Supporting Information

Evidence of a two-step process and pathway dependency in the thermodynamics of poly(diallyldimethylammonium chloride)/ poly(sodium acrylate) complexation

L. Vitorazi[1,2], N. Ould-Moussa[1], S. Sekar[3], J. Fresnais[4], W. Loh[2], J.-P. Chapel[3] and J.-F. Berret[1]

[1]Matière et Systèmes Complexes, UMR 7057 CNRS Université Denis Diderot Paris-VII, Bâtiment Condorcet, 10 rue Alice Domon et Léonie Duquet, 75205 Paris, France.
[2]Institute of chemistry, Unversidade Estadual de Campinas (UNICAMP), Caixa Postal 6154, Campinas, São Paulo, Brazil.
[3]Centre de Recherche Paul Pascal (CRPP), UPR CNRS 8641, Université Bordeaux 1, 33600 Pessac, France
[4]Physicochimie des Electrolytes et Nanosystèmes interfaciaux (PHENIX) UMR 7195 CNRS-UPMC, 4 place Jussieu, 75252 Paris, France

Outline

S1 - Determination of degree of ionization of poly(acrylic acid)/poly(sodium acrylate) as a function of pH

Fig. S1 shows the acido-basic titration of poly(sodium acrylate) (M_w = 2100 g mol^{-1}) by addition of sodium hydroxide solution (NaOH). The continuous line corresponds to the derivative of the pH as a function of the number of added moles, dpH/dn_{NaOH}. In this experiment, 0.1284 g of PANa, corresponding to 1.36 10^{-3} mole of carboxylic groups was titrated with 7.388 mL (distance between the two maxima) of NaOH prepared at the concentration of 0.133 mol L^{-1}. From the titration, we found that the amount of carboxylic groups represent 72% of the monomers. There is thus less carboxylic acid monomers as expected from the calculation. This discrepancy could originate, in part from the presence of bound water molecules in the polymer powder. The percentage of 72% was used in the estimation of the anionic charge coming from the PANa chains.

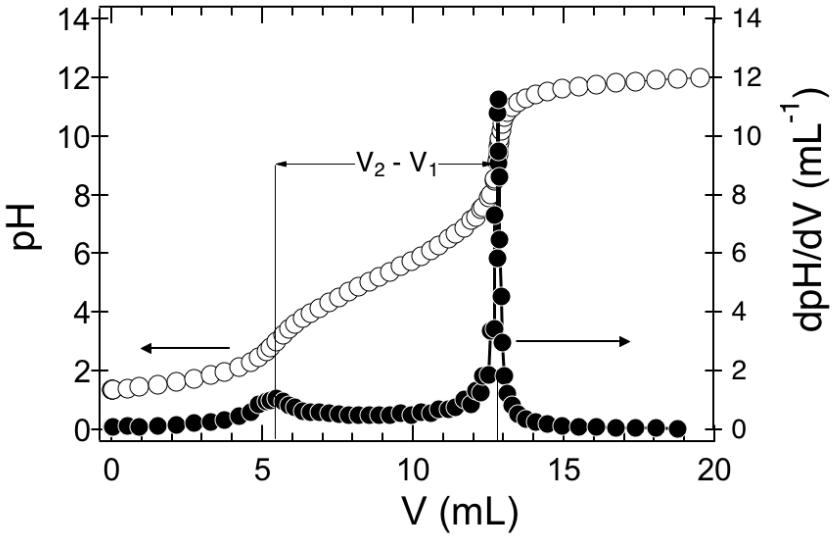

Figure S1: Potentiometric curves for the increment addition of NaOH to poly(acrylic acid) of molecular weight 2100 g mol^{-1}.

S2 – Images of dispersions prepared by direct mixing at pH7

Fig. S2 displays images of PDADMAC/ $PANa_{2K}$ mixed solutions obtained at pH7. The solutions were obtained by direct mixing protocols. Turbid samples are associated with a liquid-liquid phase separation (coacervation).

