SORPTION OF PROTEINS ONTO POROUS MULTILAYER THIN FILMS BASED ON POLY(VINYL AMINE)

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CONTENT OF PRESENTATION

- Motivation
- Objectives
- Results and Discussion
- Conclusions and Outlook
- Acknowledgements

MOTIVATION

- Biological properties of surfaces can be controlled by the sorption/embedding of proteins or nucleic acids in multilayer thin films, because the "electrostatic cage" formed by polyelectrolytes preserves the protein structure [1,2];

- Multilayer thin films can be constructed on various substrates by alternate deposition of the building blocks according to the layer-by-layer self-assembly technique [3];

1. Lvov, Y. M.; Lu, Z.; Schenkman, J. B.; Zu, X.; Rusling, J. F. *J. Am. Chem. Soc*. 1998, *120*, 4073.
2. Shutava, T. G.; Kommireddy, D. S.; Lvov, Y. M. *J. Am. Chem. Soc*. 2006, *128*, 9926.
3. Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* 1992, *210*, 831.

MOTIVATION

- Multilayer thin films are usually di- or multicomponent, their properties depending on the nature of the assembled species and on the deposition conditions (pH, ionic strength, temperature) [4];

- Weak polyelectrolytes are very attractive building blocks to design multilayer thin films because they allow a fin control of the layer thickness, surface roughness, and film morphology by their complex behavior as a function of pH [5];

[4] Dragan, E. S.; Bucatariu, F. *Self-Assembled Multilayers: Construction, Properties and Applications*, In: New Trends in Ionic (Co)Polymers and Hybrids, Ed. Dragan, E. S.; Nova Science Publishers, NY, 2007, pp 165-234.

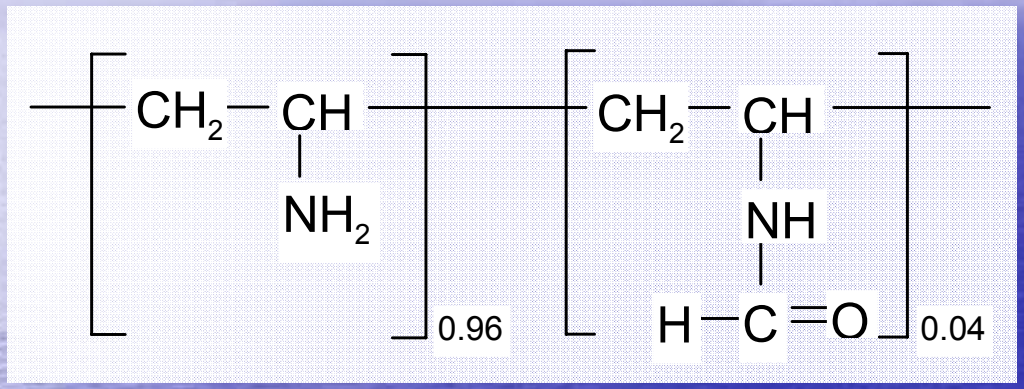
[5] Simon, F.; Dragan, E. S.; Bucatariu, F. *React. Funct. Polym*. 2008, *68*, 1178.

OUR OBJECTIVES

- Construction of novel porous single component multilayer thin films based on poly(vinyl amine) (PVAm).
- Sorption tests of proteins (HSA and BSA) onto the multilayer thin films of $(PVAm)_n$.
- Characterization of multilayer thin films before and after the sorption of proteins.

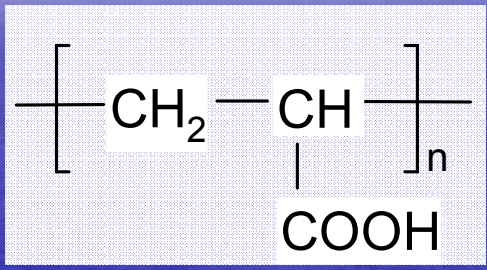
- Dragan, E. S.; Bucatariu, F. *Macromol. Rapid Commun*. 2010, 31, 317.
- Dragan, E. S.; Bucatariu, F. *Bull. Inst. Pol. Iasi* 2009, Tom LV (LIX), Fasc. 4, 167.
- Dragan, E. S.; Bucatariu, F.; Hitruc, G. E. *Biomacromolecules,* revised manuscript submitted on January 22nd.

