Supporting Information

Synthesis of double hydrophilic block copolymers and induced assembly with oligochitosan for the preparation of polyion complex micelles

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^{1}H NMR spectra

PEO macroinitiator:

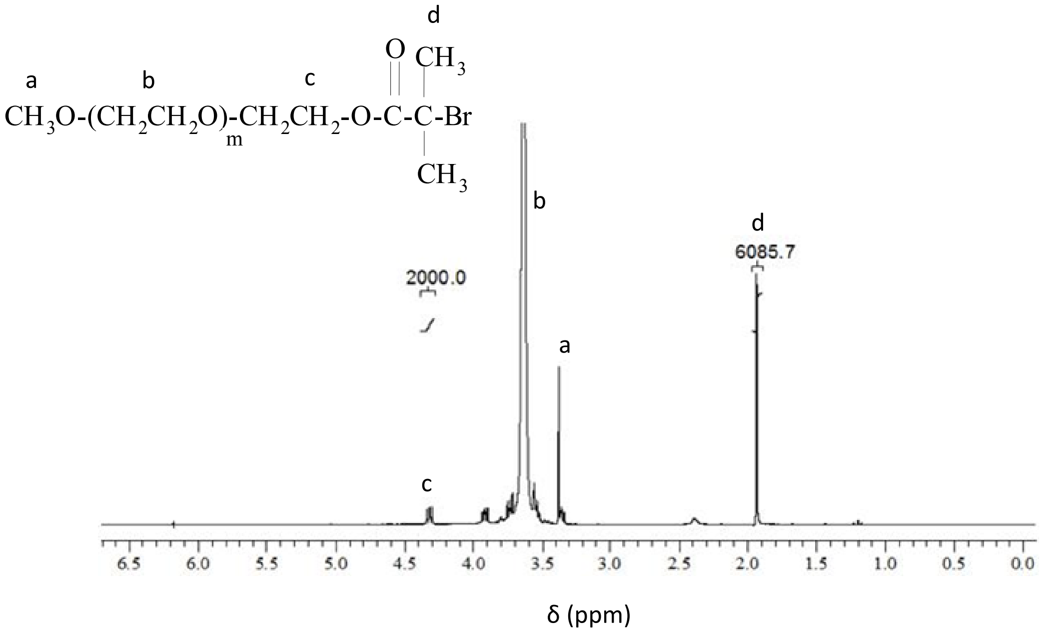

Figure S1. ^{1}H NMR spectrum of the PEO macroinitiator in $CDCl_3$.

PEO-*b*-PtBuA:

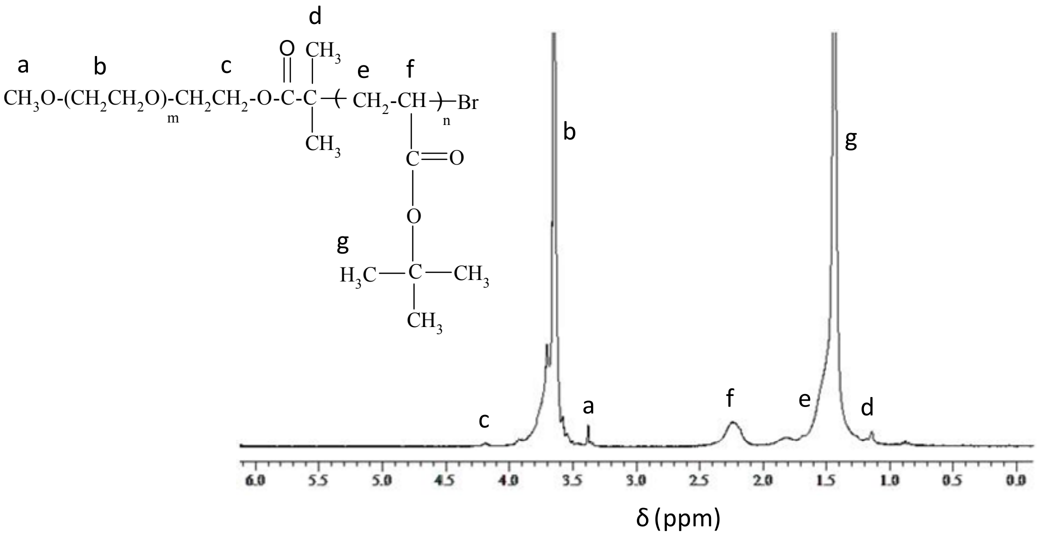

Figure S2. ^{1}H NMR spectrum of PEO113-*b*-PtBuA33 (diblock copolymer 4 in Table 1) in $CDCl_3$.