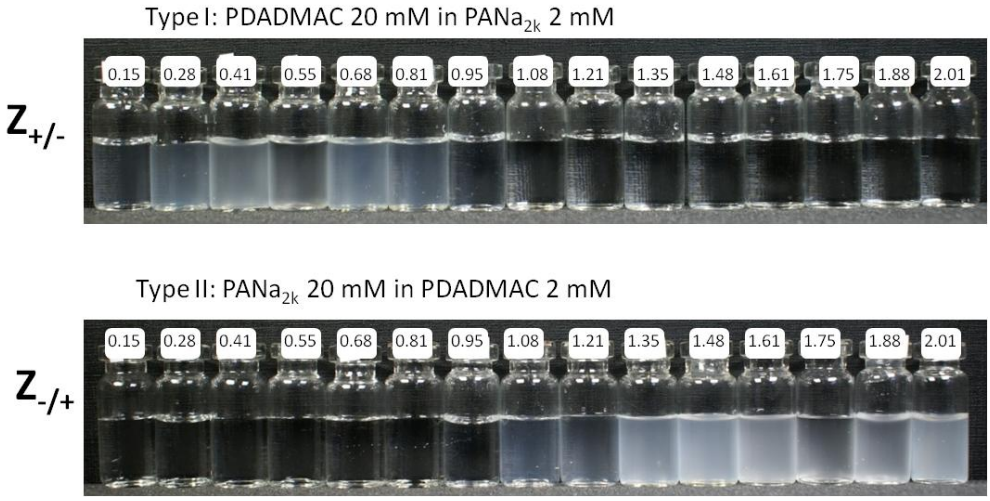

Figure S2: Direct mixtures of $PANa_{2K}$ and PDADMAC for Type I and II experiments at pH 7.