Weak polyelectrolytes used in the preparation of dicomponent multilayers



poly(vinyl amine) (PVAm)

M_v = 15000 g·mol^{-1}; 340000 g·mol^{-1}



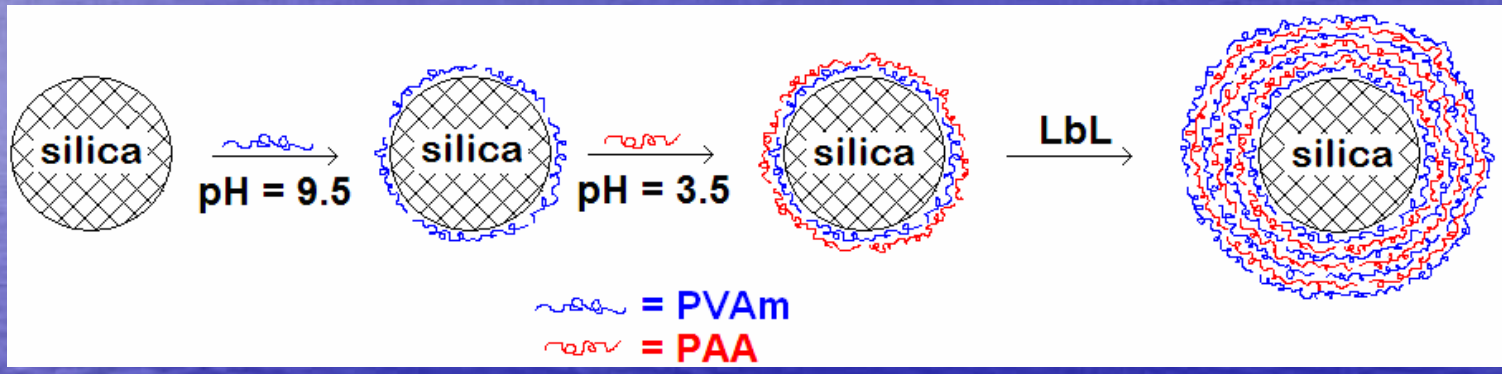
poly(acrylic acid) (PAA)

M_v = 11000 g·mol^{-1}; 58000 g·mol^{-1}

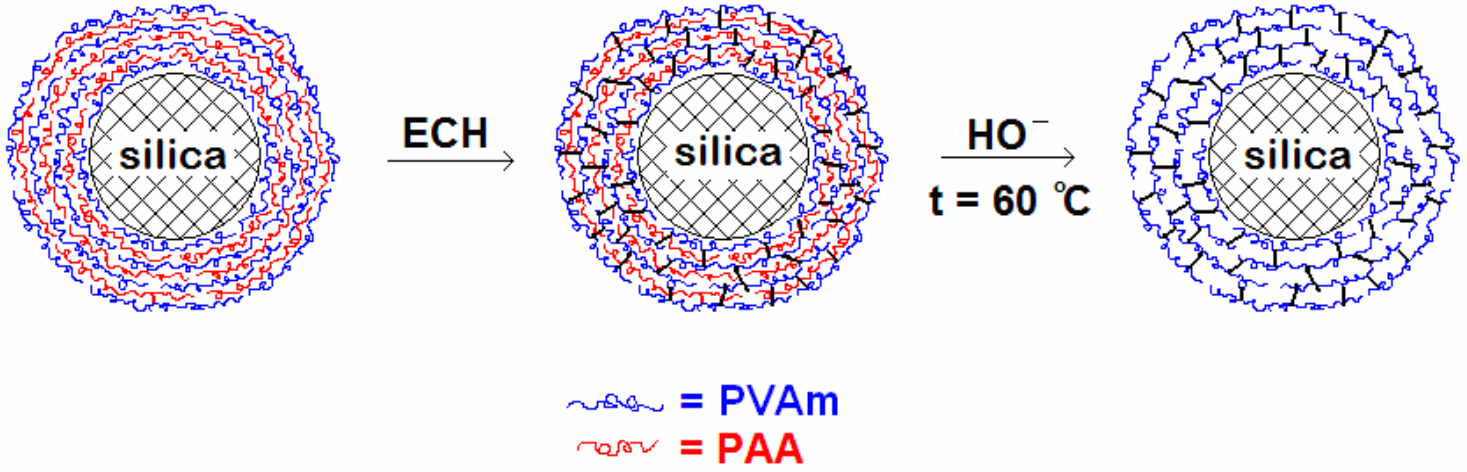
Our strategy used in the construction of porous single component multilayer thin films

Substrates: silica microparticles 15 - 40 μm, with pores of 5 nm, and Si/SiO_2 wafers

