

Electronic Supporting Information

Hole formation induced by ionic strength increase in exponentially growing multilayer films

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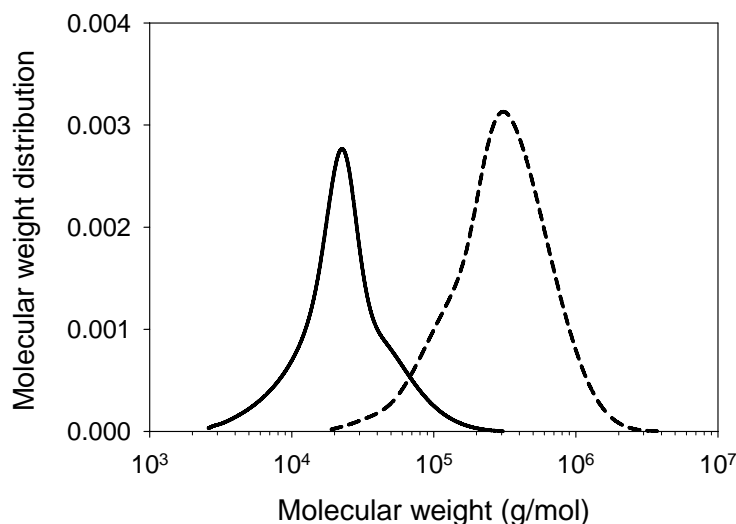
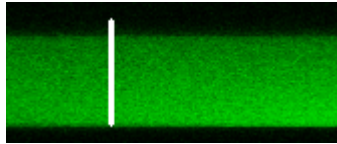
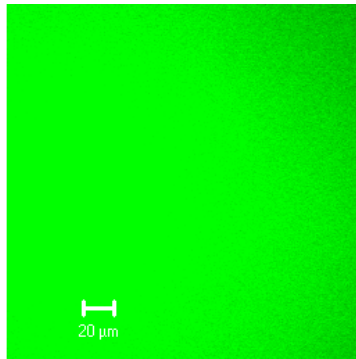


Fig. S-1: Molecular weight distribution of PLL (—) and HA (---) obtained by Steric Exclusion Chromatography - Multi Angle Light Scattering (SEC-MALS). PLL have a mean molecular weight of $M_w = 2.92 \times 10^4$ g/mol, $M_w/M_n = 1.64$. HA have a mean molecular weight of $M_w = 3.81 \times 10^5$ g/mol and a polydispersity $M_w/M_n = 1.76$. The measurements were performed using an Agilent 1100 Permeation Chromatograph (Agilent Technologies) equipped with multi light angle scattering detector DAWN HELEOS (Wyatt Techn.) and with a differential refractive index detector OPTILAB rEX (Wyatt Techn.). A precolumn [10 μ m, 8 x 50 mm] and 3 columns [10 μ m, 8 x 300 mm each] PSS NOVEMA were used. Two columns were linear and one was a 10000 Å column. 100 μ L of the polyelectrolyte solution were injected with a flow rate of 0.50 mL/min. For the determination of the mass distribution of PLL, PLL was dissolved at 2.25 g/L in an aqueous solution of 0.1 M NaCl- 0.1% vol trifluoroacetic acid. For the determination of the mass distribution of HA, HA was dissolved at 1.5 g/L in an aqueous solution of 0.1 M NaNO₃ - 0.05 M NaN₃.



Video 1. Swelling and dissolution of PLL/HA film built at 0.15 M NaCl and put into contact with 0.48 M NaCl followed by CLSM in vertical section. The scale bar represents 50 μm .



Video 2. Behavior of a PLL/HA film built at 0.15 M NaCl and put into contact with 0.48 M NaCl followed by CLSM in the (x, y) plane at half-height of the film.

