Electronic Supplementary Material (ESI) for Soft Matter.

Poly(acrylic acid) Interpolymer Complexes

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Supporting Information:

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Modelling information:

Calculations are based on the assumption of ideality in the thermodynamics. A symmetry number of 1 is used in the rotational entropy calculation and the entropies converted to energies by multiplication by the temperature (298.15 K). Internal Energy = Electronic Energy + Zero Point Energy + Thermal Corrections for Vibrations, Rotations and Translations. Enthalpy = Internal Energy + kB·T. Entropy = T·(Entropy for electronic, vibration, rotation and translation).

Monomer Calculations

PAM - Aliphatic Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-248.39778148	-248.41484558
Enthalpy	-248.39683727	-248.41390138
Entropy	0.03423091	0.03423091
Free Energy	-248.43106818	-248.44813229

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.01706411 Eh (-44.80 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-248.72650352	-248.83043011
Enthalpy	-248.72555931	-248.82948590
Entropy	0.03415123	0.03413530
Free Energy	-248.75971054	-248.86362119

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.103910654 Eh (-272.82 kJ·mol^{-1})

PAM - Vinyl Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-247.19450012	-247.50204371
Enthalpy	-247.19355591	-247.21053054
Entropy	0.03403968	0.03397593
Free Energy	-247.22759559	-247.24450647

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.016910885 Eh (-44.40 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-247.52504967	-247.62786691
Enthalpy	-247.52410546	-247.62692270
Entropy	0.03381657	0.03375283
Free Energy	-247.55792203	-247.66067553

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.102753495 Eh (-269.78 kJ·mol^{-1})

PNIPAM - Aliphatic Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-366.22036044	-366.23504984
Enthalpy	-366.21941623	-366.23410563
Entropy	0.04203964	0.04216713
Free Energy	-366.26145587	-366.27627276

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.014816889 Eh (-38.90 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-366.55962917	-366.64669556
Enthalpy	-366.55868496	-366.64575135
Entropy	0.04181653	0.041864342
Free Energy	-366.60050149	-366.68761569

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.087114199 Eh (-228.72 kJ·mol^{-1})

PNIPAM - Vinyl Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-365.01904551	-365.03343786
Enthalpy	-365.01810130	-365.03249365
Entropy	0.04277270	0.04256553
Free Energy	-365.06087400	-365.07505918

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.01418518 Eh (-37.24 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-365.35982123	-365.44594916
Enthalpy	-365.35887702	-365.44500495
Entropy	0.04248585	0.042406172
Free Energy	-365.40136287	-365.48741112

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.086048249 Eh (-225.92 kJ·mol^{-1})

PDMAM - Aliphatic Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-326.92870318	-326.94190462
Enthalpy	-326.92775897	-326.94096041
Entropy	0.03917113	0.03923487
Free Energy	-326.96693010	-326.98019528

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.01326518 Eh (-34.83 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-327.27283508	-327.36160462
Enthalpy	-327.27189087	-327.36066041
Entropy	0.03913926	0.03923487
Free Energy	-327.31103013	-327.39989528

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.088865157 Eh (-233.32 kJ·mol^{-1})

PDMAM - Vinyl Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-325.72483100	-325.73793472
Enthalpy	-325.72388679	-325.73699051
Entropy	0.03985638	0.03977670
Free Energy	-325.76374317	-325.77676721

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.013024039 Eh (-34.19 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-326.07099293	-326.15875751
Enthalpy	-326.07004872	-326.15781330
Entropy	0.03960140	0.03937830
Free Energy	-326.10965012	-326.19719160

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.087541473 Eh (-229.84 kJ·mol^{-1})

PVP - Aliphatic Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-365.03080926	-365.04529577
Enthalpy	-365.02986505	-365.04435157
Entropy	0.03923487	0.03920300
Free Energy	-365.06909992	-365.08355457

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.014454648 Eh (-37.95 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-365.37301107	-365.45992822
Enthalpy	-365.37206686	-365.45898401
Entropy	0.03942610	0.03936236
Free Energy	-365.411492966	-365.49834637

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.086853405 Eh (-228.03 kJ·mol^{-1})

PVP - Vinyl Structure

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-363.83479719	-363.84801647
Enthalpy	-363.83385298	-363.84707226
Entropy	0.03979264	0.039330489
Free Energy	-363.87364562	-363.88640275

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.012757131 (-33.49 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-364.16967705	-364.25873685
Enthalpy	-364.16873284	-364.25779264
Entropy	0.03988826	0.03945798
Free Energy	-364.20862110	-364.29725062

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.088629523 (-232.70 kJ·mol^{-1})

PVA

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-154.94079932	-154.94955463
Enthalpy	-154.93985511	-154.94861042
Entropy	0.02962536	0.02964129
Free Energy	-154.96948047	-154.97825171

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.008771246 Eh (-23.03 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-155.23481706	-155.34653135
Enthalpy	-155.23387285	-155.34558714
Entropy	0.03110742	0.03007157
Free Energy	-155.26498027	-155.37565871

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.110678438 Eh (-290.59 kJ·mol^{-1})

PEG

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-462.42619928	-462.43935317
Enthalpy	-462.42525507	-462.43840897
Entropy	0.04524281	0.04544998
Free Energy	-462.47049788	-462.48385895

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.01336107 Eh (-35.08 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-462.75133627	-462.83565022
Enthalpy	-462.75039206	-462.83470601
Entropy	0.04486034	0.04498783
Free Energy	-462.79525240	-462.87969384

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.084441439 Eh (-221.70 kJ·mol^{-1})

PCN

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-171.96085334	-171.97240380
Enthalpy	-171.95990913	-171.97145959
Entropy	0.03166519	0.03168112
Free Energy	-171.99157432	-172.00314071

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.011566396 Eh (-30.37 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-172.26359976	-172.36354843
Enthalpy	-172.26265555	-172.36260422
Entropy	0.03177674	0.03176080
Free Energy	-172.294432291	-172.39436502

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.099932734 Eh (-262.37 kJ·mol^{-1})

PDEAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-405.48734726	-405.49951484
Enthalpy	-405.48640305	-405.49857063
Entropy	0.04603962	0.04610337
Free Energy	-405.532442671	-405.54467400

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.012231325 Eh (-32.11 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-405.83667457	-405.91990357
Enthalpy	-405.83573036	-405.91895936
Entropy	0.04589619	0.04589620
Free Energy	-405.88162655	-405.96485555

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.083229000 Eh (-218.52 kJ·mol^{-1})

PEAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-326.94232469	-326.95706633
Enthalpy	-326.94138048	-326.95612212
Entropy	0.03955360	0.03990419
Free Energy	-326.98093408	-326.99602631

