Supporting information for

Effect of Water on the Thermal Transition Observed in Poly(allylamine hydrochloride)-Poly(acrylic acid) Complexes

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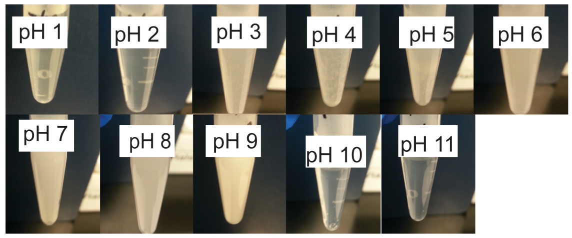


Figure S1. Digital images of PAH-PAA complexes from pH 1 to pH 11.

Proton nuclear magnetic resonance spectroscopy

Figure S2 shows the ^{1}H NMR spectra of (a) pure PAA, (b) pure PAH, (c) - (f) PAH-PAA complexes prepared from pH 3.5, 5.5, 7, and 9, respectively. The standard internal reference DSS chemical shift was assigned 0 ppm.[1] The spectra of pure PAA (Figure S2a) shows four distinct resonances centered at δ = 2.48, 2.00, 1.83, 1.69 ppm. The resonance at 2.48 ppm is assigned to α hydrogen and the three resonances between 1.6 to 2.0 ppm are assigned to β hydrogen, which is assigned to the methylene resonances of triad distribution of the *rr*, *mr*, and *mm* sequences.[2] The spectral pattern here is consistent with previous reports with peaks shifting downfield due to lower pD value.[3] For pure PAH (Figure S2b), the spectra shows three distinct resonances centered at δ = 3.14, 2.13, 1.60 ppm, which are assigned to H_c, H_d and H_e marked in Figure S2.[4]

The PAH-PAA complex NMR spectra, as shown in Figure S2 (c)-(f), show both PAH and PAA characterized chemical shifts peaks. Two notable peaks represent the H_c and H_a marked in Figure S2. The composition of the complex can be calculated using equation S(1)

$$\text{PAA mol\%} = \frac{\text{PAA}}{(\text{PAH+PAA})} = \frac{\text{A}(\text{H}_a)}{(\frac{1}{2}\text{A}(\text{H}_c)+\text{A}(\text{H}_a))} \qquad S(1)$$

Based on the spectra and equation S(1), the calculated PAA mol% were 62%, 56%, 53% and 50% for solutions of pH 3.5, 5.5,7 and 9, respectively.

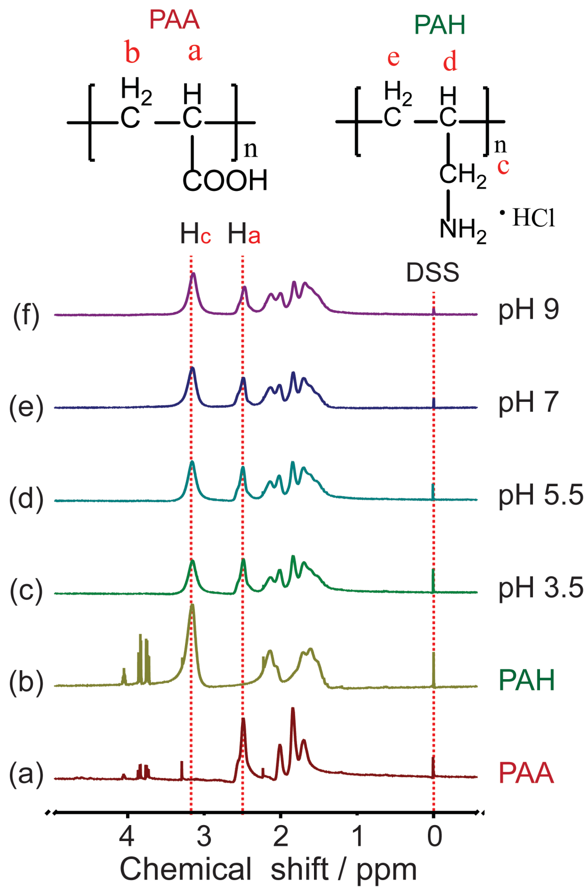


Figure S2. ^{1}H-NMR spectra for homopolymer PAA, PAH and PAH-PAA complexes prepared from pH 3.5, 5.5, 7 and 9 solutions.