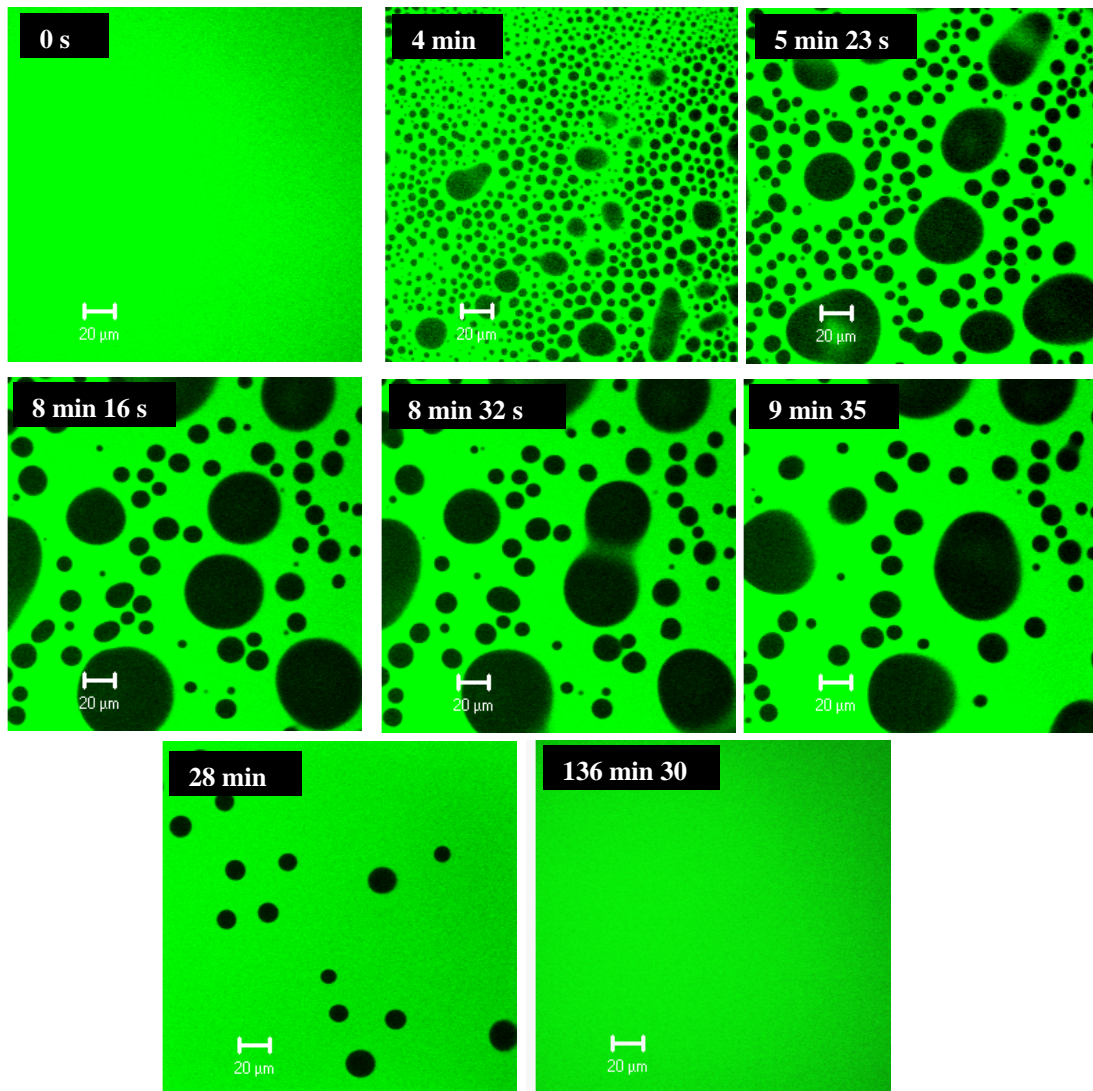


Fig. S-2. Confocal (x,y) images of a $(\text{PLL}/\text{HA})_{50}\text{-PLL}^{\text{FITC}}$ film built at 0.15 M NaCl and progressively brought into contact with a 0.48 M NaCl solution, followed as a function of time. The observation was made in the (x, y) plane at half-height of the film.