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.015092236 Eh (-39.62 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-327.28235499	-327.37347407
Enthalpy	-327.28141078	-327.37252986
Entropy	0.03963328	0.03971296
Free Energy	-327.32104406	-327.41224282

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.091198761 Eh (-239.44 kJ·mol^{-1})

PHEAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-362.89129557	-362.90817938
Enthalpy	-362.89035136	-362.90723517
Entropy	0.04019104	0.04033447
Free Energy	-362.93054240	-362.94756964

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.017027236 Eh (-44.71 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-363.22457939	-363.32299479
Enthalpy	-363.22363518	-363.32205059
Entropy	0.04057351	0.04084443
Free Energy	-363.26420869	-363.36289502

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.098686325 Eh (-259.10 kJ·mol^{-1})

Trimer Structures

PAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-779.71630677	-779.75619665
Enthalpy	-779.71536256	-779.75525244
Entropy	0.05963318	0.05993597
Free Energy	-779.77499574	-779.81518841

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.040192667 (-105.53 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-780.10276678	-780.19051618
Enthalpy	-780.10182257	-780.18957197
Entropy	0.05754554	0.05658937
Free Energy	-780.15936811	-780.24616134

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.086793229 Eh (-227.88 kcal/mol)

PNIPAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1133.20012757	-1133.22671134
Enthalpy	-1133.19918337	-1133.22576713
Entropy	0.07698768	0.07939404
Free Energy	-1133.27617105	-1133.30516117

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.028990123 Eh (-76.11 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1133.58011987	-1133.64978990
Enthalpy	-1133.57917566	-1133.64884569
Entropy	0.07660521	0.07826257
Free Energy	-1133.6557809	-1133.72710826

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.071327393 (-187.27 kJ·mol^{-1})

PDMAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1015.31983559	-1015.34367251
Enthalpy	-1015.31889138	-1015.34272830
Entropy	0.07220683	0.07153751
Free Energy	-1015.39109821	-1015.41426581

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.0231676 Eh (-60.83 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1015.70630195	-1015.77651528
Enthalpy	-1015.70535774	-1015.77557107
Entropy	0.07335423	0.07276459
Free Energy	-1015.77871197	-1015.84833566

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.069623691 Eh (-182.80 kJ·mol^{-1})

PEAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1017.75388403	-1017.78258206
Enthalpy	-1017.75293982	-1017.78163785
Entropy	0.06986421	0.07281240
Free Energy	-1017.82280403	-1017.85445025

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.031646223 Eh (-83.09 kJ·mol^{-1})

Protonated Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1018.12456613	-1018.20081994
Enthalpy	-1018.12362192	-1018.19987573
Entropy	0.06909927	0.07303551
Free Energy	-1018.19272119	-1018.27291124

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.08019005 Eh (-210.54 kJ·mol^{-1})

PDEAM

Neutral Molecule

Components	Gas Phase (Eh)	Water Solvated (Eh)
Internal Energy	-1253.39861234	-1253.42131534
Enthalpy	-1253.39766814	-1253.4203711
Entropy	0.08087611	0.08218287
Free Energy	-1253.47854425	-1253.50255400

$\Delta G_{solv} = G_{aq} - G_{gas}$ = -0.024009757 Eh (-63.038 kJ·mol^{-1})

Calibration of pK_a calculations

The pK_as for a selection of carboxylic acids, amides and alcohols (Table S1) were calculated by the same methodology as the polymer monomers. A calibration curve (Figure S1) was constructed, using the known experimental values to correct the pK_a values of systems with unknown experimental pK_a values.

Table S1. Calculated and Experimental pKa values for calibration systems

System	Experimental pK_a[1]	Calculated pK_a
Formic acid	3.77	6.95
Acetic acid	4.76	10.22
Chloroacetic acid	2.86	5.31
Dichloroacetic acid	1.29	2.72
Trichloroacetic acid	0.65	0.33
Acetamide	-0.51	-5.75
Phenol	9.95	17.15
Methanol	15.54	29.11
Ethanol	15.9	28.48
Urea	0.18	-3.67