S3 - Evidence of pH changes during titrations performed at pH7

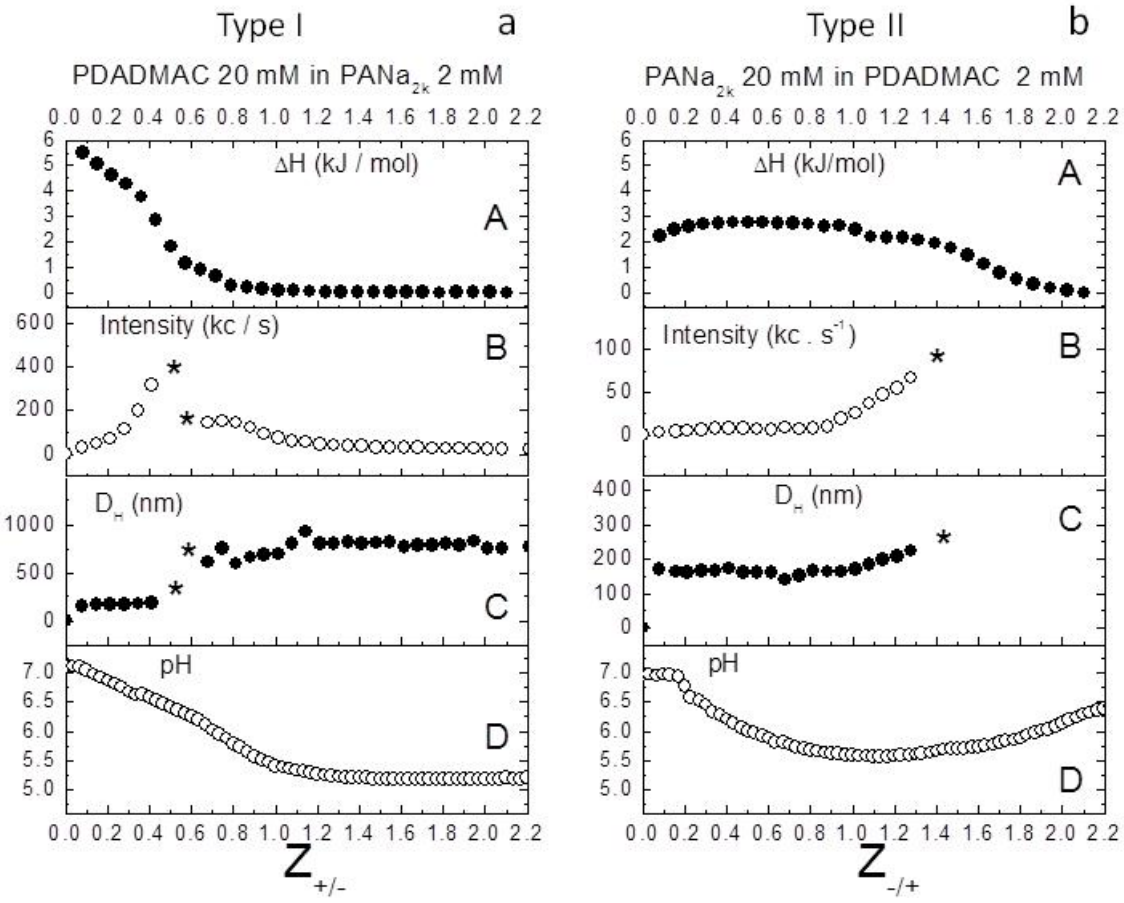

Figure S3: Binding enthalpy (A), light scattered intensity (B), hydrodynamic diameter (C) and pH measurements (D) found by titration of $PANa_{2K}$ by PDADMAC (Type I experiment) and of PDADMAC by $PANa_{2K}$ (Type II experiment). Prior to titration, the pH of the initial polymer solutions was set at pH 7.

S4 - ITC experiments between PDADMAC and $PANa_{2K}$ at pH7

Figs. S4 show the thermograms (a,d) and binding isotherms with (b,e) for Type I and II titrations between PDADMAC in $PANa_{2K}$ at $^{pH}7$. The characteristic features of the ITC curves are identical to those observed with $PANa_{2K}$ at pH10. Upon addition of $PANa_{2K}$ to PDADMAC or *vice-versa*, ITC reveals the existence of two sequential processes, one endothermic at low charge ratio, and the second being either exo- or endothermic depending on the mixing order.

