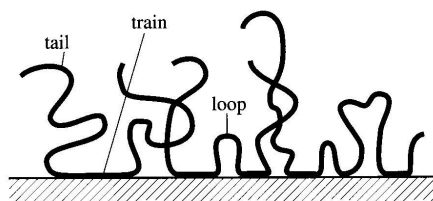


polimeri na površini; adsorpcija polimera



IUPAC Gold Book

polyelectrolyte
Synonym: polymer electrolyte, polymeric electrolyte

Polymer composed of macromolecules in which a substantial portion of the constitutional units contains ionic or ionizable groups, or both.

Notes:

1. The terms polyelectrolyte, polymer electrolyte, and polymeric electrolyte should not be confused with the term solid polymer electrolyte.
2. Polyelectrolytes can be either synthetic or natural. Nucleic acids, proteins, tricholic acids, some polypeptides, and some polysaccharides are examples of natural polyelectrolytes.

Source:
IUPAC, 2006, 78, 2067. (Terminology of polymers containing ionizable or ionic groups and of polymers containing ions (IUPAC Recommendations 2006)) on page 2072 [Turns] [Paper]

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Polyelectrolytes Are Superheroes

Guest Editor:

Dr. Ranjit De
Department of Life Sciences,
Pohang University of Science and
Technology (POSTECH), Pohang
37673, Korea
deranjit@postech.ac.kr

Message from the Guest Editor

Polyelectrolytes are a special class of polymers with ionizable groups in each of their repeating units which can influence surface properties and interactions. The presence of various types of such interactions among polymer chains can have applications in various fields. They can also contribute to protecting sensitive molecules from losing their inherent properties.

polikationi i polianioni; ponašanje na površini

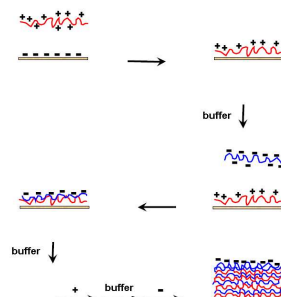
polielektrolitni višesloj (*polyelectrolyte multilayer*)

- nastaju naizmjeničnom adsorpcijom polikationa i polianiona na čvrstu površinu
- najčešća metoda naizmjenično uranjanje u otopinu polielektrolita
- intenzivno istraživan posljednjih petnaestak godina (preko 100 radova godišnje)
- istražuju se uglavnom jaki polielektroliti

polikationi i polianioni; ponašanje na površini

- adsorpcija polielektrolita na kovinskim oksidima
- izmjenično dodavanje pozitivno i negativno nabijenih polielektrolita $\Rightarrow$ nastajanje višesloja na površini metalnog oksida
- izrastanje višesloja je karakterizirano porastom adsorbirane mase $\Rightarrow$ metoda praćenja reflektometrija

polyelectrolyte multilayers



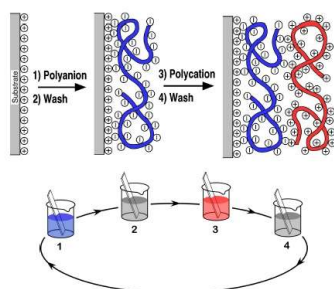


Fig. 1: Formation of PE multilayers

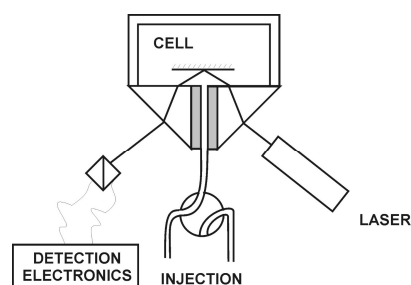
otvorena pitanja

- ponašanje slabih polielektrolita
- mehanizam nastajanja višeslojeva
- polielektrolitni višeslojevi su ravnotežne strukture?
- eksponencijalni vs. linearni rast

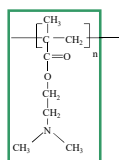
eksperimentalne metode:

- Elipsometrija
- **Optička reflektometrija**
- Quartz crystal microbalance (QCM)
- Atomic force microscopy (AFM)
- Optical waveguide lightmode spectroscopy
- Surface plasmon resonance spectroscopy
- Neutron reflectometry
- FTIR-IR, itd, itd...