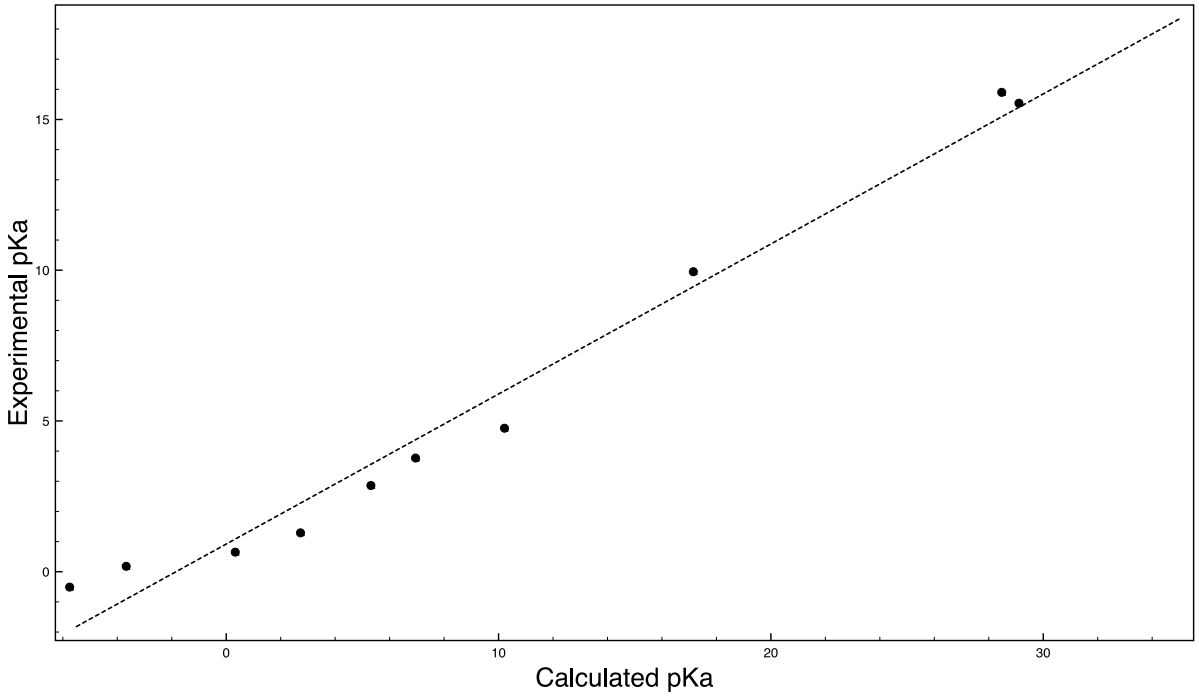
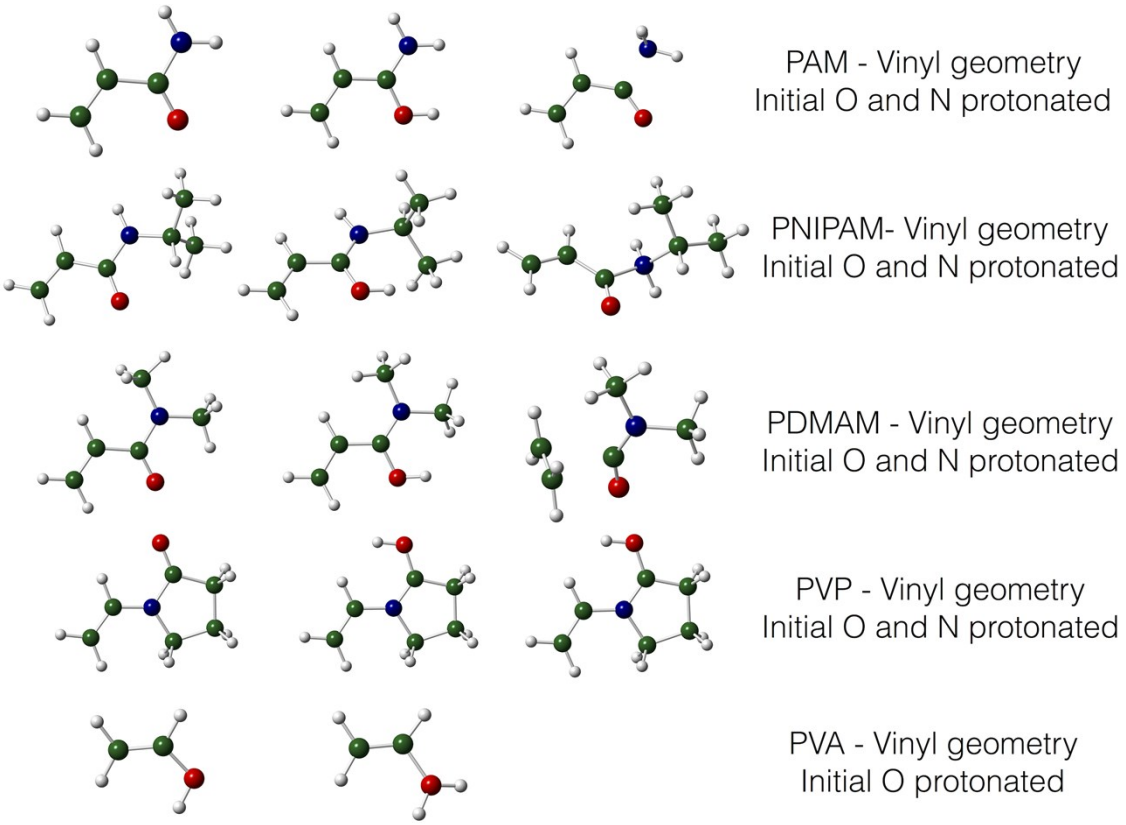


Figure S1. Calibration curve derived from set of references structures. Regression line has equation y = 0.4967x + 0.9184, R^2 = 0.97759.

Optimised Structures for Vinyl Monomers



Analysis of Fluorescence Labels

When covalently attached to the PAA polymer the fluorescence intensity of the ACE fluorophore does not respond significantly to the pH of the solution, although there is some slight quenching at higher pH (Figure S2). As the ACE-label is covalently bound to the polyacrylic acid chain the expansion/contraction of the polymer chain has no effect on the wavelengths or intensity of the label's luminescence. PAA in dilute solution does not fluoresce in this region without the ACE label[1].

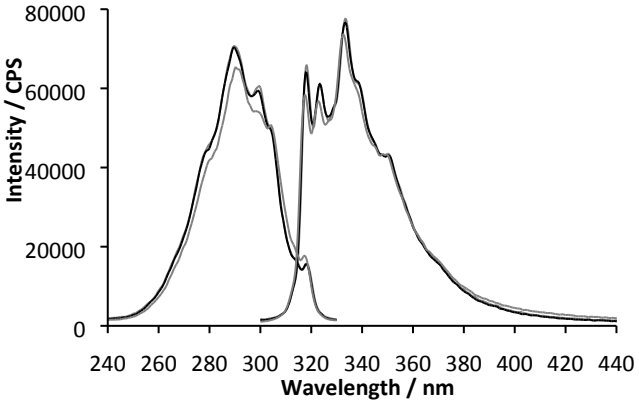


Figure S2 – Emission/Excitation intensities of ACE-Labelled PAA polymers at pH 2 (solid black line), pH 4 (dark grey line) and pH 12 (light grey line).

Fluorescent label ACE has a peak excitation/emission wavelength of 295 / 340 nm. The label was studied by Time Correlated Photon Counting (TCPC) in 1,4-dioxane and was shown to have a lifetime (τ) of 11.6 ns (standard deviation 0.04 ns, χ^2 3.41) and a correlation time (τ_c) of 0.17 ns (standard deviation 0.01 ns, χ^2 1.05). The τ_c of the label in solution is significantly smaller than when it was bound to a poly(acrylic acid) backbone (approx. 10 - 30 ns, pH dependant) because the free label rotates freely in solution at a speed that exceeds the lifetime of its excited state[1]. The decay in anisotropy of the free label and the label attached to PAA is shown in Figure S3. When bound to PAA the decay in anisotropy of the label is determined by the state of segmental rotations, affected by the conformational state of the polymer chain. This is in turn affected by the complexation of the polymer which leads to a long component in the loss of anisotropy that lasts beyond 200 nanoseconds. This is fitted using a dual exponential function as described in previous publications (Figure S4)[1-2].