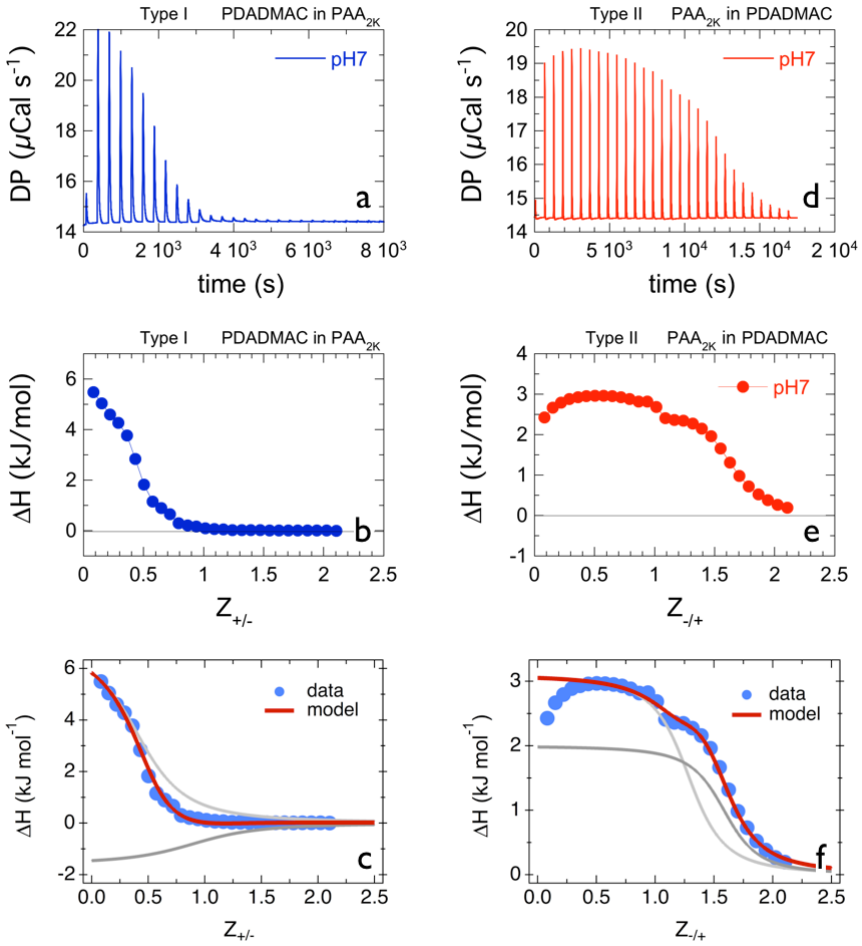

Figure S4: ITC curves for addition of PDADAMAC in $PANa_{2K}$ (a,b,c) and $PANa_{2K}$ in PDADMAC (d,e,f) at pH7. In c) and f) the binding enthalpy curves are adjusted using the model described in the main text (Eq. 3).

In Figs. S4c and S4f are plotted the binding isotherms together with the adjustments using Eq. 3. The different parameters retrieved from the adjustment are listed in Table S4. The legends are the same as those of Fig. 7. The present approach shows that at pH7 and pH10, the thermodynamics of titration remains the same, and that the molecular weight of the polymer does not play a major role in the sequence of reactions.

Primary process	ΔH_b^A $(kJ\ mol^{-1})$	K_b^A (M^{-1})	n_A	ΔG^A $(kJ\ mol^{-1})$	ΔS^A $(J\ mol^{-1}K^{-1})$
Type I PDADMAC in $PANa_{2K}$ pH7 (20/2)	+ 7.0	5.0 x 10^3	0.5	- 21.0	+94.3
Type II $PANa_{2K}$ in PDADMAC pH7 (20/2)	+ 3.1	2.5 x 10^4	1.3	- 25.1	+ 94.6

Secondary process	ΔH_b^C $(kJ\ mol^{-1})$	K_b^C (M^{-1})	n_C	ΔG^C $(kJ\ mol^{-1})$	ΔS^C $(J\ mol^{-1}K^{-1})$
Type I PDADMAC in $PANa_{2K}$ pH7 (20/2)	- 1.6	5.0 x 10^3	1.0	- 21.1	+ 65.4
Type II $PANa_{2K}$ in PDADMAC pH7 (20/2)	+ 2.0	3.3 x 10^4	1.6	- 25.8	+ 93.2

Table S4: List of the thermodynamic parameters determined for the binding enthalpies between PDADMAC and $PANa_{2K}$ at pH7.

S5 - ITC experiments between PDADMAC and $PANa_{100K}$

Figs. S5 show the thermograms (a,d) and binding isotherms with (b,e) for Type I and II titrations between PDADMAC in $PANa_{100K}$. The ITC data were obtained at pH 10 and T = 25 °C. The characteristic features of the ITC curves are identical to those observed with $PANa_{2K}$. Upon addition of $PANa_{100K}$ to PDADMAC or *vice-versa*, ITC reveals the existence of two sequential reactions, one endothermic at low charge ratio, and the second being either exo- or endothermic depending on the mixing order.