optička reflektometrija



P-AMA Poli(di-metil-Amino-etil-MetAkrilat)

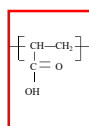


$M_w = 20 \text{ kg/mol}$

$M_s = 157 \text{ g/mol}$

PAA

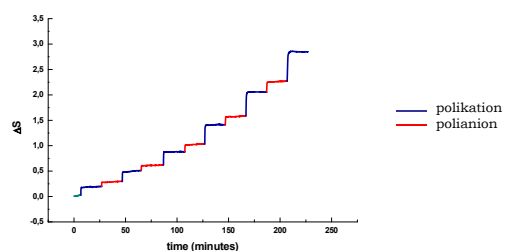
Poli Akrilna kiselina (**A**cid)

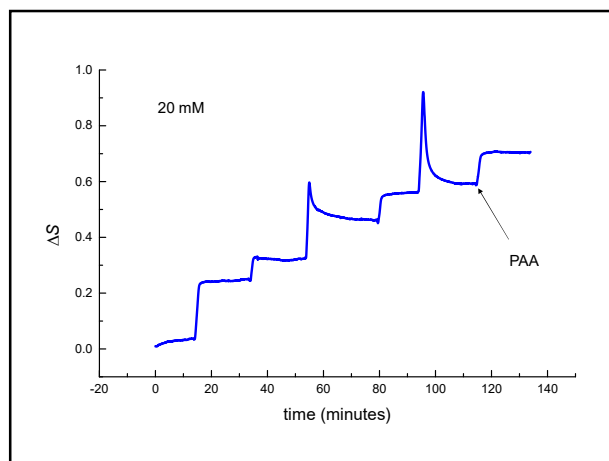
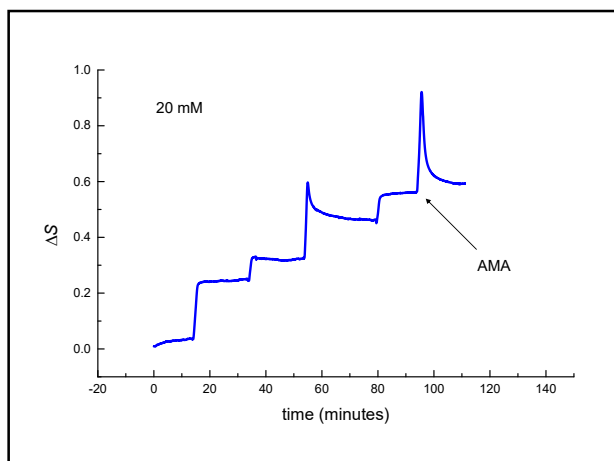
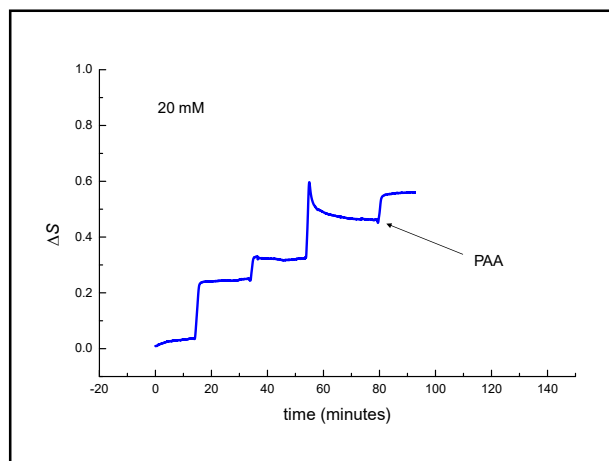
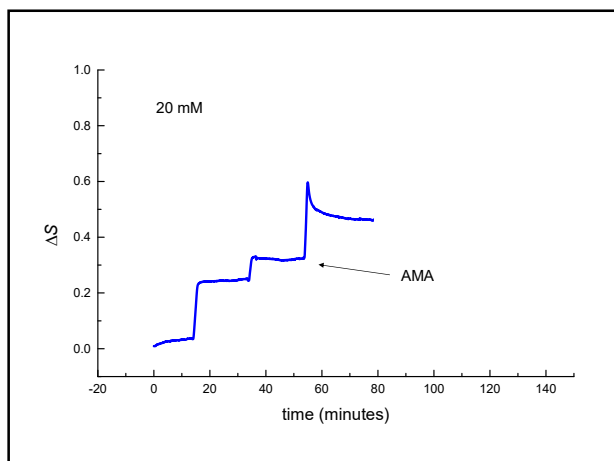
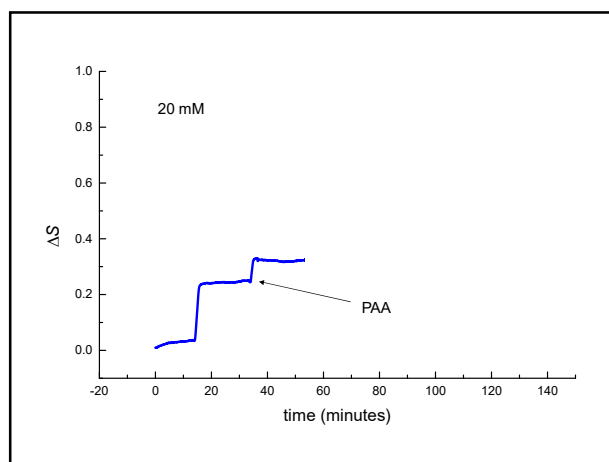
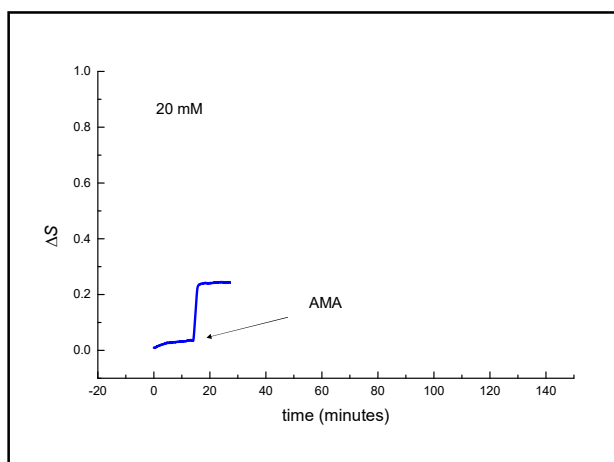