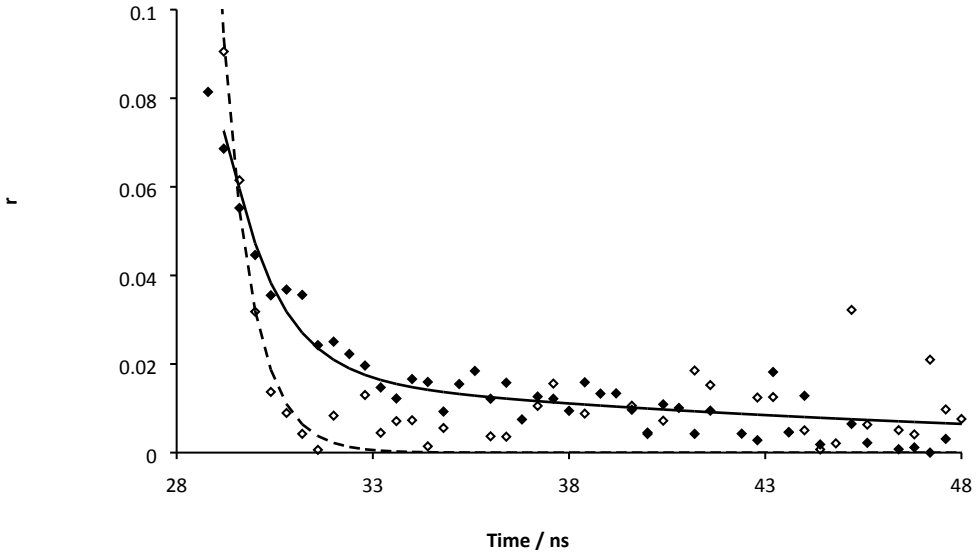


Fig. S3 – Anisotropy profile following excitation pulse of ACE label in dioxane (clear diamonds) with fitted profile (dashed line, $\chi^2 = 3.41$) compared to p(AA-*co*-ACE) in water (black diamonds) with fitted profile (solid line, $\chi^2 = 1.02$).