First step

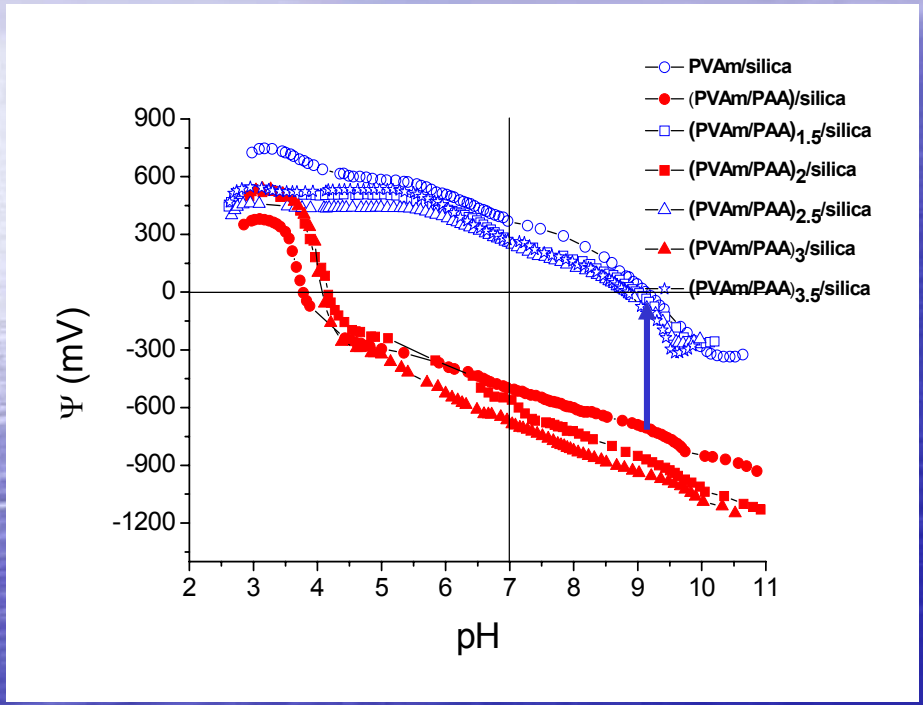


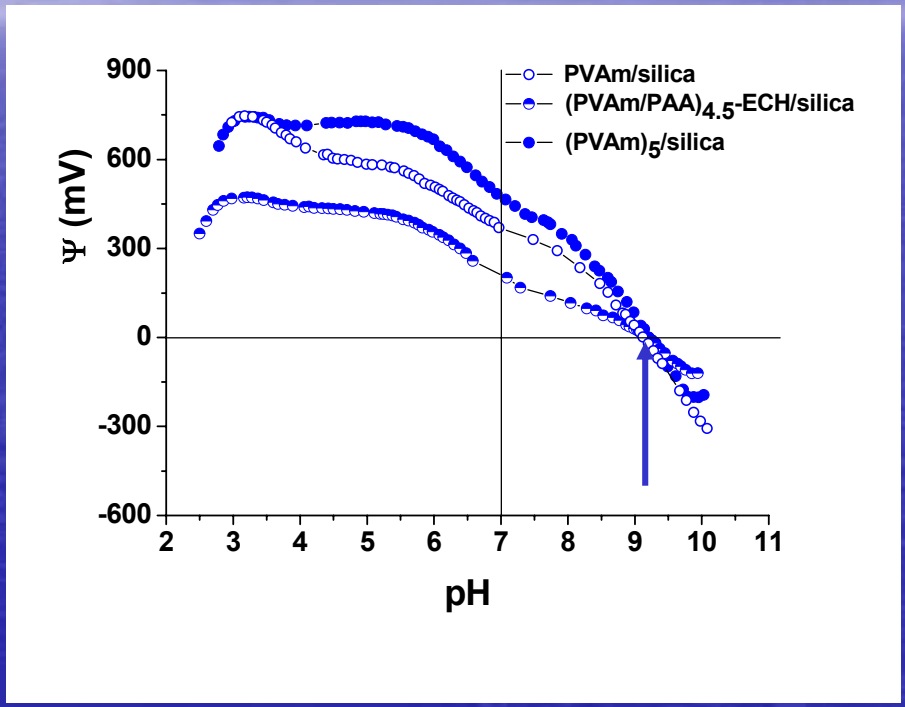
Second step



Characterization of multilayer thin films

Multilayer thin film deposited on silica microparticles

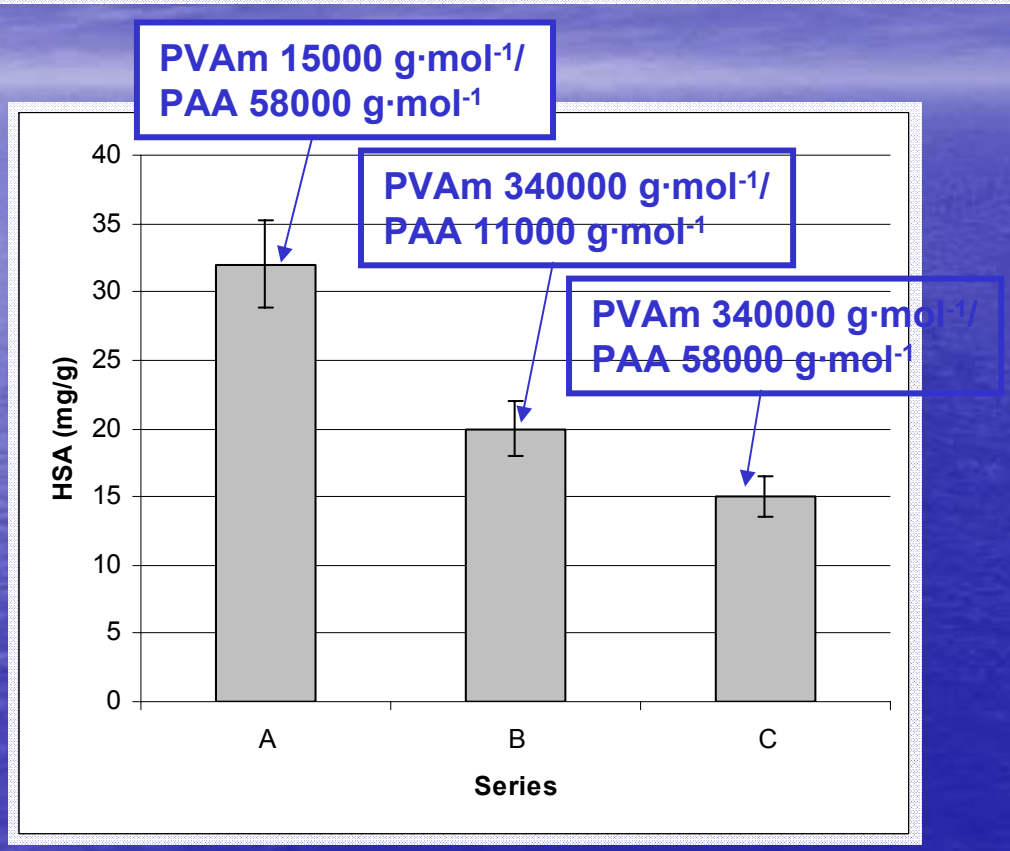