PEO-*b*-PAA:

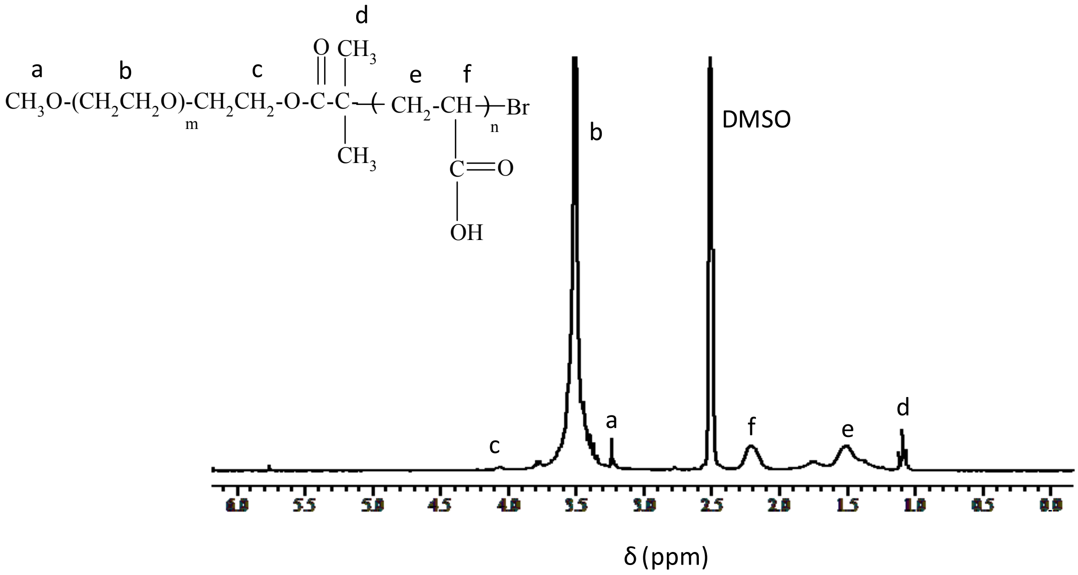

Figure S3. ^{1}H NMR spectrum of PEO113-*b*-PAA33 (diblock copolymer 4' in Table 2) in DMSO-^{6}d.

Determination of effective charge density of PAA_{1290}-PEO_{5000}, PAA_{650}-PEO_{2000} and PAA_{4600}-PEO_{2000} diblock copolymers.

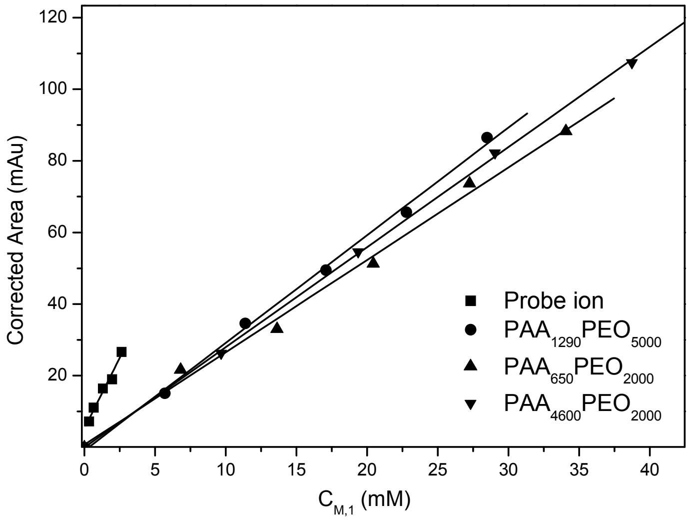

Figure S4: Calibration curves obtained by indirect UV detection CE for diblock copolymers. Electrophoretic conditions as in figure 2. $C_{M,1}$ is the molar concentration of charged monomers (AA). Each data point is the average of nine measurements. Least square regression equations: y=2.61x (r^2=0.989) for *f*=0.16; y=2.96x (r^2=0.995) for *f*=0.13; y=2.67x (r^2=0.984) for *f*=0.58.

Dynamic Light Scattering analysis of copolymers and oligochitosan studied individually as a function of pH.