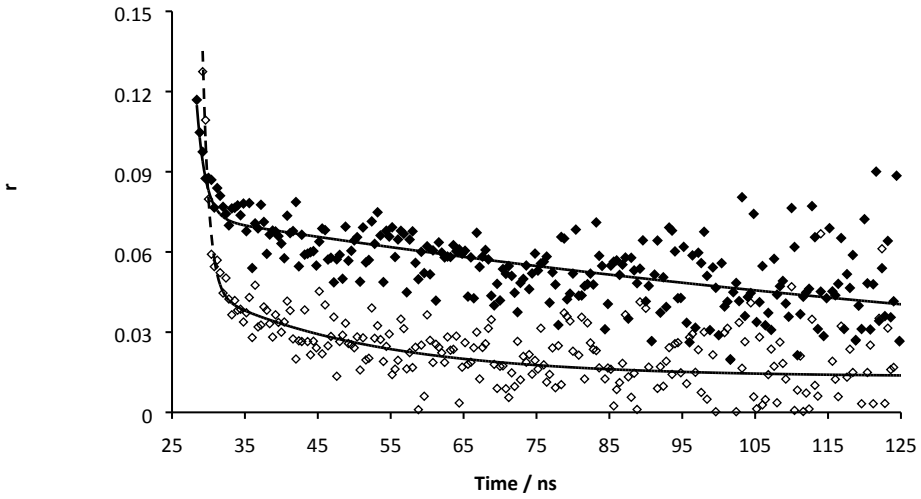
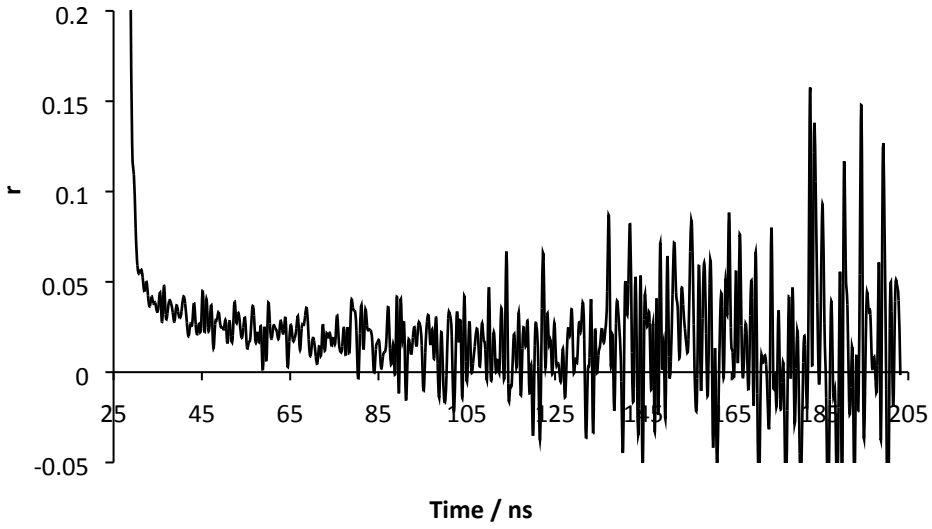
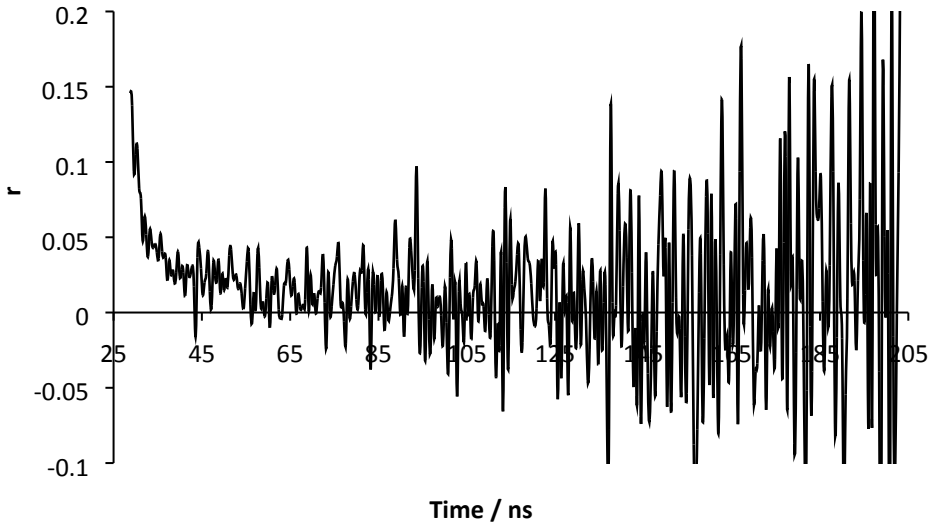
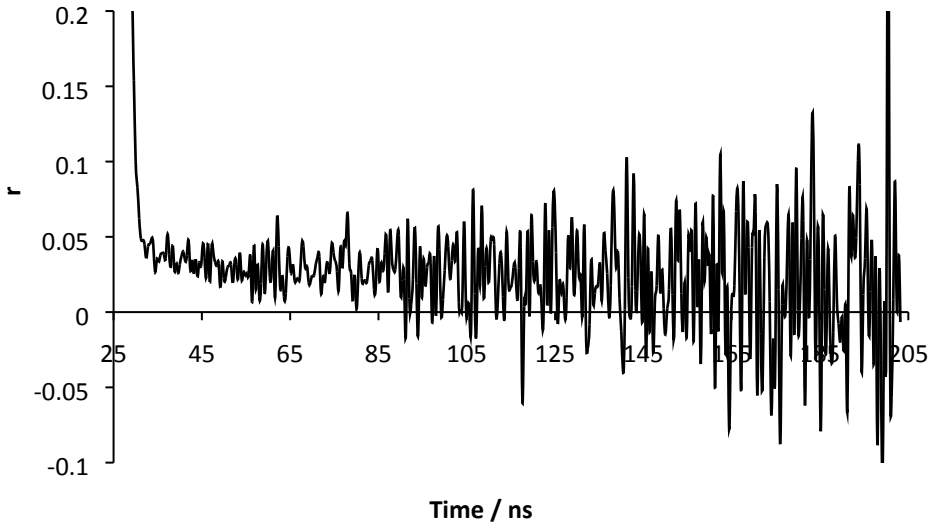
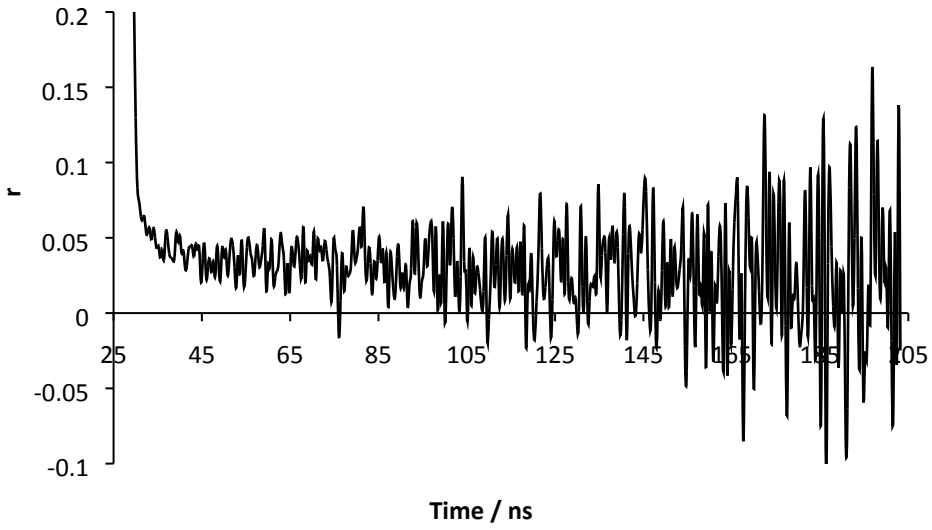
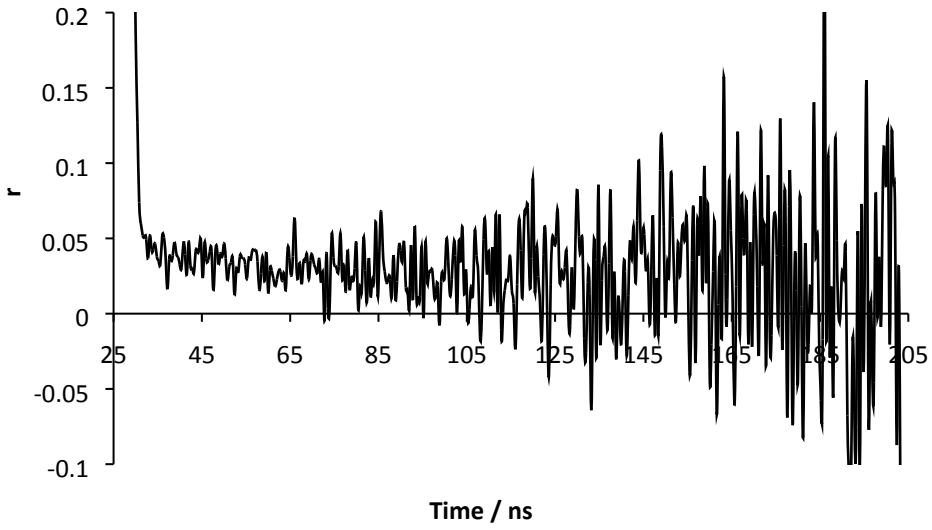
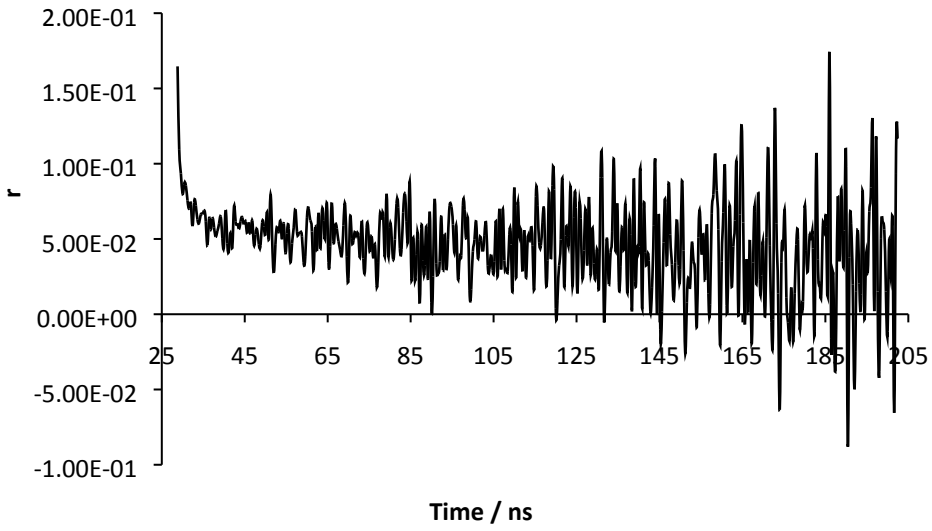
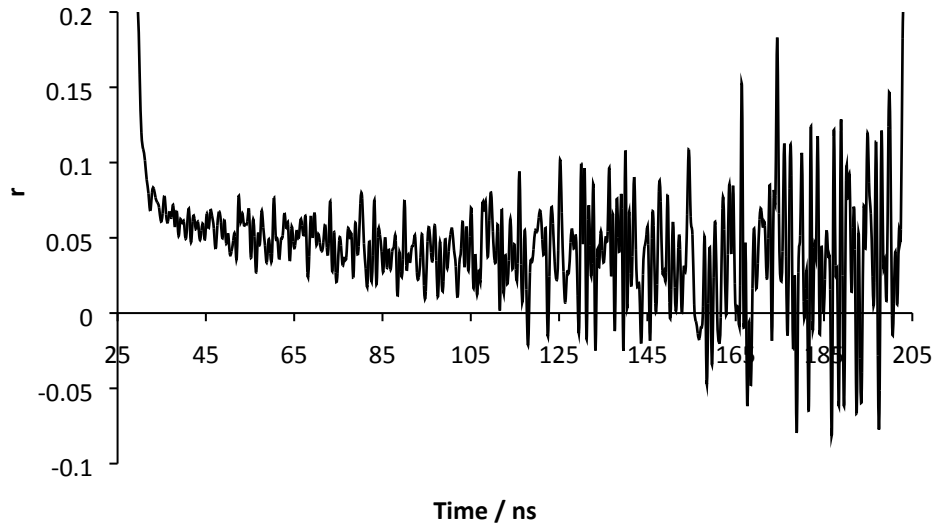
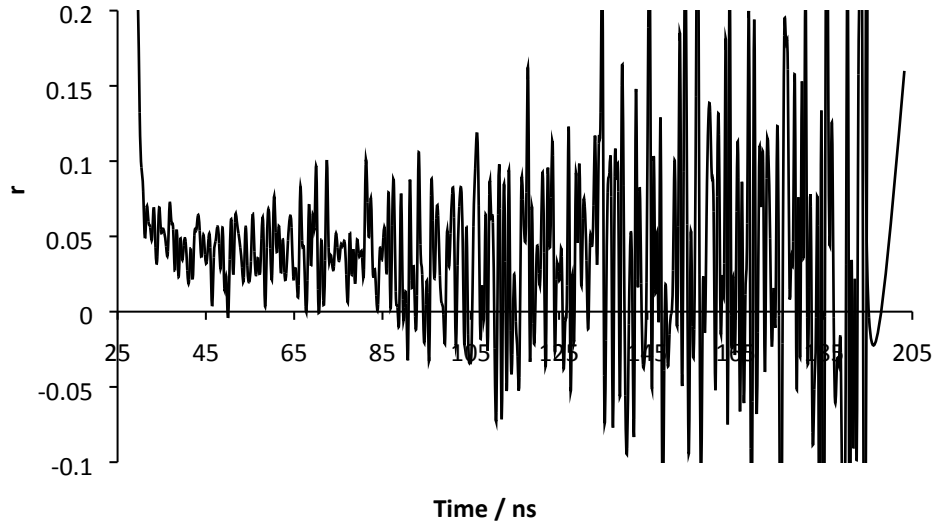