Potentiometric titration of hybrid particles consisting of LbL multilayers constructed with: PVAm cu M_v = 15000 g·mol^{-1};PAA cu M_v = 58000 g·mol^{-1}

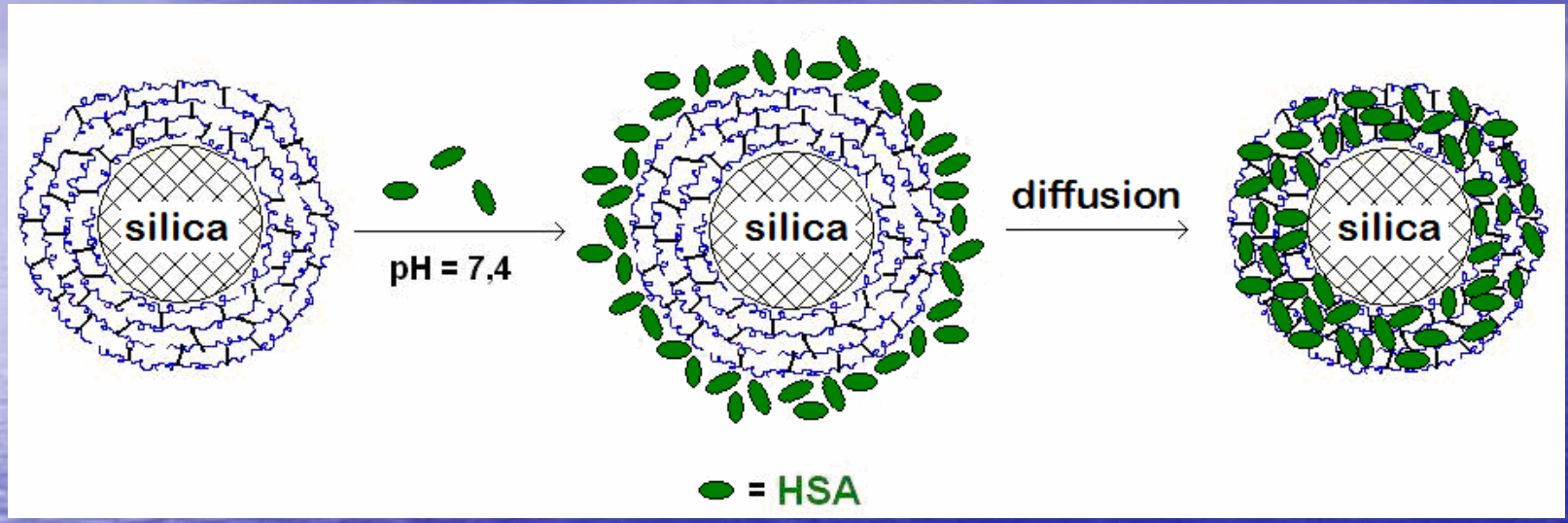
Sorption of HSA onto the single component multilayer thin films

