SUPPORTING INFORMATION

Surface grafted chitosan gels. Part II. Gel formation and characterization.

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Content:

1) Stability of the multilayer film prior to cross-linking. The multilayer tends to dissolve at low pH and high ionic strength salt solutions. In Figure S1, the starting point that defines zero frequency and dissipation shift corresponds to one surface grafted layer of chitosan in 30 mM NaCl at pH 5.7. The second set of points correspond to an 11 multilayer film (6 chitosan and 5 PAA layers) deposited *in situ* and measured at the same solution conditions. As expected, this results in a large decrease in resonance frequency as well as a large increase in energy dissipation. Finally, when this multilayer is exposed to a 100 mM NaCl solution at pH 2.7 both frequency and dissipation return back to the starting value, showing that the multilayer was completely disintegrated due to the reduced electrostatic interaction between chitosan and PAA.[1, 2] At pH 2.7 the chitosan segments (bulk $pK_a \approx 6.0$-6.5) are positively charged, whereas the PAA segments (bulk $pK_a \sim 4.8$) are neutralized. Thus the multilayer becomes unstable due to internal charge imbalance, resulting in film decomposition. We note that the first chitosan layer, which was grafted to the surface, remains intact.

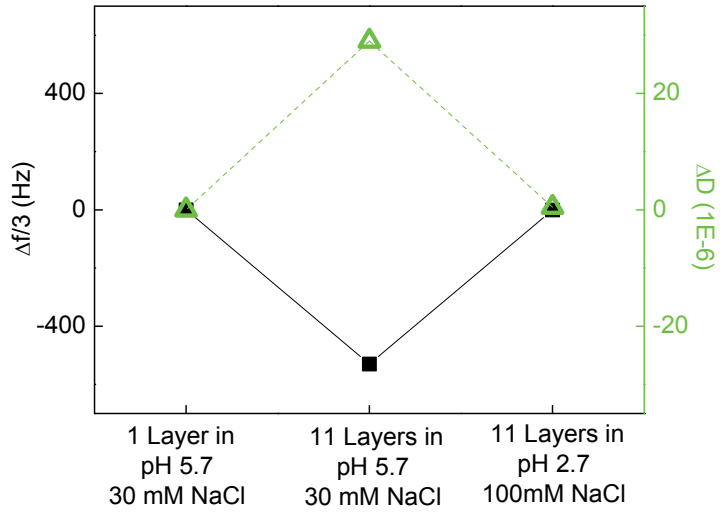

Figure S1. Changes in frequency (black squares) and dissipation (open green triangles) relative to the values for one grafted chitosan layer. Middle points are for a multilayer film consisting of 11 layers (6/5 CHI/PAA) measured in 30 mM NaCl at pH 5.7. Rightmost points are for the same layer after exposure to 100 mM NaCl at pH 2.7. After this treatment the frequency and dissipation values are the same as for one grafted chitosan layer (leftmost points).

2) Raman spectra from glutaraldehyde. Raman spectra were collected for a 2.5wt% glutaraldehyde aqueous solution. In Figure S1, the contributions of water vibrational modes were removed by subtraction using as reference the pure water spectrum. Note that besides the carbonyl stretch (C=O) of the aldehyde at ~1715 cm^{-1}, no additional bands are observed in the double bond region. This indicates that polymeric species of glutaraldehyde containing unsaturated ethylenic bonds (i.e. C=C) are, within our detection limit, absent in the reaction solution prior to contact with the chitosan/PAA multilayer. The large number of bands in the fingerprint region, however, clearly indicates that the dialdehyde is not the only molecular structure present in solution. Moreover, the flat background after subtraction from the water spectral contributions clearly indicates that the glutaraldehyde solution is not fluorescent at the frequency of our excitation source (532 nm).