Fig. S4 - Anisotropy decays following excitation pulse of p(AA-*co*-ACE) with PAM (black diamonds) with fitted profile (black line, $\chi^2 = 1.12$) and PEO (clear diamonds) with fitted profile (dashed line, $\chi^2 = 1.05$) at pH 2.

Example raw anisotropy data for PAA with each of the complexed polymers is shown below:

PEO Weak increase in long component – increase in τ_c from 5 to 50 ns	
PVA Weak increase in long component – increase in τ_c from 5 to 40 ns	
PAM Strong second component as documented previously[1-2]. Increase in τ_c from 5 to 190 ns.	

PNIPAM Strong second component. Increase in τ_c from 5 to 150 ns.	
PDMA Strong second component. Increase in τ_c from 5 to 200 ns.	
PVP Strong second component. Increase in τ_c from 5 to 190 ns.	

PDADMAC Strong second component. Increase in τ_c from 5 to 90 ns.	
PDAEC Strong second component. Increase in τ_c from 5 to 160 ns. However strong noise over this range.	

Datasets shown in Fig. 4 and 5:

Table S2 – pH, Tc and SD data of complexed PAA probes shown in Fig. 4

	pH	Tc / ns	SD / ns	χ^2
PEO	3.81	32.39	3.15	1.905
PEO	5.04	4.64	0.35	1.260
PEO	1.05	15.92	1.13	1.050
PEO	1.68	49.75	4.42	1.680
PEO	2.81	46.73	6.79	1.405
PEO	6.36	3.42	0.38	1.590
PEO	8.10	2.75	0.38	2.025
PEO	1.50	32.77	4.73	1.500
PEO	4.46	19.60	7.43	1.115
PVA	4.26	4.457	0.40	1.420
PVA	1.07	37.94	3.16	1.070
PVA	1.7	35.53	3.642	1.700
PVA	3.5	7.015	0.865	2.750
PVA	7.6	2.498	0.190	1.450
PVA	4.65	2.211	0.309	2.325
PVA	2.5	28.201	2.992	1.250
PVA	2.65	25.80	2.61	1.325
PVA	0.86	38.540	3.455	1.290
PVA	2.1	37.08	2.938	1.260
PVA	3.67	7.006	1.088	2.202

Table S3 - pH, Tc and SD data of complexed PAA probes shown in Fig. 5

	pH	Tc / ns	Sd / ns	χ^2
PAM	1.70	179.90	5.66	1.350
PAM	8.92	2.84	0.14	1.792
PAM	5.00	13.56	1.68	1.400
PAM	3.19	20.56	2.53	1.548
PAM	1.20	183.02	8.53	1.200
PAM	2.52	120.43	9.04	1.760
PAM	2.95	16.08	1.30	1.488
PAM	3.64	19.77	2.87	1.660
PAM	0.96	196.64	6.58	1.156
PAM	0.64	214.38	7.55	1.224
PAM	2.16	181.77	9.42	1.580
PAM	2.30	119.17	8.32	1.650
PAM	7.21	2.75	0.34	1.621
PAM	6.15	3.19	0.46	1.515
PDMA	5.44	5.740	0.83	1.813
PDMA	4.36	37.97	3.57	1.353
PDMA	1.53	177.49	9.69	1.530
PDMA	1.99	185.23	5.95	1.393

PDMA	2.78	172.16	6.18	1.390
PDMA	4.81	2.244	0.72	2.405
PDMA	0.68	154.64	7.23	1.360
PDMA	1.09	158.713	8.67	1.090
PDMA	6.61	2.5035	0.39	3.305
PDMA	7.97	2.881	0.27	3.985
PDMA	3.5	148.939	5.76	1.750
PDMA	3.79	124.355	9.77	1.895
PNIPAM	4.20	82.75	8.76	1.680
PNIPAM	1.63	138.01	9.06	1.630
PNIPAM	1.08	125.36	9.08	1.080
PNIPAM	2.43	140.76	9.20	1.944
PNIPAM	3.39	133.198	8.66	1.356
PNIPAM	5.74	2.412	0.21	1.837
PNIPAM	6.71	3.283	0.33	2.147
PNIPAM	7.66	3.065	0.24	2.451
PNIPAM	9.07	2.377	0.21	2.902
PNIPAM	4.64	29.600	4.52	1.485
PNIPAM	4.79	18.744	2.86	1.533
PVP	0.69	203.01	9.39	2.550
PVP	1.94	198.26	8.62	2.250
PVP	2.65	143.77	5.33	2.050
PVP	2.99	130.54	6.99	4.940
PVP	3.60	99.80	4.44	4.400
PVP	4.10	77.38	9.17	3.475
PVP	4.50	51.60	7.12	1.075
PVP	4.61	55.65	3.06	1.650
PVP	4.86	23.60	3.33	3.180
PVP	6.36	2.33	0.18	1.395
PVP	6.95	3.42	0.73	2.705
PVP	8.80	3.50	0.29	1.380
PVP	9.88	3.53	0.31	1.940