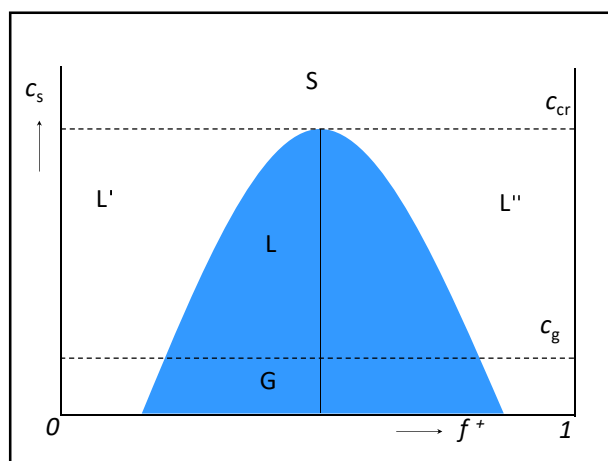
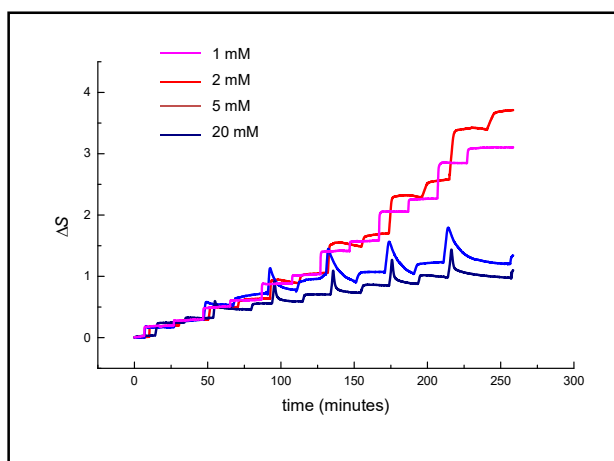
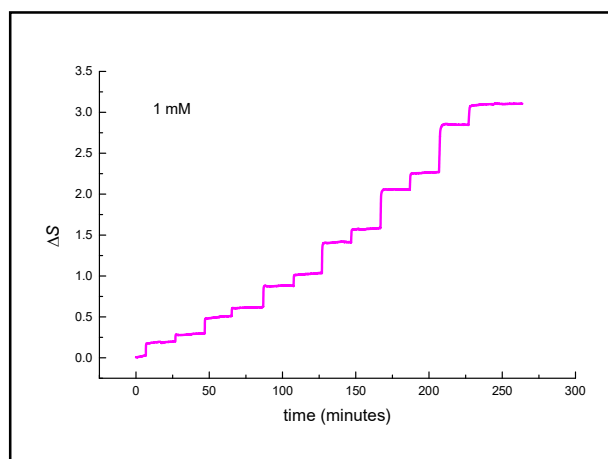
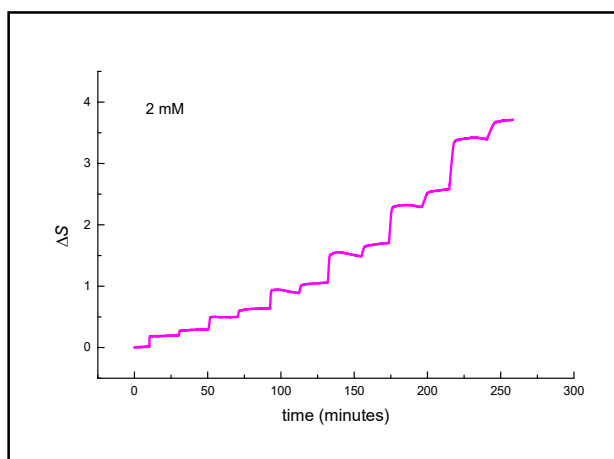
$M_w = 12.5 \text{ kg/mol}$