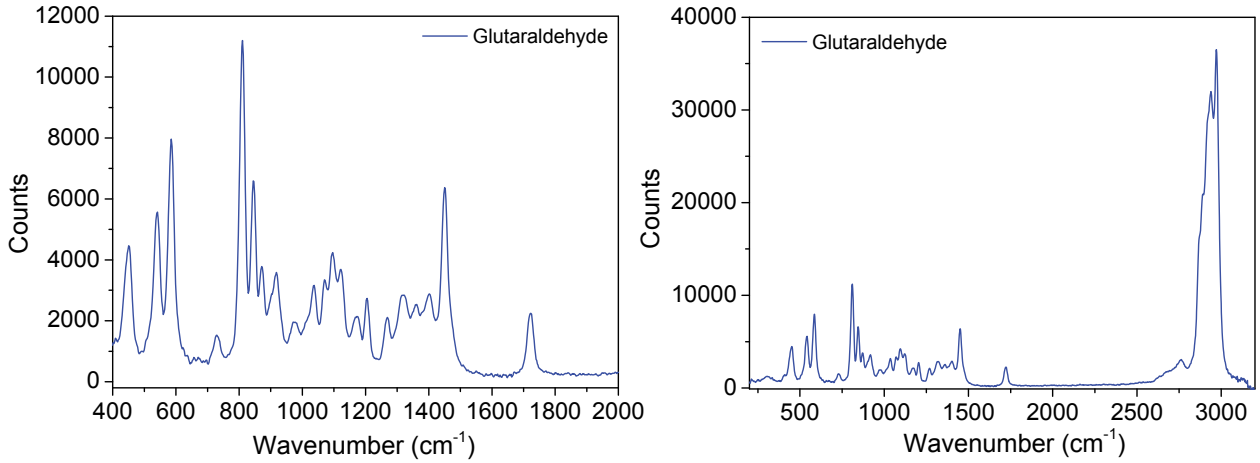

Figure S2. Raman spectra of glutaraldehyde. Spectra was collected using a 532 nm CW laser (250 mW) in a 90° scattering configuration. The analyzer was set with the polarization plane parallel to that of the incoming laser.

3) Calculation of dry and wet mass of the hydrogels by the Johannsmann model. In order to determine the dry mass of the gel films in air the data was evaluated with the Johannsmann model, see Figure S3 (top frame). A close to perfect straight line is obtained allowing us to determine the mass of the LC-gel to be 57mg/m^2. The mass of the HC-gel is significantly larger, 83mg/m^2. The Johannsmann model could not be equally successfully used for determining the wet mass as illustrated in Figure S3 (bottom frame). However, an approximate value of the sensed mass can still be obtained by extrapolation of the line obtained from the two lowest frequencies (overtone 3 and 5) to zero frequency. Thus, we prefer to use the Voigt model (see main article) to calculate the wet mass.

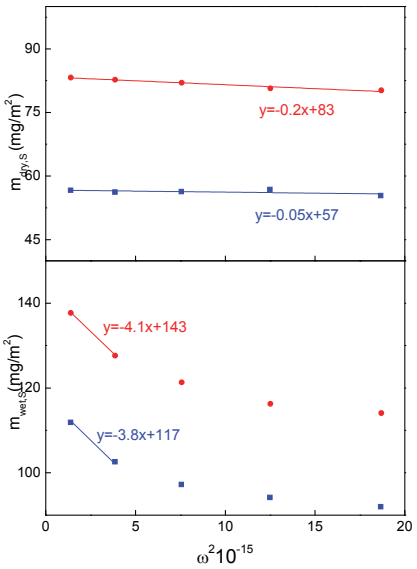

Figure S3. Plot of dry mass and wet mass versus ω^2 (Eq. 2) for the LC-gels (blue) and HC-gels (red). The upper and lower frames show data from measurements in air and 30 mM NaCl at pH 5.7, respectively. The frequency independent Johannsmann mass in air and water obtained by a linear fit to the mass calculated using the first five overtones for the measurements in air and the first two overtones for the measurements in water.

4) TIRR (total internal reflection Raman): pK_as determination. Selected spectra used for the determination of the dissociation constants of the amine and carboxylic acid groups in chitosan and PAA, respectively, are shown in Figures S4 and S5. The spectra shown in Figure S4, correspond to subtracted data in the NH stretching region for the LC-gel at different pHs, having as subtraction reference the spectrum at pH 2. The two clear bands centred at 3315 cm^{-1} and 3370 cm^{-1} are the symmetric and asymmetric NH_2 stretches, respectively. They are only observed at basic pHs when the chitosan amine groups are uncharged. The spectra were fitted using two Lorentzian peaks to extract the relative amplitudes as a function of pH. During the fitting procedure the peak positions and bandwidths were constrained to be constant at all pHs. For PAA both the protonated and deprotonated forms could be targeted directly. Figure S5 (left) and S5(right) show the variations of the symmetric carboxylate and carbonyl stretch, respectively, as a function of pH. Note that the subtraction reference for Figure S5(left) was the spectrum at pH 2, while for Figure S5(right) the reference was that at pH 9.5, when the carbonyl group is fully deprotonated. Similarly, peak positions were constrained to a constant value when fitting the spectra.

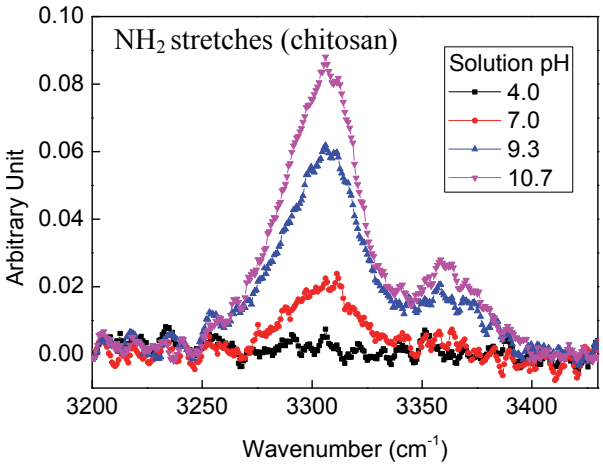

Figure S4. TIRR spectra of the LC-gel in the NH stretching region as a function of pH. The spectrum collected at pH 2 has been used as reference for subtraction.