Table S4 - pH, Tc and SD data of complexed PAA probes shown in Fig. 11

	pH	Tc / ns	Sd / ns	χ^2
PDAEC	3.80	138.28	9.40	1.074
PDAEC	1.43	3.83	0.56	1.013
PDAEC	9.80	159.89	5.41	1.026
PDAEC	2.90	131.17	9.77	1.187
PDAEC	7.75	168.08	9.03	1.061
PDAEC	6.71	162.30	5.84	1.051
PDAEC	2.85	105.35	26.55	1.330
PDAEC	1.80	8.66	1.15	1.047
PDAEC	3.19	120.57	17.15	1.194
PDAEC	0.76	0.62	0.06	1.136

PDAEC	5.55	167.27	30.94	1.151
PDAEC	2.65	119.24	38.03	1.172
PDAEC	4.45	144.55	12.78	1.140
PDADMAC	4.42	97.14	7.97	1.002
PDADMAC	7.96	48.40	9.98	1.191
PDADMAC	1.51	9.82	1.11	1.094
PDADMAC	1.90	1.11	0.09	1.043
PDADMAC	4.90	102.08	6.98	1.008
PDADMAC	5.56	110.15	9.69	1.028
PDADMAC	2.30	5.40	0.99	1.001
PDADMAC	3.68	102.33	10.28	1.102
PDADMAC	1.31	10.60	1.39	1.007
PDADMAC	9.80	31.56	2.05	1.082
PDADMAC	0.72	11.07	0.99	1.072
PDADMAC	3.31	100.66	4.60	1.113
PDADMAC	3.95	106.29	7.69	1.172
PDADMAC	8.99	29.96	2.93	1.140
PDADMAC	3.05	104.00	6.31	1.133

Characterisation of Poly(N-isopropylacrylamide)

A sample of poly(N-isopropyl acrylamide) (PNIPAM) was donated by Yuanbo Zhao for use in IPC complexation studies with PAA. The polymer had a stated M_n of 22,301, M_w of 36,347 and a polydispersity of 1.89, determined by DMF GPC. PNIPAM undergoes an LCST behaviour at 33°C[3], and this was confirmed via the increased absorbance a dilute solution (1 mg ml^{-1}) shows when heated beyond this transition a visible cloud point can be observed at 34°C (Figure S5).

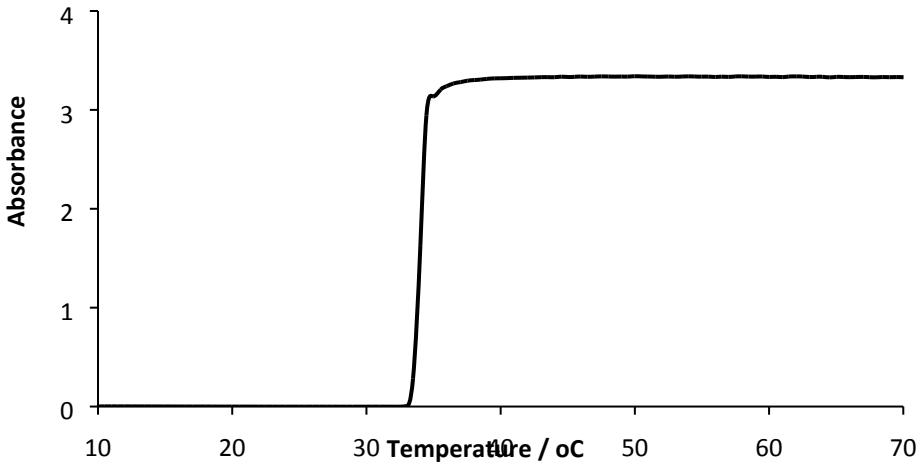


Figure S5 – Absorbance of 1 mg ml-1 sample of PNIPAM with varying temperature

Particle Size:

Data shown in Fig. S6 is mean particle size data.

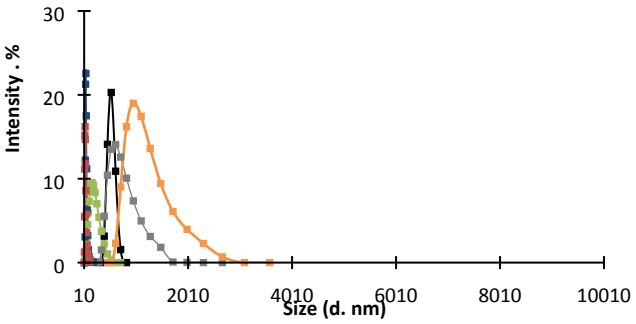


Fig. S6. Particle distributions of PAM (black), PVP (Green), PNIPAM (grey), PDMA (orange), PEO (Blue) and PVA (Red) 1 mg ml^{-1} in dispersion with equal conc. of PAA at pH 2.

Carbon NMR

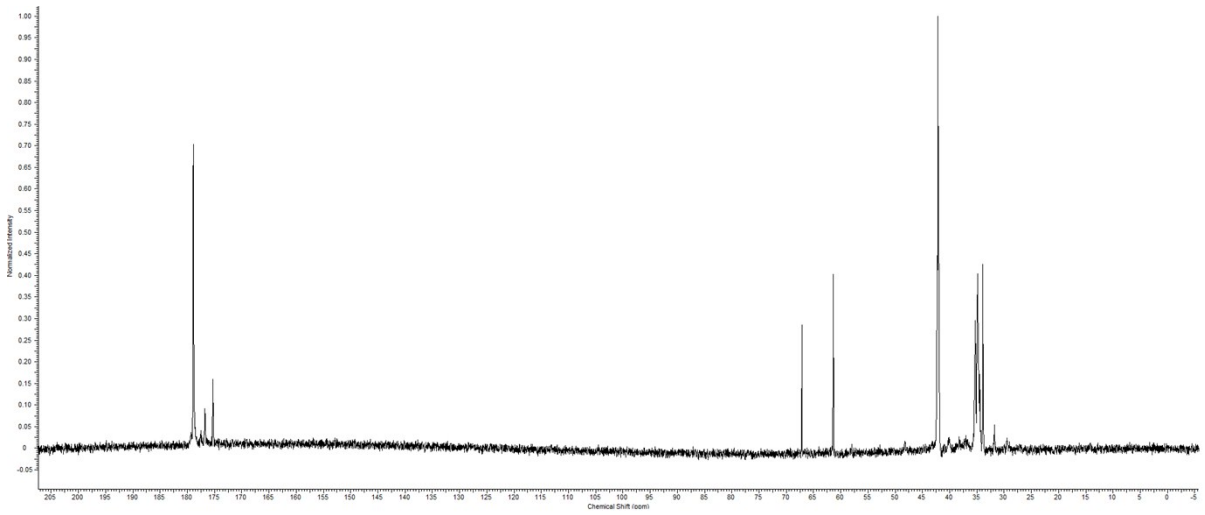


Fig. S7. ^{13}C NMR spectra of PAA homopolymer.

