Crouzier and Picart, Supporting Information
"Ion pairing and hydration in polyelectrolyte multilayer films containing polysaccharides"

Estimation of the diffusion coefficient from the FRAP experiments.

The expression of the relative intensity in the bleach area was given in ref. Picart et al. *Micro. Res. Tech* 2005.

If $\tau = \frac{4Dt}{a^2}$ (D being the diffusion coefficient in $\mu m^2/s$ and a the bleached diameter in μm) < 1, then the expression of the relative intensity in the bleached area given in (1) (see eq A30) can be approximated by :

$$\frac{c(t)}{c_0} = \alpha + (1-\alpha)\frac{\sqrt{4Dt}}{a\sqrt{\pi}}\left(1 - \frac{Dt}{4a^2}\right) \quad (1)$$

When t tends to 0, this can be approximated by :

$$\frac{c(t)}{c_0} \to \alpha + b\sqrt{t} \quad (2)$$

Thus, α and b were easily deduced from the linear regression obtained by plotting $\frac{c(t)}{c_0} = f(\sqrt{t})$.

From the slope b, a first approximation of D can be easily deduced :

$$D = \frac{\pi a^2 b^2}{4(1-\alpha)^2} \quad (3)$$

Of note, D estimated here is a mean coefficient measurement obtained by assuming that all the molecules are diffusing.

Figure SI 1. Calibration curves of the polyelectrolytes in solution (15 mg/mL) in contact with the ATR-FTIR crystal.

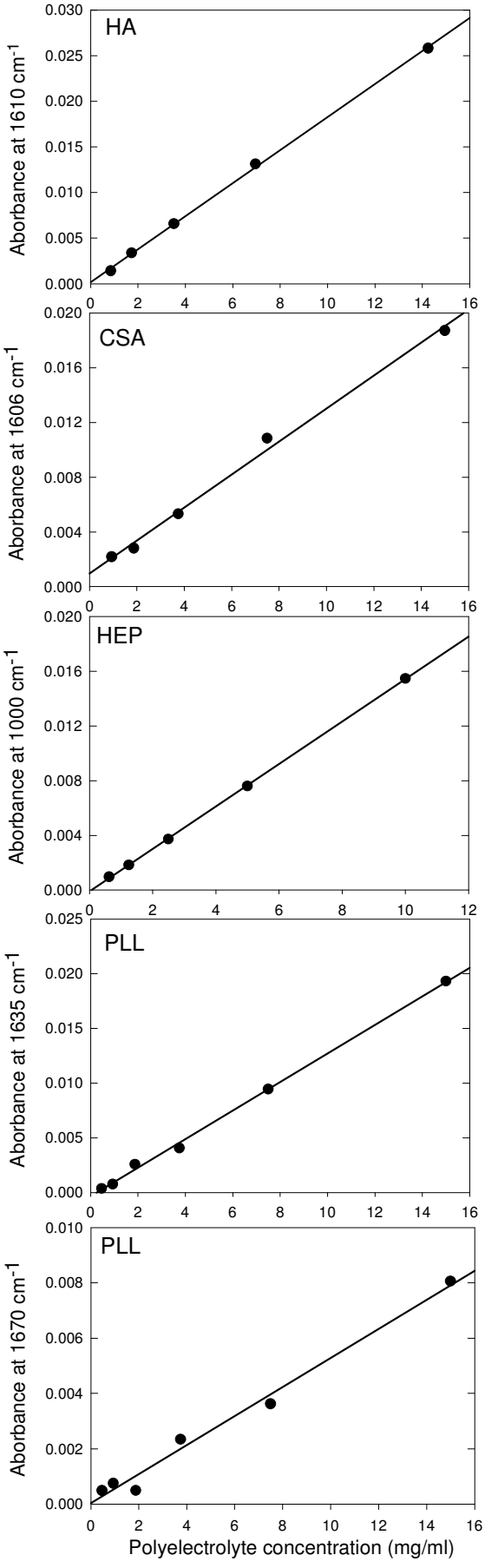
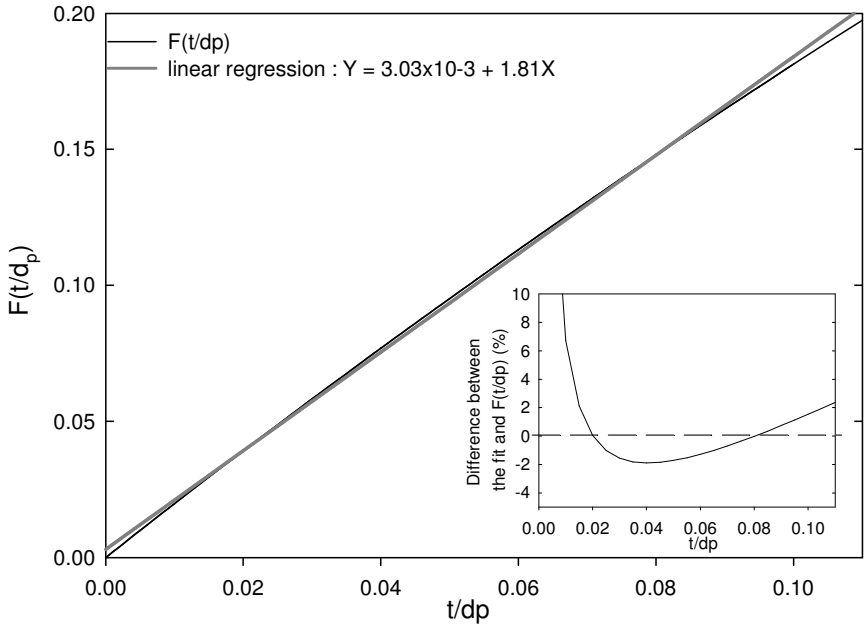


Figure SI 2. Representation of the function $F(t/d_p) = 1 - \exp(-2\frac{t}{d_P})$ as a function of t/d_P and the corresponding linear fit. Insert : difference (in %) between the linear fit and $F(t/d_p)$.



By considering eq (6) (see main text) and rewriting it differently: $F(t/d_p) = A\frac{n_2}{n'_2 K\rho_F}$

Considering that A_{max} ~ 0.25 in our experiments (See Figure 5), K ~ $1.2\text{x}10^{-3}$ (see Table 1), and using the values of n'_2, n_2, ρ_F given in the text, this gives an upper value of F(t/dp) of ~ 0.2

Thus, even for the highest absorbance measured in this work, we remain in the limit of validity of the approximated linear equation which deviates only very slightly from the full exponential form by few percents.

1. Picart, C., Mutterer, J., Arntz, Y., Voegel, J. C., Schaaf, P., and Senger, B. (2005) Application of fluorescence recovery after photobleaching to diffusion of a polyelectrolyte in a multilayer film. *Microscopy Research Technique* **66:**43-57.