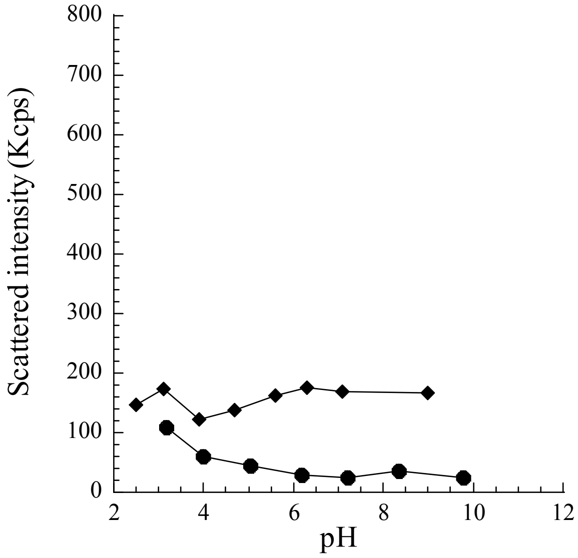

Figure S5. Scattered intensity of an aqueous solution of PEO113-b-PAA33 diblock copolymer (circles) or oligochitosan (diamonds) analyzed individually as a function of the pH of the solution.

Dependence of ionization degrees of the PAA block (a weak polyacid) and of oligochitosan (a weak polybase) with pH

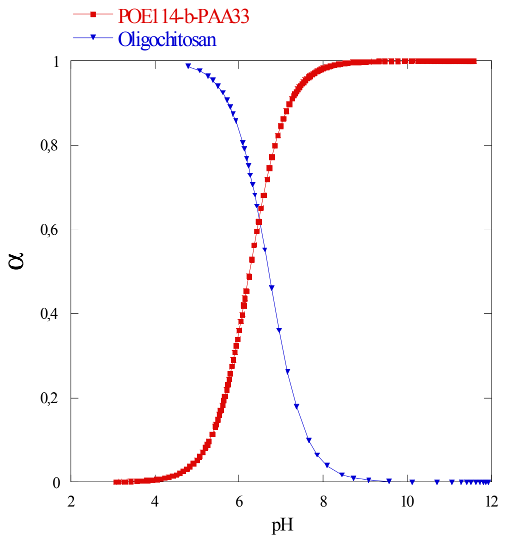

Figure S6. Theoretical dependence of the ionization degrees of the PAA block and oligochitosan with pH.

Effect of salt concentration on the existence of the complex micelles

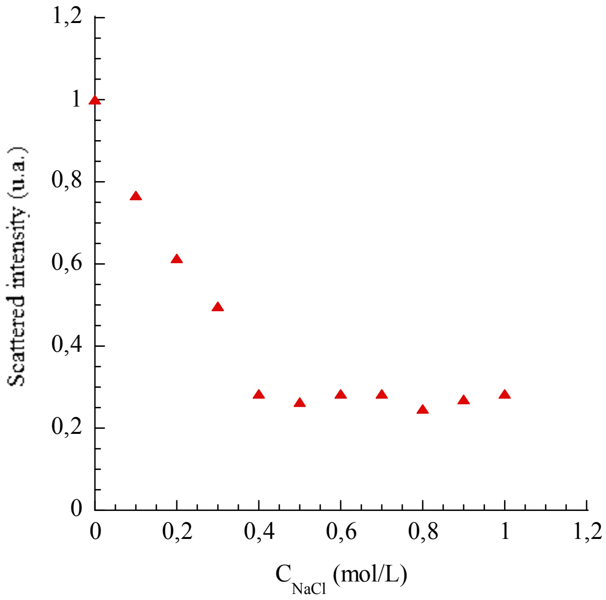

Figure S7: Normalized intensity as a function of NaCl concentration (mol.L^{-1}) for the PEO113-*b*-PAA33/oligochitosan complex system.

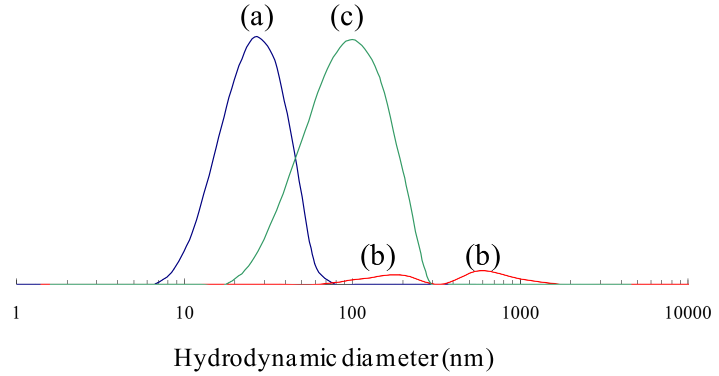

Figure S8: Size distribution of aggregates formed at pH=6 with the PEO113-*b*-PAA33/oligochitosan complex system before salt addition, (b) after salt addition and (c) after removal of salt by dialysis.

