

## MECHANICALLY RESPONDING NANOVALVES BASED ON POLYELECTROLYTE MULTILAYERS

D. Mertz<sup>a</sup>, J. Hemmerlé<sup>a</sup>, J.-C. Voegel<sup>a</sup>, P. Schaaf<sup>b</sup>, Ph. Lavallo<sup>a</sup>

<sup>a</sup>INSERM Unité 595 "Biomaterials", University Louis Pasteur, 11 rue Humann, 67085 Strasbourg, France

<sup>b</sup>Institut Charles Sadron, CNRS, 6 rue Boussingault, Strasbourg, France

The alternate deposition of polyanions and polycations on charged surfaces leads to the formation of nanostructured films called polyelectrolyte multilayers [1,2]. The layer-by-layer deposition constitutes a formidable tool to functionalize surfaces and its potential applications are optical coatings, filtration devices, self-supported membranes with highly enhanced Young's moduli, fuel cell membranes, drug release or biologically active coatings [3,4]. The layer by layer deposition process of polyelectrolytes is used to construct films equipped by compartments containing "free" polymers or biomolecules [5-8]. Each compartment corresponds to a stratum of an exponentially growing polyelectrolyte multilayer film and two consecutive compartments can be separated by a stratum composed of linearly growing multilayers that act as a barrier preventing polyelectrolyte diffusion from one compartment to another.

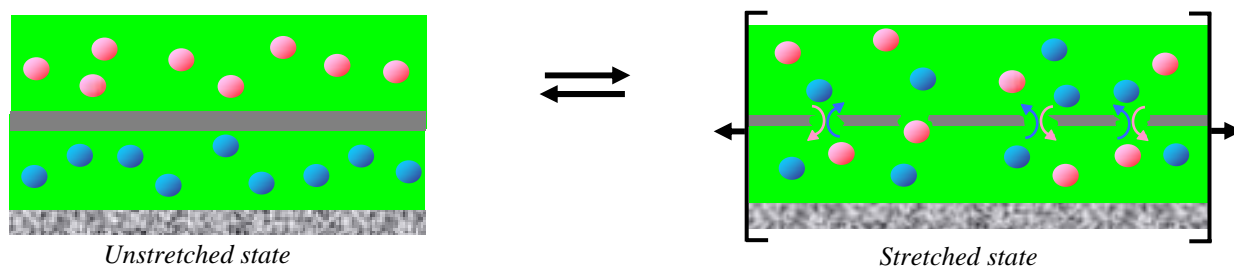
Whereas a first generation of polyelectrolyte multilayers was designed to functionalize a surface in a stable way, such multicompartiment films may constitute a new generation of functionalized coatings leading to *adaptative surfaces*. Most reported adaptative surfaces are aimed to respond, reversibly if possible, to external stimuli as for example pH, temperature or electrical stimuli and they are usually obtained by grafting polymers to solid substrates. The multilayer technology constitutes also an original way to develop these adaptative coatings and a second generation of multilayers responding to similar external stimuli is now emerging [9]. These films are usually designed to deliver active compounds consecutively to a change of pH [10] or temperature [11]. These stimuli, even if of great interest do not cover the whole possible stimuli range and others stimuli are envisioned for these surfaces. To our knowledge, only very few adaptative films responding to mechanical stimuli were reported up to now [12], despite the fact that mechanical stimuli can be of great convenient applications. One can, for example, anticipate their use in drug delivery patches, self repairing systems or nano-bio-sensor technology. We thus wish to make use of the great versatility of the multilayer technology to develop mechanically responding polyelectrolyte multilayers.

Such multicompartiment films are now built up on an extensible silicon sheet to design stimuli responding films [13]. Nanometer-sized multilayer barriers deposited on or between multilayer compartments will act as nanovalves [14]. For the investigated system, the stretching induces the formation of pores in the barriers once a critical stretching degree is reached and consequently allows a diffusion process through the barrier of polyelectrolyte chains initially contained in the different compartments. This critical stretching degree depends upon the number of bilayers constituting the barrier.

Finally, the diffusion of polyelectrolytes through the barrier from one compartment to another can be switched on/off by tuning the mechanical stretching and thereby opening or closing nanopores in the barrier. This work represents a first step toward the design of chemically or biologically active films responding to mechanical stresses.

**References:**

- [1] Decher, G., *Science*, 277, 1232 (1997).
- [2] Picart, C., Mutterer, J., Richert, L., Luo, Y., Prestwich, G. D., Schaaf, P., Voegel, J.-C., Lavallo, Ph., *Proc. Natl. Acad. Sci. USA*, 99, 12531 (2002).
- [3] Jessel, N., Lavallo, Ph., Meyer, F., Audouin, F., Frisch, B., Schaaf, P., Ogier, J., Decher, G., Voegel, J.-C., *Adv. Materials*, 16, 1507 (2004).
- [4] Jessel, N., Oulad-Abdelghani, M., Meyer, F., Lavallo, P., Haikel, Y., Schaaf, P., Voegel, J. C., *Proc. Natl. Acad. Sci. U.S.A*, 103, 8618 (2006).
- [5] Garza, J. M., Schaaf, P., Muller, S., Ball, V., Stoltz, J.-F., Voegel, J.-C., Lavallo, Ph., *Langmuir*, 20, 7298 (2004).
- [6] Garza, J. M., Jessel, N., Ladam, G., Dupray, V., Muller, S., Stoltz, J.-F., Schaaf, P., Voegel, J.-C., Lavallo, Ph., *Langmuir*, 21, 12372 (2005).
- [7] Vodouhe, C., Le Guen, E., Garza J.M., Francius, G., Dejugnat, C., Ogier, J., Schaaf, P., Voegel, J.C., Lavallo, Ph., *Biomaterials*, 27, 4149 (2006).
- [8] Jourdainne, L., Arntz, Y., Senger, B., Debry, C., Voegel, J.-C., Schaaf, P., Lavallo, Ph., *Macromolecules*, 40, 316 (2007).
- [9] Sukhishvili, S. A., *Curr. Opinion Colloid Interf. Sci.*, 10, 37-44 (2005).
- [10] Izumrudov, V. A., Kharlampieva, E.; Sukhishvili, S. A., *Biomacromolecules*, 6, 1782-1788 (2005).
- [11] Quinn, J. F.; Caruso, F., *Macromolecules*, 38, 3414-3419 (2005).
- [12] Russell, T. P., *Science* 297, 964-967 (2002).
- [13] Hemmerlé, J., Roucoules, V., Fleith, G., Nardin, M., Ball, V., Lavallo, Ph., Marie, P., Voegel, J.-C., Schaaf P., *Langmuir*, 21, 10328 (2005).
- [14] Mertz, D., Hemmerlé, J., Mutterer, J., Ollivier, S., Voegel, J.-C., Schaaf, P., Lavallo, Ph., *Nano Letters*, 7, 657 (2007).

**Figure:**

*Schematic representation of a multicompartiment film before and during the stretching state. The gray line corresponds to the barrier that allows diffusion of molecules from one compartment to the other when the stretching is applied and nanopores are formed.*