$M_s = 72 \text{ g/mol}$

polielektrolitni višeslojevi (*Polyelectrolyte Multilayers*)

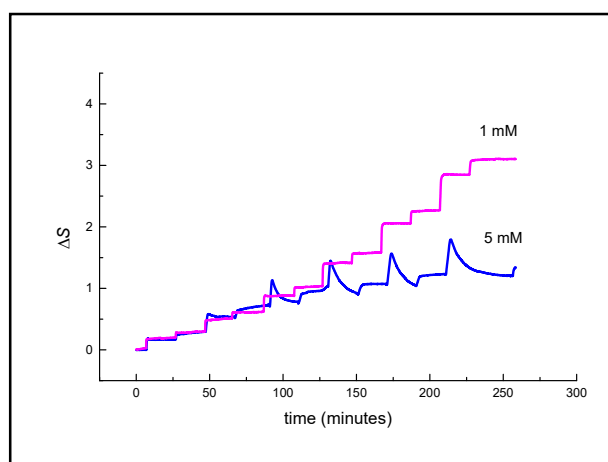






AFM mjerenja

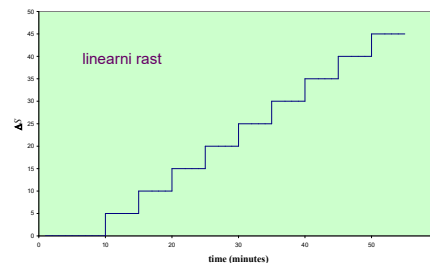
- usporedba između uzoraka pripremljenih pri 1 mM i 5 mM
- contact mode AFM



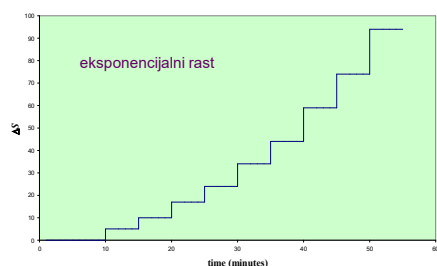
otvorena pitanja

- ponašanje slabih polielektrolita
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- eksponencijalni vs. linearni rast