Multilayer thin films deposited onto silica microparticles



HSA amount (mg/g) sorbed on the $(PVAm)_5$ film as a function of the polyion pair used in the construction of LbL dicomponent film

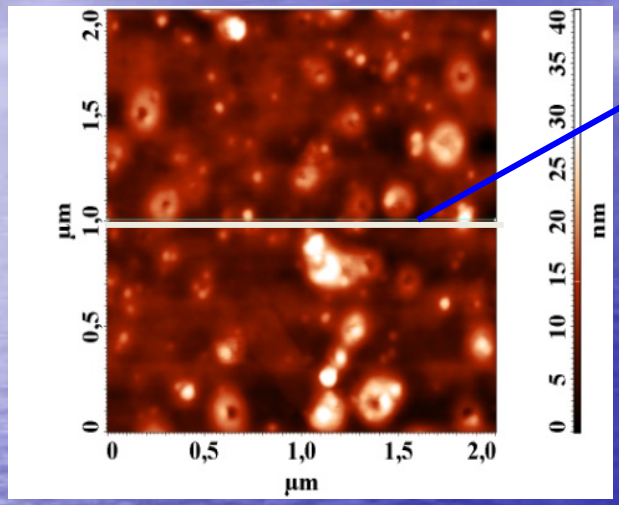
Modalities of protein sorption onto the single component multilayer thin films of $(PVAm)_n$

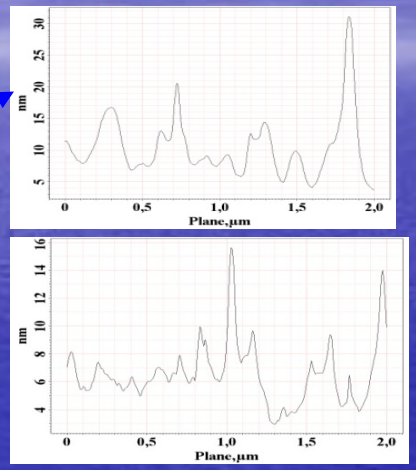


To evaluate which sorption process is the most probable, AFM and contact angle measurements were performed on the films deposited on silicon wafers

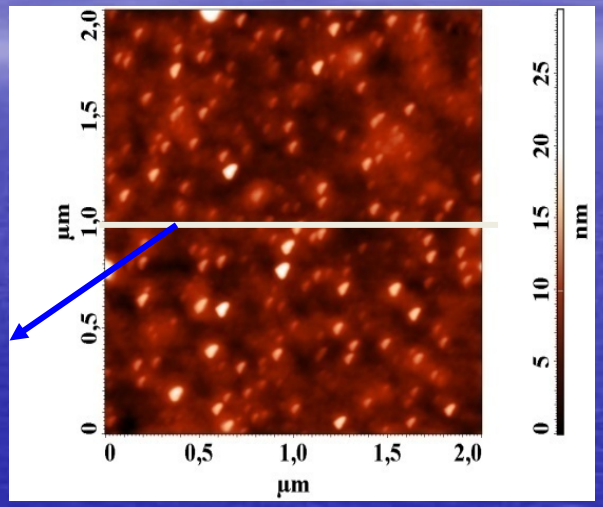
Height AFM images of the $(PVAm)_n$ multilayer thin films before and after the sorption of HSA