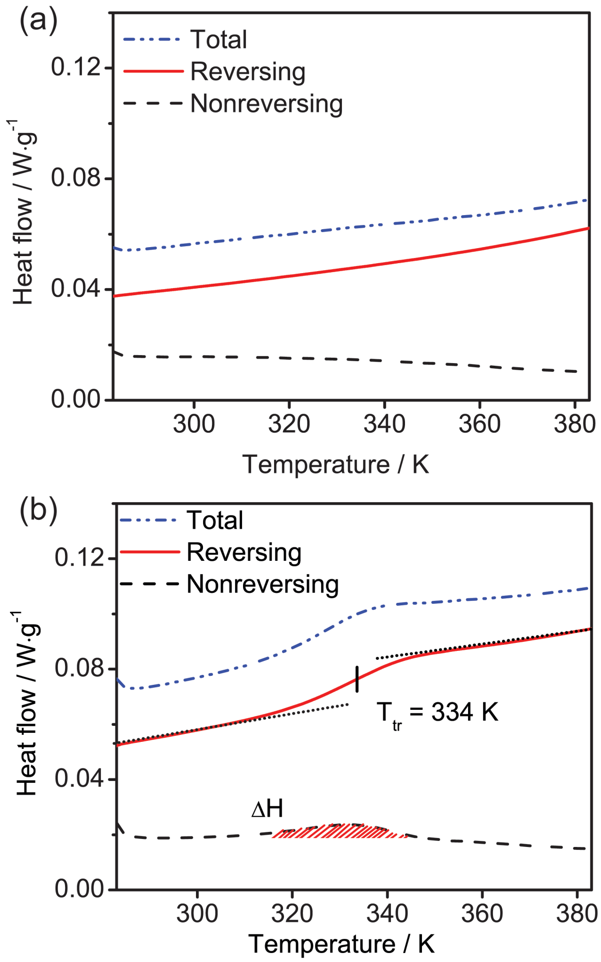


Figure S3. (a) Modulated DSC heating scans of (a) dried and (b) 15.3% hydrated $(PAH\text{-}PAA)_{3.5}$. The 2nd heating scans are shown. The T_{tr} and ΔH (enthalpic relaxation change, shaded area in (b)) are labeled.

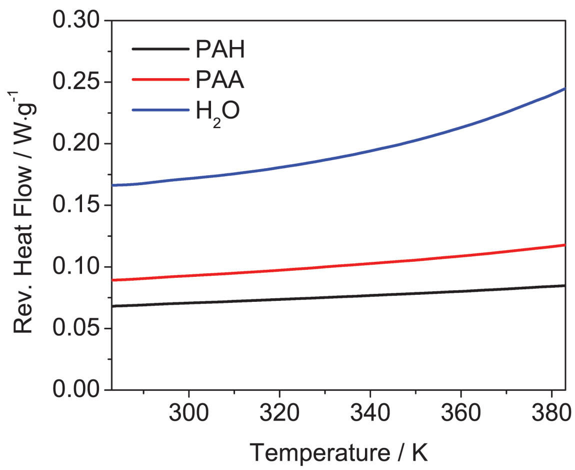
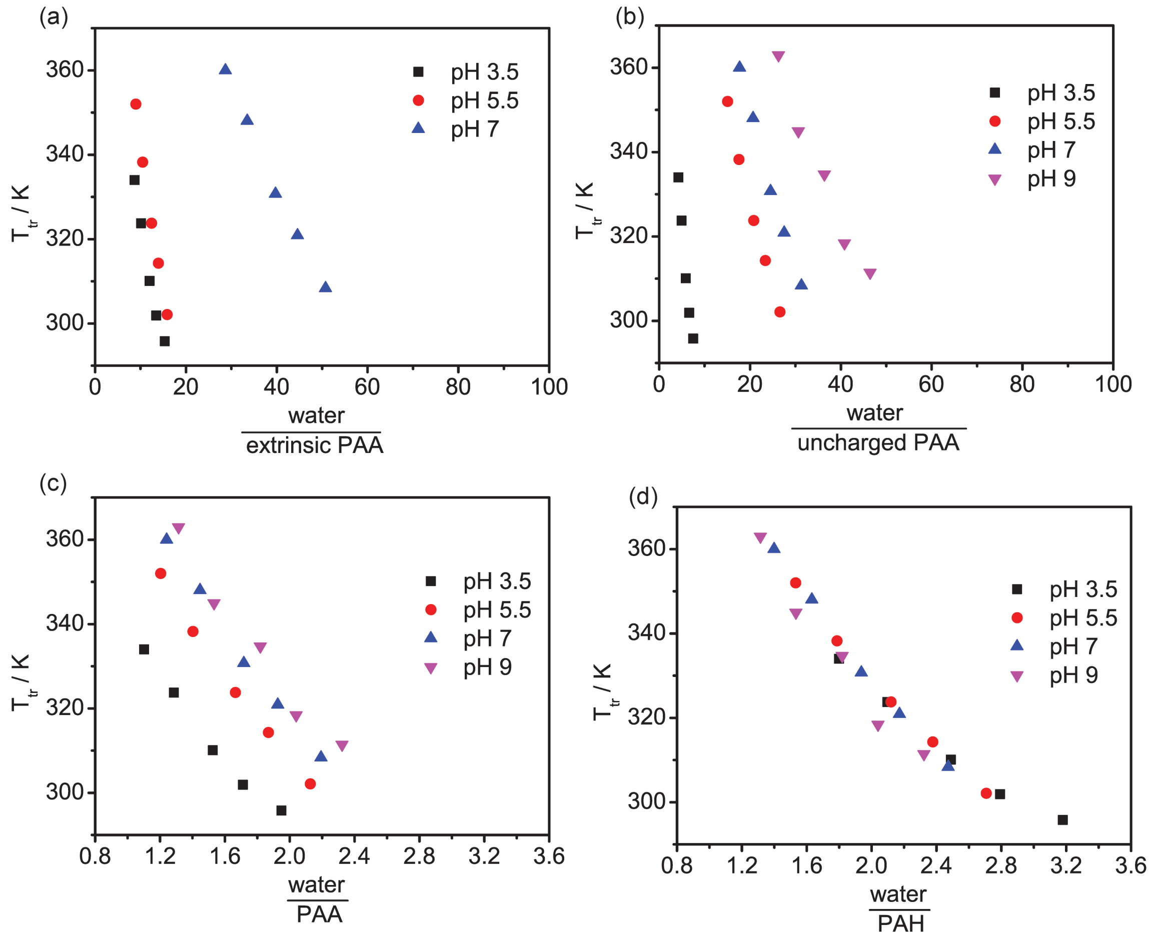