Effect of block length variation on complex micelle morphology. Scaling relationships

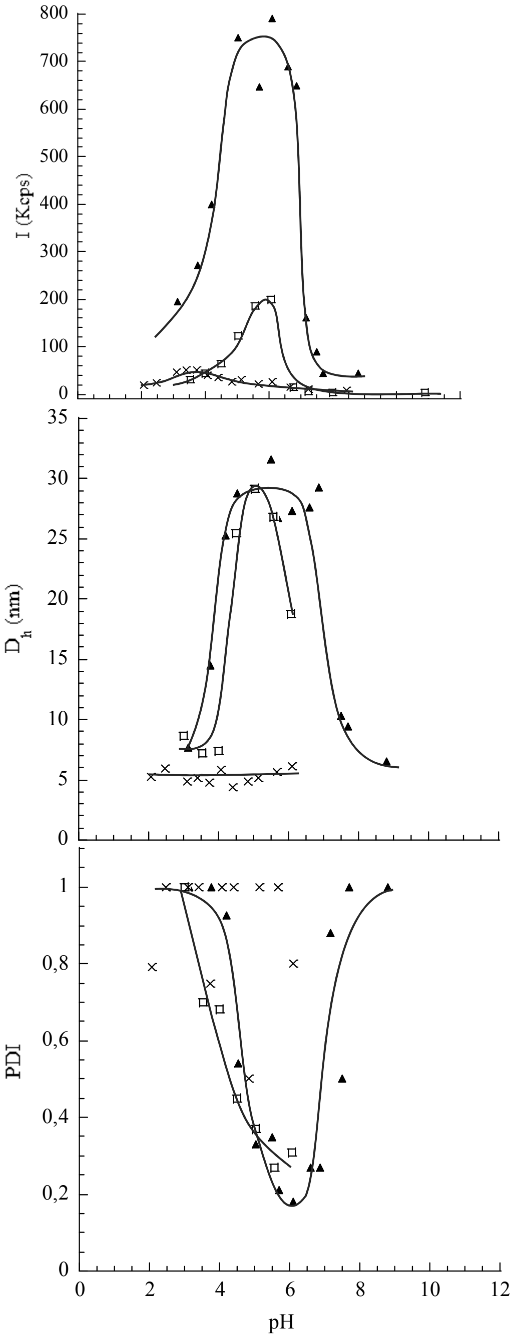

Figure S9: Scattered intensity, hydrodynamic diameter and polydispersity indexes plotted as a function of pH for mixtures composed of diblock copolymers with DP_{PAA} = 9 (crosses), 22 (empty squares) and 33 (triangles).

Cohen Stuart qualitatively studied the effect of block length variation on complex micelle morphology[1] by making analogies with hydrophobically associating systems for which scaling relationships have been determined.[2,3] For micelles composed of strongly asymmetric diblock copolymers with a neutral-hydrophobic architecture, two critical cases can be distinguished depending on the length of the neutral (hydrophilic) and hydrophobic blocks : *starlike* micelles are obtained when DPcorona >> DPcore, they are constituted of a very small core compared to the overall dimensions of the micelles; and *crew-cut* micelles are obtained when DPcore>>DPcorona, in that case, the micellar dimensions are dominated by the size of the core. In both cases, the block length ratio governs the physics of the micellization process, the aggregation number and micelle radius.

In the case of starlike micelles, the value of the aggregation number N_{agg} at the equilibrium is given by Equation S1[1]:

$$N_{agg} \sim (DP_{core}\,\gamma)^{4/5}\left(\ln \frac{R_{corona}}{R_{core}}\right)^{-6/5} \qquad \text{Equation S1}$$

With γ the interfacial tension between the core and the solvent and R_{corona} and R_{core} the radii of corona and core respectively.

In the case of crew-cut micelles, Equation S2 holds[1]:

$$N_{agg} \sim DP_{core}^{\;2}\,\gamma^{7/11}\,DP_{corona}^{\;-18/11}\,\upsilon^{-6/11} \qquad \text{Equation S2}$$

With υ the solvent quality for the corona blocks.

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[1] M. A. Cohen Stuart, N. A. M. Besseling and R. G. Fokking, *Langmuir*, 1998, **14**, 6846.
[2] A. Halperin and S. Alexander, *Macromolecules*, 1989, **22**, 2403.
[3] O. V. Borisov and E. B. Zhulina, *Macromolecules*, 2002, **35**, 4472.