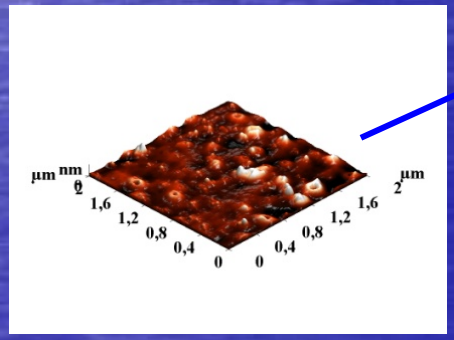
$(PVAm)_6$

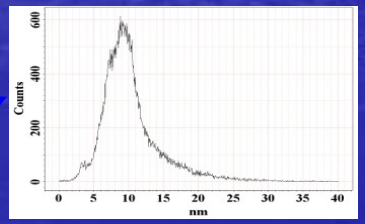


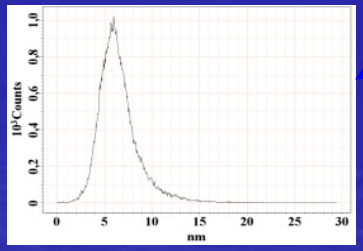


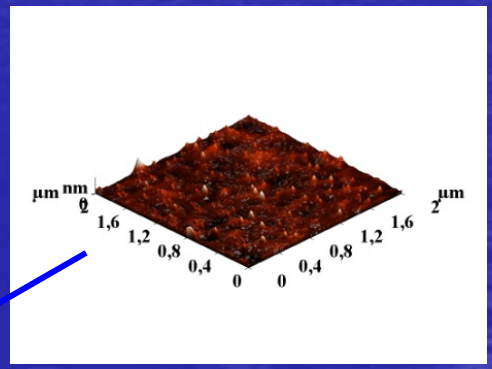
$HSA-(PVAm)_6$









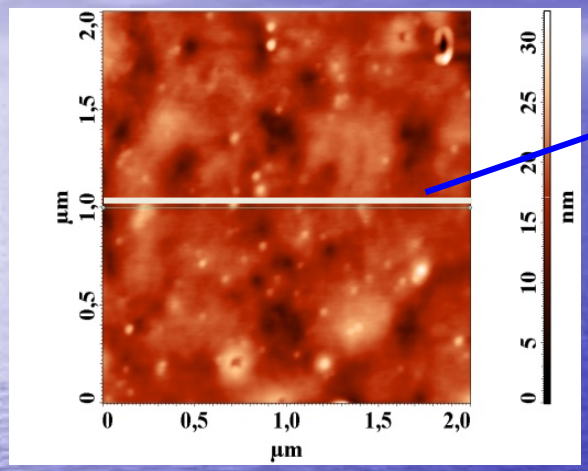


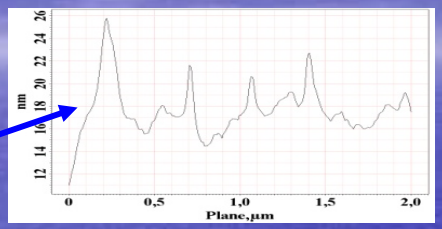
R_a = 4.38 nm

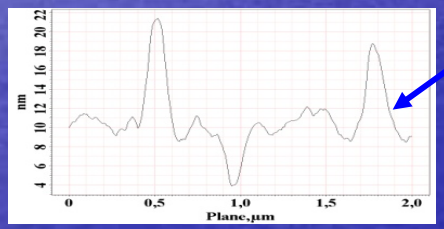
R_a = 2.27 nm

Height AFM images of the $(PVAm)_n$ multilayer thin films before and after the sorption of HSA