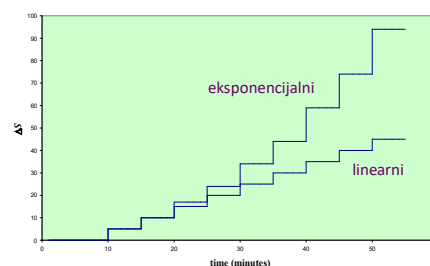
eksponencijalni vs. linearni rast



eksponencijalni vs. linearni rast



eksponencijalni vs. linearni rast

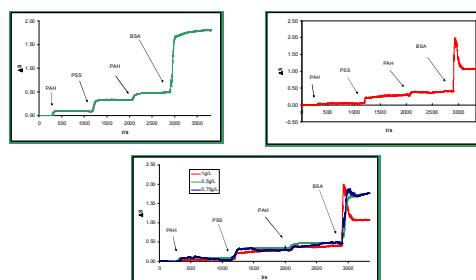


eksponencijalni vs. linearni rast

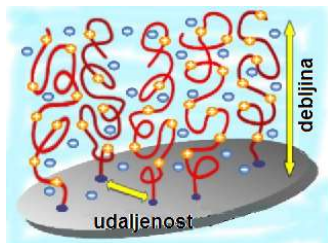
Faktori koji utječu na tip rasta:

- kemijska priroda polielektrolitnog para
- vrsta dodanog elektrolita
- ionska jakost
- temperatura
- metoda pripreme

adsorpcija BSA na prethodno formirani polielektrolitni višesloj



polielektrolitne "četke" (Polyelectrolyte Brushes)



polyelectrolyte multilayers - applications

Biomedicine and pharmaceutical industry

• Surface modification (thickness, charge, etc...)

• Drug delivery

• Formation of stimuli responsive systems (e.g. mechanical, temperature, pH)

• Surfaces with antibacterial properties

nature
materials

REVIEW ARTICLE

Emerging applications of stimuli-responsive polymer materials

Marlene A. Cohen Stuart, Willem T. S. Huck, Jan Geniesse, Marcus Müller, Christopher Ober, Manfred Stamm, Oleg B. Sukhorukov, Igor Schiller, Vladimir V. Tsudikov, Marek Urban, François Winnik, Stefan Zauscher, Igor Luzinov and Sergey Minko*

Responsive polymer materials can adapt to surrounding environments, regulate transport of ions and molecules, change wettability and adhesion of different species on external stimuli, or convert chemical and mechanical signals into optical, electrical, thermal and mechanical signals, and vice versa. These materials are playing an increasingly important role in a diverse range of applications, such as drug delivery, diagnostics, tissue engineering and smart material systems, as well as laboratory microelectromechanical systems, catalysis and energy. The underlying science and principles in the field are rapidly expanding, leading to a wide range of applications of stimuli-responsive polymer materials that are self-assembled from nanostructured building blocks. We also provide a critical review of emerging developments.

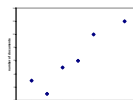
BioMACROMOLECULES

Drastically Lowered Protein Adsorption on Microbicidal Hydrophobic/Hydrophilic Polyelectrolyte Multilayers

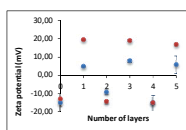
Sze Yee Wong,^{1,2} Lin Han,³ Kasia Tomczak,⁴ Jonasz Vondraniec,^{1,2} Md Nasim Huda,¹ Christine Oke,¹ Alexander M. Kabanov,^{1,2} and Dalia T. Hristova^{1,2}

¹Department of Chemical Engineering, ²Institute for Surface Nanotechnology, ³Department of Materials Science and Engineering, ⁴Department of Chemistry, ⁵Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

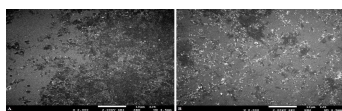
Supporting Information



adhesion of bacteria on polyelectrolyte multilayers



PAH/PSS multilayer



adhesion of bacteria *Pseudomonas aeruginosa* on PAH/PSS multilayer (SEM).
(A) five layers with positive terminating layer (PAH)
(B) six layers with negative terminating layer (PSS)

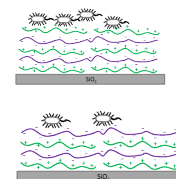
polymers

MDPI

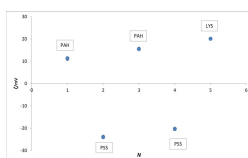
Influence of Polyelectrolyte Multilayer Properties on Bacterial Adhesion Capacity

