

# Supporting Information

## Simultaneous spray coating of interacting species : General rules governing the system poly(styrene sulfonate)/poly(allyl amine)

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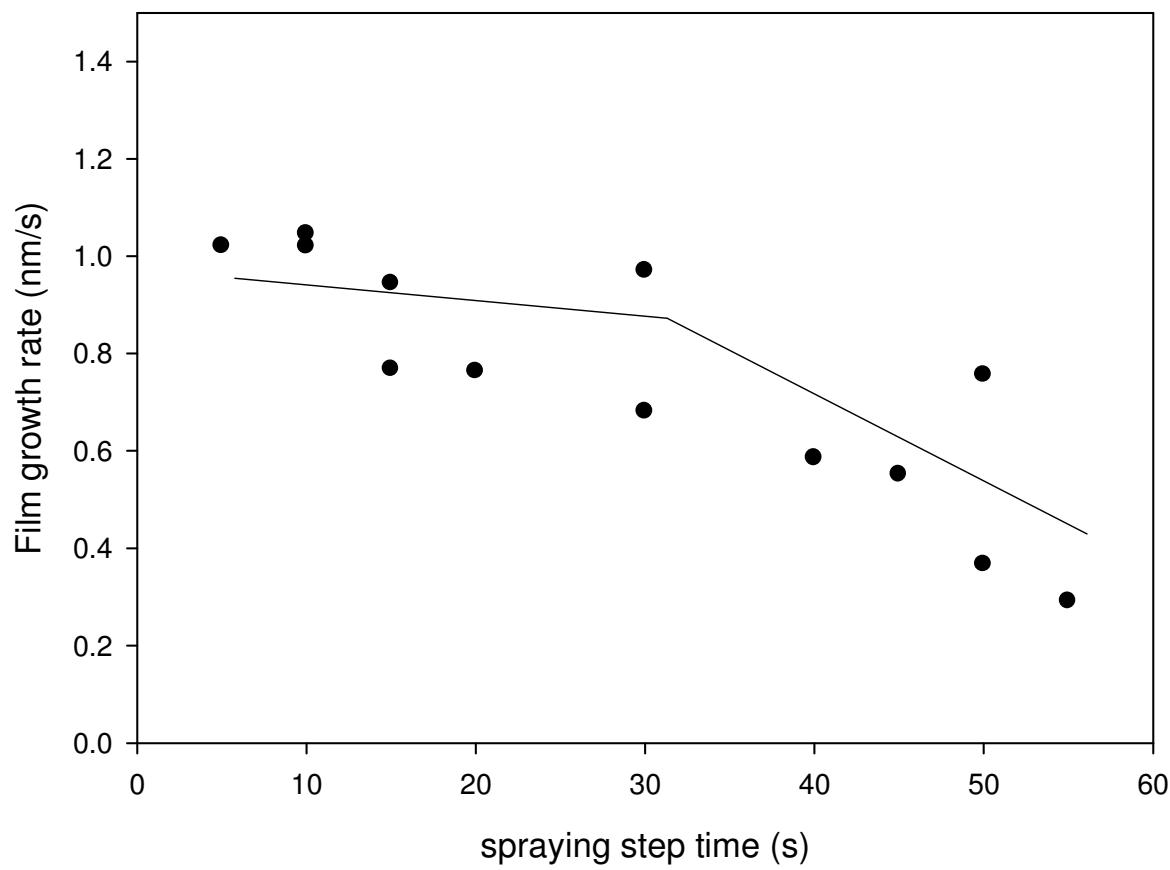
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Figure S 1: Variation of the growth speed of a PAH/PSS film sprayed simultaneously versus the spraying step duration.