Figure S4. MDSC thermograms of 15.3% hydrated homopolymer PAH, PAA and water. The 2nd heating scans are shown.

Table S1. Enthalpy change associated with T_{tr} of PAH-PAA complexes prepared from different pH solutions.

sample	wt% water	ΔH(J/g)
pH 3.5	15.3%	3.81
	17.4%	3.36
	20%	2.98
	21.9%	1.37
	24.2%	0.52
pH 5.5	15.3%	3.58
	17.4%	3.44
	20%	3.14
	21.9%	2.48
	24.2%	1.98
pH 7	15.3%	3.33
	17.4%	3.64
	20%	3.08
	21.9%	2.73
	24.2%	2.46
pH 9	15.3%	3.56
	17.4%	3.58
	20%	3.08
	21.9%	2.77
	24.2%	2.00



Figures S5. T_{tr} with number of water molecules per (a) extrinsic PAA, (b) neutral PAA, (c) PAA, (d) PAH repeat unit.

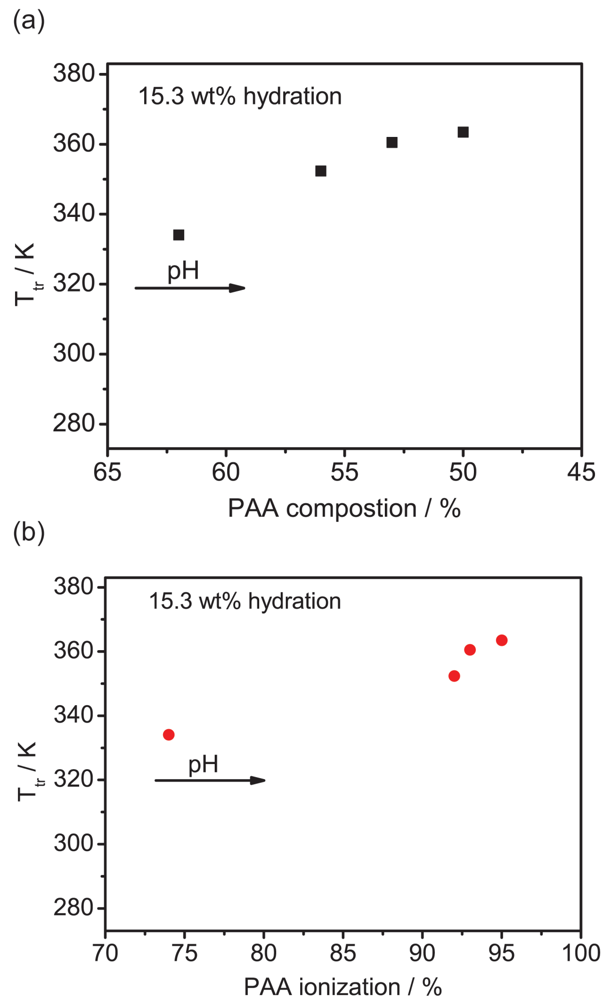


Figure S6. $(PAH\text{-}PAA)_{3.5}$ complex T_{tr} as a function of (a) PAA composition and (b) PAA ionization.

Reference

1. Chollakup, R.; Beck, J. B.; Dirnberger, K.; Tirrell, M.; Eisenbach, C. D. Polyelectrolyte Molecular Weight and Salt Effects on the Phase Behavior and Coacervation of Aqueous Solutions of Poly(acrylic acid) Sodium Salt and Poly(allylamine) Hydrochloride. *Macromolecules* **2013,** 46, (6), 2376-2390.
2. Chang, C.; Muccio, D. D.; St. Pierre, T. Determination of the tacticity and analysis of the pH titration of poly(acrylic acid) by proton and carbon-13 NMR. *Macromolecules* **1985,** 18, (11), 2154-2157.
3. Garces, F. O.; Sivadasan, K.; Somasundaran, P.; Turro, N. J. Interpolymer complexation of poly(acrylic acid) and polyacrylamide: structural and dynamic studies by solution- and solid-state NMR. *Macromolecules* **1994,** 27, (1), 272-278.
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