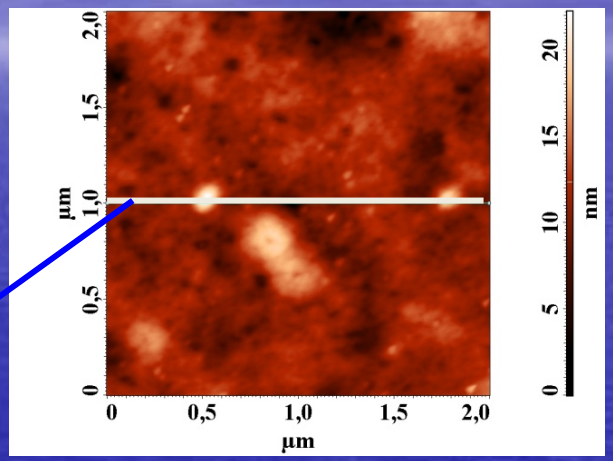
$(PVAm)_8$

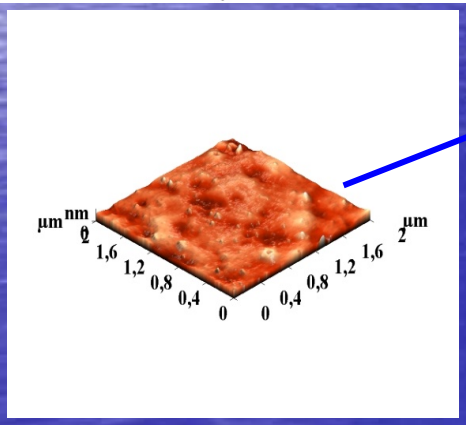


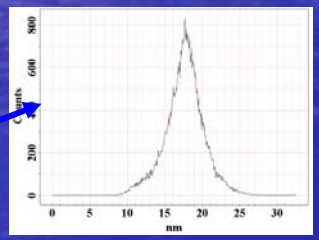


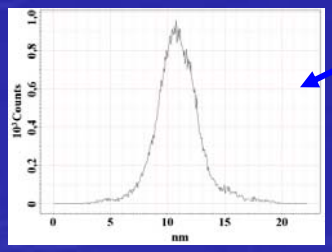


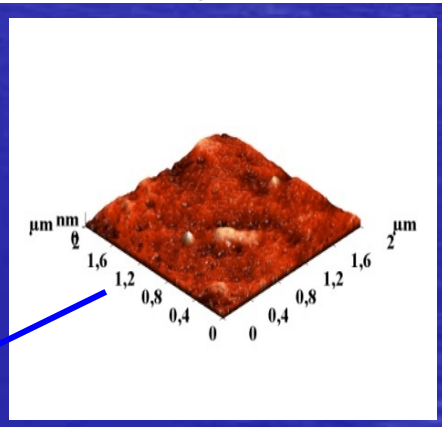
$HSA/(PVAm)_8$









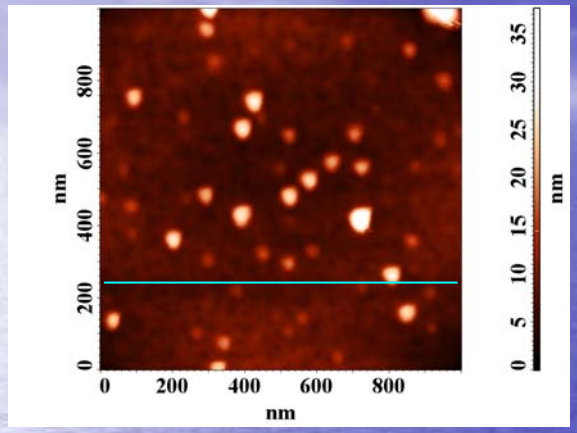


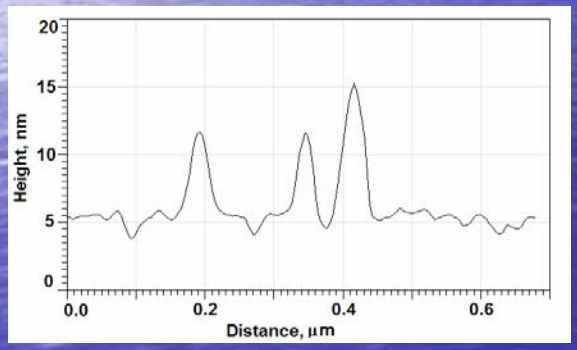
R_a = 2.63 nm

R_a = 2.11 nm

Characterization by AFM of the $(PVAm)_n$ multilayer thin films after the sorption of BSA