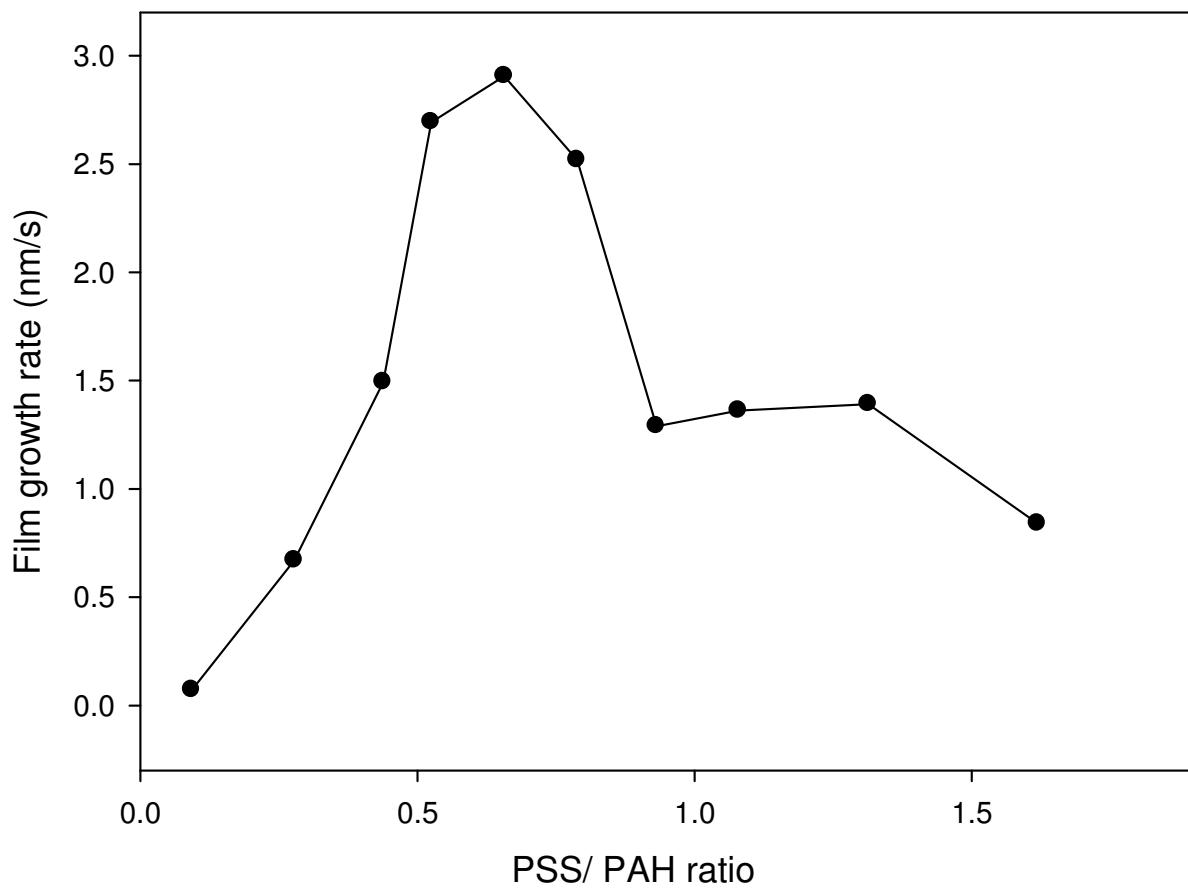
Figure S 2: Variation of the growth speed of a PAH/PSS film sprayed simultaneously versus PSS/PAH ratio with different flow rates.

Figure S 3: AFM pictures showing the changes in the morphology of a PAH/PSS film sprayed simultaneously versus the PSS/PAH spraying rate ratio.

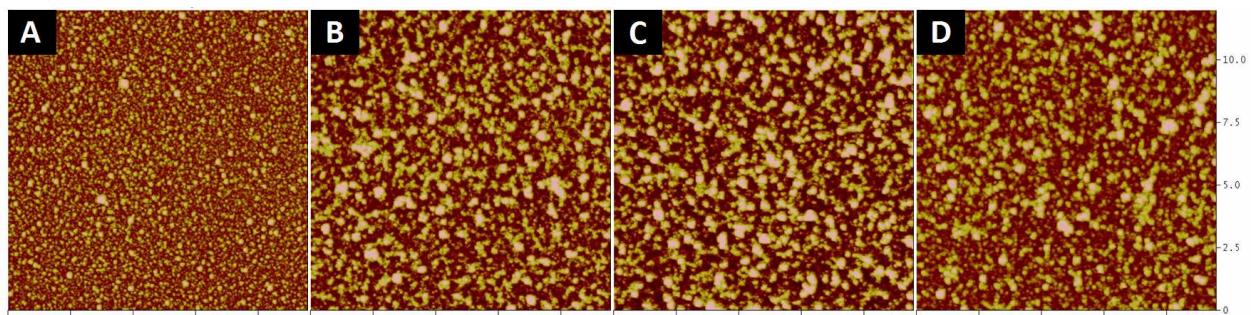
Figure S 4: XPS spectrum obtained from a PAH/PSS film sprayed simultaneously