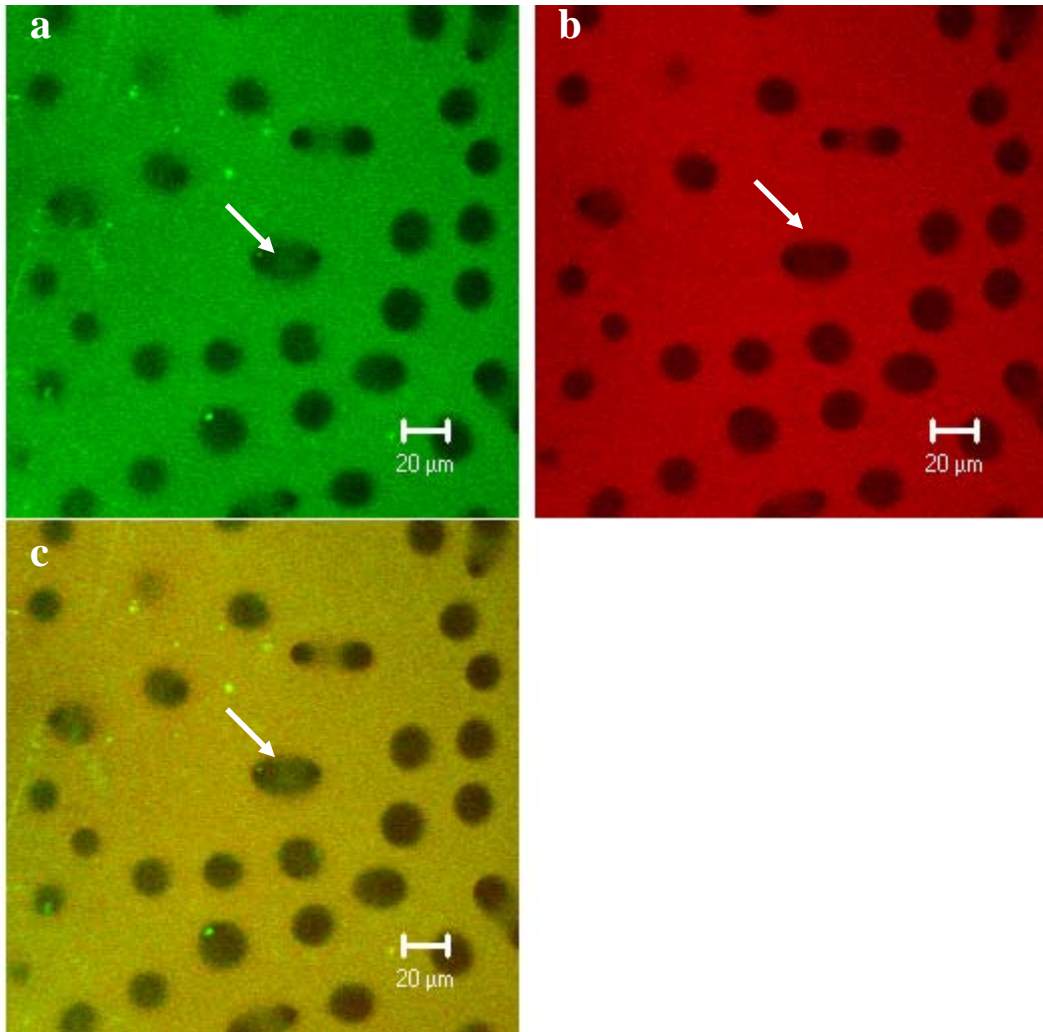


Fig S-3: CLSM (x,y) plane of $(\text{PLL}/\text{HA})_{50}\text{-PLL}^{\text{Rho}}\text{-HA}^{\text{FITC}}$ built at 0.15 M NaCl and progressively brought into contact with a 0.48 M NaCl solution, 1900 s after the incubation, (a) in green channel, (b) in red channel, (c) in green and red channel. The arrows show the presence of both labeled polyelectrolytes inside the holes.

