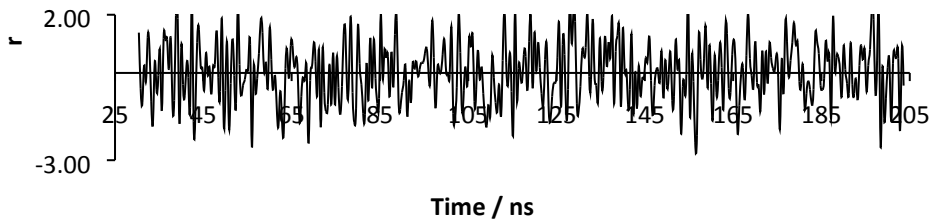


Table SM5 - Experimental conditions of data shown in Fig. 11, with PAA* conc. at 200ppm and pH fixed to 2, A fixed to zero.

Conc PAM / ppm	**τ_c / nS**	**ChiSq**
0.0	16.32	1.08
2.1	34.66	1.02
5.3	61.00	1.09
10.6	80.12	1.05
18.5	107.86	0.96
21.2	101.88	1.05
31.8	123.42	1.09
53.0	153.81	1.06
58.0	165.68	1.06
74.2	150.56	1.12
84.8	162.93	1.00
106.0	177.78	1.03

The ChiSq value (representing goodness of fit) shows that the fit is most difficult when the concentration of PAM is very low (between 5 and 20 ppm). It is at these low levels of complexing polymer, where the majority of the PAA is not involved in IPC formation, that It is most difficult to apply a mathematically good fit.