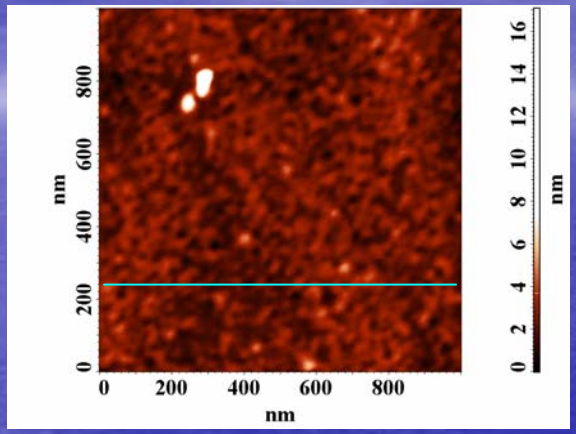
n = 4

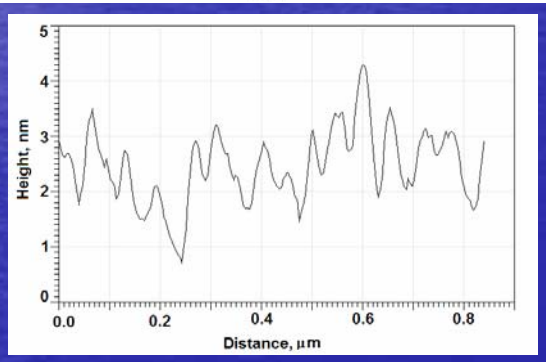




h_a = 5.2 nm; R_a = 1.7 nm

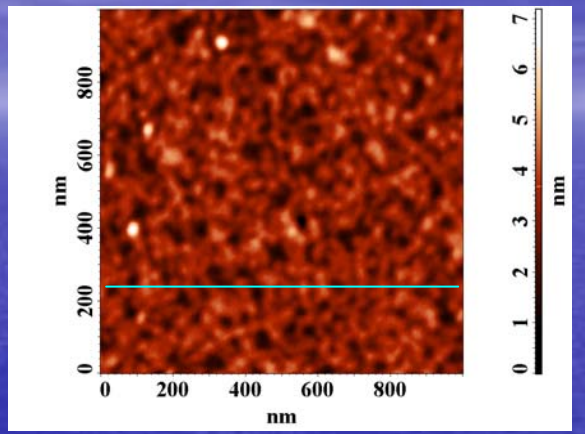
n = 6

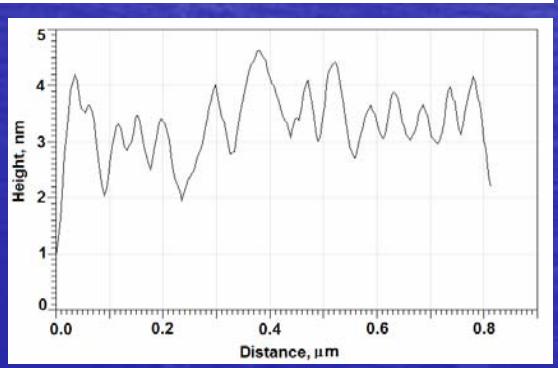




h_a = 4.8 nm; R_a = 1.4 nm

n = 8





h_a = 3.2 nm; R_a = 0.5 nm

Upper: height AFM images of the cross-linked single component $(PVAm)_n$ films after the sorption of BSA; scan size: 1 x 1 μm^2 in all images;
Down: the height profiles generated along the horizontal lines.

Contact angle measurements on the porous $(PVAm)_n$ multilayer thin films

Contact angle and standard deviations of the film surface before and after the sorption of HSA

n	$(PVAm)_n$	$HSA/(PVAm)_n$
4	88.8 ± 1.0	85.5 ± 0.4
6	95.3 ± 1.2	85.1 ± 0.7
8	95.0 ± 0.2	89.2 ± 0.1

- Contact angle decreased after the sorption of HSA, the main decrease being observed for the films with 6 and 8 layers of PVAm.
- The increase of the film wettability after the sorption of HSA suggests the protein has been absorbed into the porous thin film.

Contact angle measurements on the porous $(PVAm)_n$ multilayer thin films

Contact angle and standard deviations of the film surface before and after the sorption of BSA

n	$(PVAm)_n$	BSA/$(PVAm)_n$
4	88.8 ± 1.0	70.5 ± 2.0
6	95.3 ± 1.2	74.4 ± 0.5
8	95.0 ± 0.2	77.8 ± 0.1

- After the sorption of BSA, the contact angle decreased even more than in the case of HSA sorption, supporting the same mechanism of interaction between the porous film and protein, i.e., the absorption of protein inside the porous thin film.
- Even if the HSA and BSA are very similar concerning their molar mass and isoelectric point, differences in their sorption on the $(PVAm)_n$ thin films have been observed, as for other substrates.

CONCLUSIONS AND OUTLOOK

- It was shown, for the first time, that porous cross-linked multilayer thin films containing only PVAm as single component can be designed.

- $(PVAm)_n$ multilayer thin films constitute potential reservoirs for proteins and other biologic active compounds.

- Finding the best conditions for controlled release of biologic active compounds from the $(PVAm)_n$ multilayer thin films is the main task in the near future.

- Influence of the preparation conditions of the starting dicomponent multilayer on the properties of the final single component thin film is of interest for the future investigations.

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Thank you
for your
kind attention!