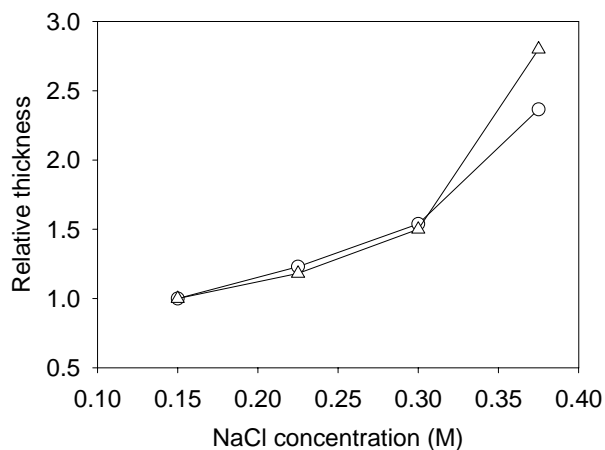


Fig. S-4. Swelling ratio of (△) (PLL/HA)₅₀-PLL^{FITC}-(PSS-PDADMAC)₅ and (○) (PLL/HA)₅₀-PLL^{FITC} films as a function of the ionic strength after 15 min of contact. All the films were built and maintained in 0.15 M NaCl before the swelling process. The film was put step by step in contact with more and more concentrated NaCl solutions during 15 min at each step. The relative thickness was calculated by dividing the thickness at a given NaCl concentration by the thickness measured after its buildup at 0.15 M NaCl. The film thicknesses were evaluated from the vertical sections of CLSM images.

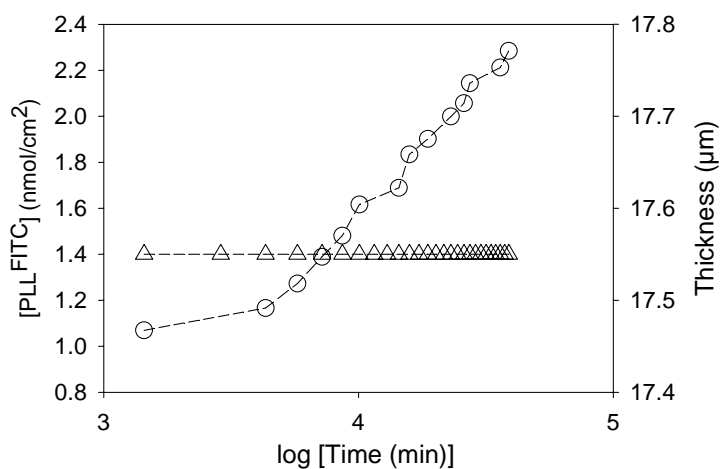


Fig. S-5. PLL^{FITC} released (○) and thickness (△) of (PLL/HA)₅₀-PLL^{FITC} built at 0.15 M NaCl and raised to 0.225 M NaCl as a function of time. The film was swelled by contact with more and more concentrated NaCl solutions (15 min of contact for each step).

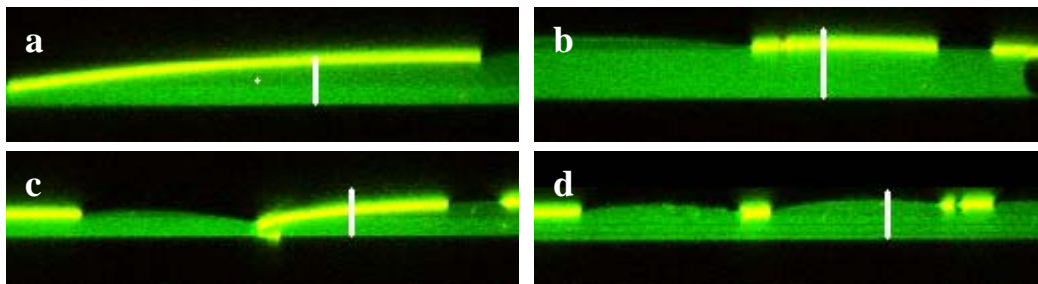


Fig. S-6: Vertical section images of different areas of $(\text{PLL}/\text{HA})_{50}\text{-PLL}^{\text{FITC}}\text{-}(\text{PSS}/\text{PDADMAC})_5\text{-PSS}^{\text{Rho}}$ built at 0.15 M NaCl after (a, b) 780 min and (c,d) 8 days of contact with 0.375 M NaCl. The film was progressively swelled by contact with solutions of increasing NaCl concentrations up to 0.375 M. The scale bars represent respectively 20 μm for images (a), (c), (d) and 30 μm for image (b).