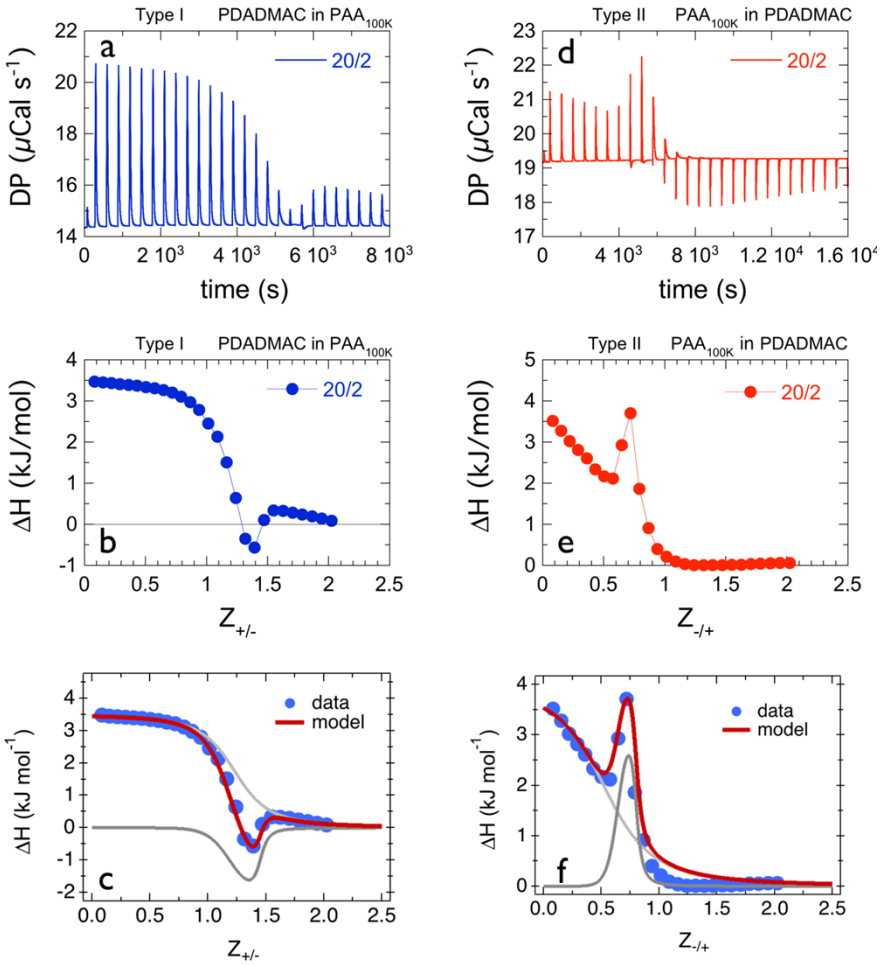

Figure S5: ITC curve for addition of PDADAMAC in $PANa_{100K}$ at pH 10 (a,b,c) and $PANa_{100K}$ in PDADMAC (d,e,f). In c) and f) the binding enthalpy curves are adjusted using the model described in the main text (Eq. 2).

In Figs. S5c and S5f are plotted the binding isotherms together with the adjustments using Eq. 3. The different parameters retrieved from the adjustment are listed in Table S5. The legends are the same as those of Fig. 7. The present approach shows that for $PANa_{2K}$ and

$PANa_{100K}$, the thermodynamics of titration remains the same, and that the molecular weight of the polymer does not play a major role in the sequence of reactions.

Primary process	ΔH_b^A $(kJ\ mol^{-1})$	K_b^A (M^{-1})	n_A	ΔG^A $(kJ\ mol^{-1})$	ΔS^A $(J\ mol^{-1}K^{-1})$
Type I PDADMAC in $PANa_{100K}$ 20/2	+ 3.5	2.5 x 10^4	1.25	- 25.1	+ 95.9
Type II $PANa_{100K}$ in PDADMAC 20/2	+ 4.0	6.3 x 10^3	0.6	- 21.6	+ 86.1

Secondary process	ΔH_b^C $(kJ\ mol^{-1})$	K_b^C (M^{-1})	n_C	ΔG^C $(kJ\ mol^{-1})$	ΔS^C $(J\ mol^{-1}K^{-1})$
Type I PDADMAC in $PANa_{100K}$ 20/2	- 2.2	5.0x 10^5	1.45	- 32.5	+ 101.7
Type II $PANa_{100K}$ in PDADMAC 20/2	+ 3.5	5.0 x 10^5	0.8	- 32.5	+ 120.8

Table S5: List of the thermodynamic parameters determined for the binding enthalpies between PDADMAC and $PANa_{100K}$ at pH10.