Đorđe Koraćević,¹ Bek Prizmić,² Kamren Gofid Torkay,³ Jasmina Salopek,¹ Goran Džalić,^{1,4,5} Anđel Abram,^{1,4,5} and Klemen Bohinc,^{1,2}

	PAH as terminating layer (5 layers)	PSS as terminating layer (5 layers)
Fraction of the multilayer surface covered with <i>P. aeruginosa</i>	20.4 % ± 4.8 %	9.0 % ± 3.1 %
Contact angle	48.9° ± 2.5°	46.9° ± 5.0°
Roughness	0.017 μm ± 0.004 μm	0.019 μm ± 0.006 μm

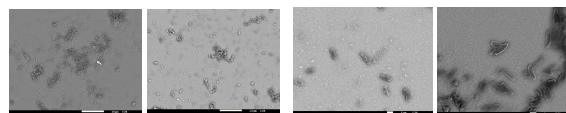


adhesion of bacteria on protein-terminating polyelectrolyte multilayers



	Lysozyme as terminating layer (5 layers)	BSA as terminating layer (5 layers)	Glucanase as terminating layer (5 layers)
Contact angle	63.2° ± 0.1°	63.2° ± 6.0°	66.7° ± 9.4°
Roughness/μm	0.120 ± 0.00	0.072 ± 0.00	0.018 ± 0.006
z-potential/mV	20.10 ± 0.35	7.24 ± 0.74	-11.77 ± 0.40

adhesion of bacteria on protein-terminating polyelectrolyte multilayers



lysozyme

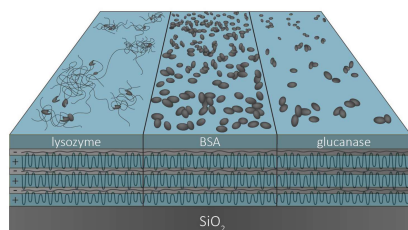
BSA

glucanase

Two types of bacteria:

- *Pseudomonas aeruginosa* - left
- *Escherichia coli* - right

adhesion of bacteria on protein-terminating polyelectrolyte multilayers



bacterial adhesion capacity of uropathogenic *Escherichia coli* to polyelectrolyte multilayer coated urinary catheter surface

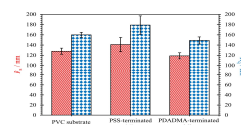


Table 1. Quantitative measurements of the local average surface roughness (R_a) and root-mean-square (R_q) surface roughness (R_z) inside the PVC catheter sample and the same material covered with PSS/P2VP/MAA thin film.

Sample	R _a /nm	R _z /nm
PVC substrate	120 ± 5	360 ± 5
PVC substrate coated with PSS-terminated multilayer	141 ± 14	379 ± 16
PVC substrate coated with PSS-MAA-terminated multilayer	110 ± 5	349 ± 7

Model catheter surface:
PVC surface
Key surface properties:
charge
hydrophobicity
roughness

Table 2. Zeta potential of untreated and coated PVC surfaces at pH = 7.2

Sample	ζ , mV
PVC substrate	+15.96 $\pm$ 2.0
PVC substrate coated with PSS-terminated multilayer	-63.25 $\pm$ 0.35
PVC substrate coated with PDADMA-terminated multilayer	+6.19 $\pm$ 0.25

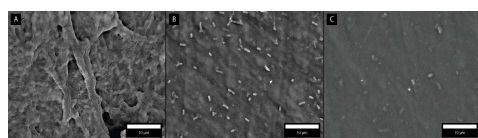
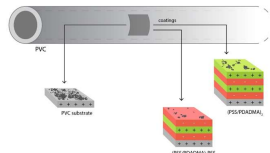


Table 3. Number of adhered bacteria per 1700 μm^2

Sample	PVC substrate	PVC substrate coated with PSS/MAA-terminated multilayer
Number of adhered bacteria per 1700 μm^2	10 ± 12	11 ± 17

K. Bohinc, L. Kukić, R. Štukelj, AM. Zore, A. Abram, T. Klačič, D. Kovačević, *Coatings*, 11 (2021) 630.



šuplje sfere