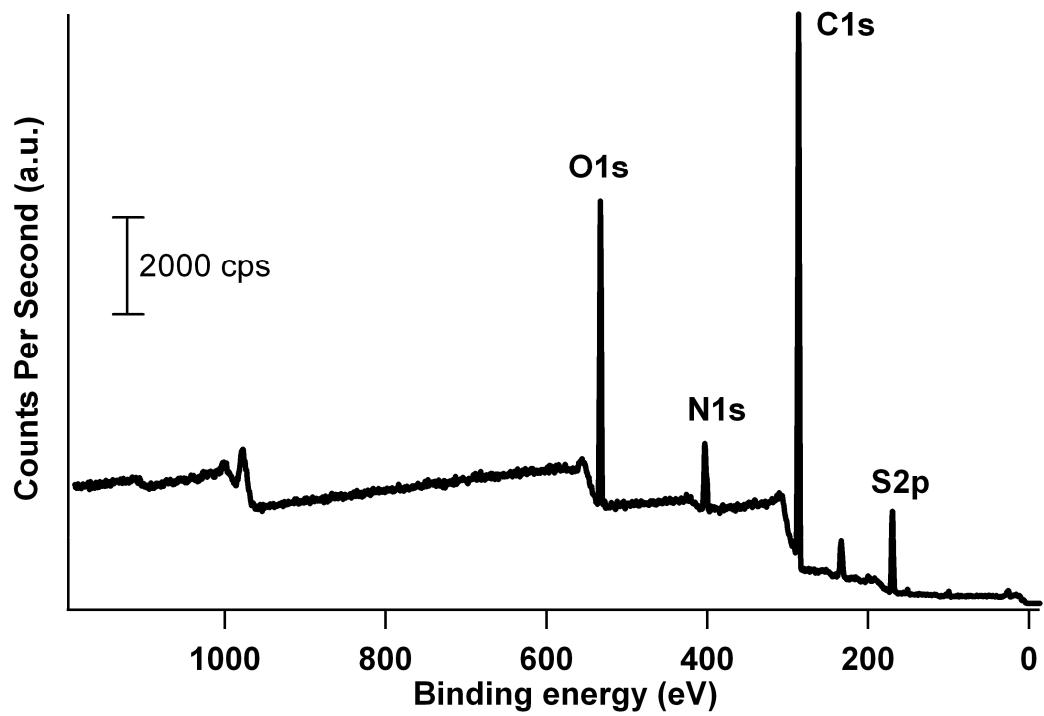
**S1 :** Evolution of the film growth rate versus the varying spraying step time. Poly(allylamine hydrochloride) (PAH) solution of  $0.5 \text{ mg.mL}^{-1}$ , sprayed at a spraying rate of  $1.5 \times 10^{-3} \pm 1.4 \times 10^{-4} \text{ mol/s}$ , poly(styrene sulfonate) (PSS) solution of  $0.5 \text{ mg.mL}^{-1}$ , sprayed at a spraying rate of  $8.0 \times 10^{-4} \pm 1.7 \cdot 10^{-5} \text{ mol.s}^{-1}$ . It corresponds to a PSS/PAH ratio of  $0.54 \pm 0.05$



**S2 :** Film growth rate (in nm/s) versus poly(allylamine hydrochloride) / poly(styrene sulfonate) ratio for PAH spraying rate constant of  $2.3 \times 10^{-3}$  mol.s<sup>-1</sup> (PAH concentration of 0.5 mg/mL) and PAH flow rate of  $24.2 \pm 1$  mL.s<sup>-1</sup> and PSS spraying rate variable and PSS flow rate of  $15.2 \pm 0.5$  mL.s<sup>-1</sup>. The solutions were at pH 7.5 and sprayed with a duration of a (single) spraying step of 5 seconds.



**S3 :** Evolution of the film morphology with the PSS/PAH spraying rate ratio. The overall morphology of the film does not change with the spraying ratio: one always obtains a granular structure. PSS/PAH (sprayed) ratio of respectively 0.15; 0.41; 0.82 and 1.15. AFM in contact mode, 12  $\mu\text{m}$  X 12  $\mu\text{m}$ , z-scale of 200 nm for A, B and C; 250 nm for D.



S4: Typical X-Ray Photoelectron Spectroscopy (XPS) spectrum of a PAH/PSS film.

Poly(allylamine hydrochloride) concentration is  $2.5 \text{ mg.mL}^{-1}$  (spraying rate of PAH of  $5 \times 10^{-3} \text{ mol.s}^{-1}$ ) and poly(styrene sulfonate) concentration is  $3 \text{ mg.mL}^{-1}$  (spraying rate of PSS of  $7.6 \times 10^{-3} \text{ mol.s}^{-1}$ ) corresponding to a PSS/PAH (sprayed) ratio of 0.66.