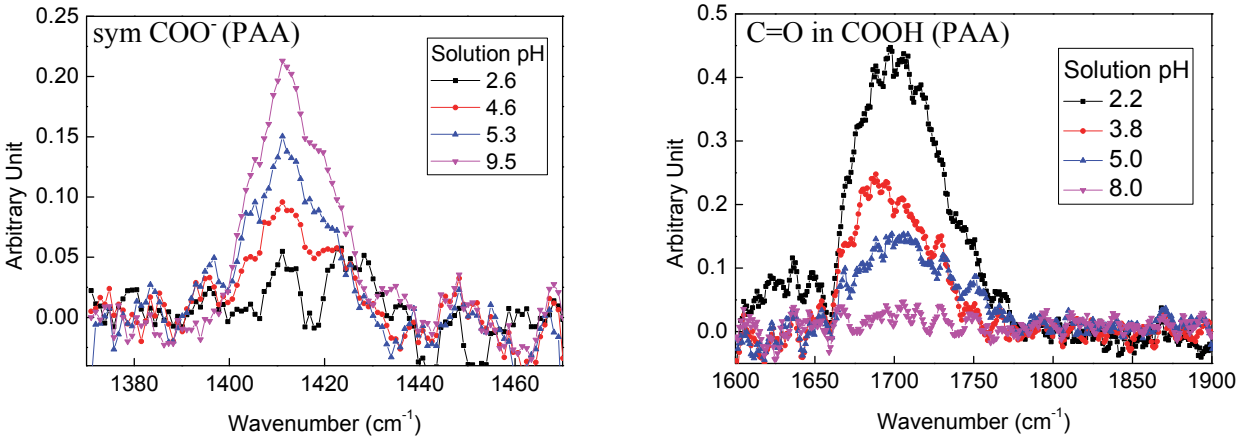

Figure S5. TIRR spectra of the LC-gel in the symmetric carboxylate (left) and carbonyl (right) stretching region as a function of pH. The spectrum collected at pH 2 (left) and pH 9.5 (right) has been used as reference for subtraction.

5) QCM-D: Response of the LC-gel at pH > 10. Figure S6 shows the changes in dissipation and frequency for the LC-gel upon changes of pH. In particular, it is observed that the sensed mass is higher (decrease in frequency) both at pH 2.7 and pH 10.9, when compared with the starting conditions (pH 5.7). The data illustrate the swelling of the surface grafted hydrogel upon breakage of the COO^-/NH_3^+ complexes between PAA and chitosan segments, which occurs at pHs lower than 3 or higher than 9 (see discussion in main article for details).

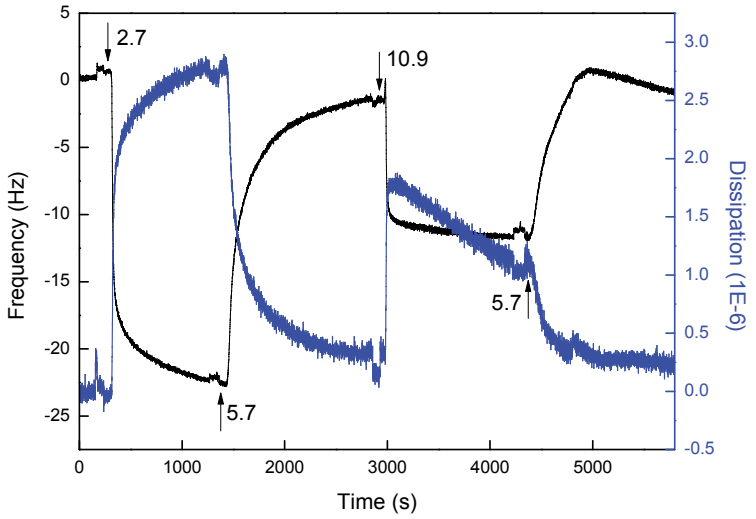

Figure S6. Variation of the frequency (black curve) and dissipation (blue curve) in the LC-gel upon changes of the solution pH in the sequence: pH 5.7 → pH 2.7 → pH 5.7 → pH 10.9 → pH 5.7.

References

1. Kovacevic, D.; van der Burgh, S.; de Keizer, A.; Cohen Stuart, M. A., Kinetics of Formation and Dissolution of Weak Polyelectrolyte Multilayers: Role of Salt and Free Polyions. *Langmuir* **2002,** 18, (14), 5607-5612.
2. Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B., Multiple Membranes from "True" Polyelectrolyte Multilayers. *J. Am. Chem. Soc.* **2001,** 123, (22), 5368-5369.