Figure 1 – Laddered / Non Ladddered Systems

Figure 1 shows the potential for IPC formation without representing this in the form of a laddered / ribbon type structure, which is the conventionally accepted model for these systems that has held for nearly thirty years. However we recently published data suggesting this model is not satisfactory, and there is little reason to assume the polymer would open form the desolvated globule to a swollen system in order to complex with another polymer. Therefore we have not demonstrated this in Fig. 1. However if this was to be represented as a laddered system Fig. 1 would appear as thus:

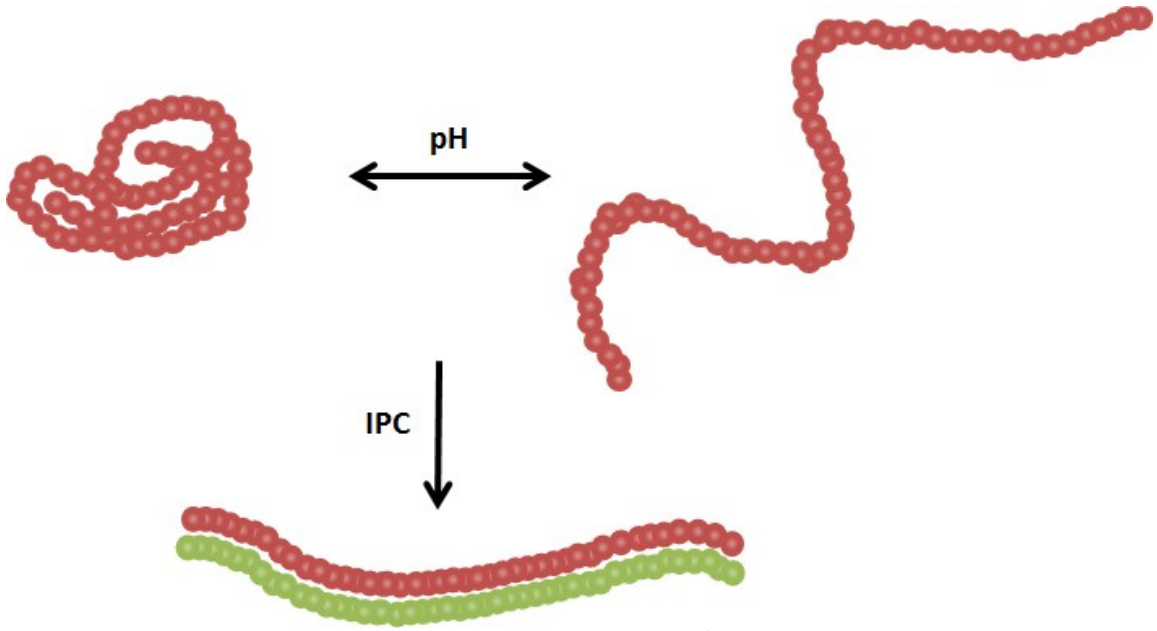


Fig. S8 – Fig. 1 alternative. A system demonstrating the laddered / ribbon type structure of IPC formation.

Concentration Sensors

The PAA-PAM complex has been proposed as a method of sensing low concentration polymers in solution. This study was repeated with PEO and PNIPAM and in both cases the anisotropic response to complexation was found to be concentration dependent. These initial studies are shown below in Fig. S9.

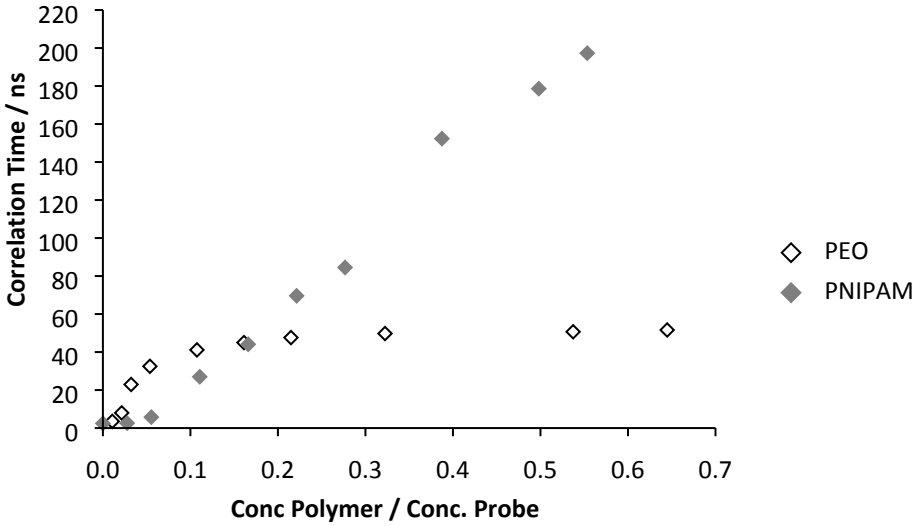


Fig. S9 – Concentration response of PAA correlation time with increasing / decreasing PEO / PNIPAM present.

References:

1. Brown, H.C. *et al.,* in Braude, E.A. and F.C. Nachod *Determination of Organic Structures by Physical Methods*, Academic Press, New York, 1955; *Handbook of Chemistry and Physics*, Editor in Chief, Charles D. Hodgman, M.S.; Chemical Rubber Publishing Company, Cleveland, OH, 1951, p. 1636-7; Ballinger, P.; Long, F.A. *J. Am. Chem. Soc.* **1960**, *82*, 795; J. T. Muckerman, J. H. Skone, M. Ning and Y. Wasada-Tsutsui, *Biochim. Biophys. Acta, Bioenerg.*, 2013, **1827**, 882–891.

[1] T. Swift, L. Swanson and S. Rimmer, *RSC Advances* **2014**, *4*, 57991-57995.

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