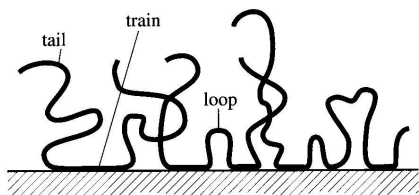


polimeri na površini; adsorpcija polimera



IUPAC Gold Book

polyelectrolyte
 Synonyms: polyelectrolyte, polymeric electrolyte

Definition: 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, trichloro acids, some polypeptides, and some polysaccharides are examples of natural polyelectrolytes.

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

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polymers

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Polyelectrolytes Are Superheroes

Guest Editor:

Message from the Guest Editor

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

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

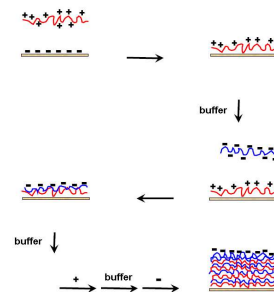
polielektrolitni višesloj (*polyelectrolyte multilayer*)

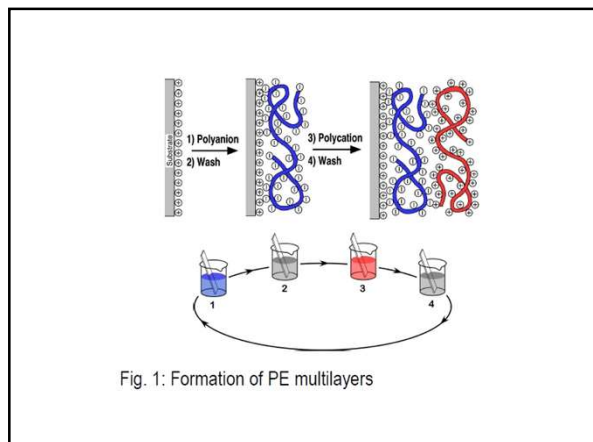
- nastaju naizmjeničnom adsorpcijom polikationa i polianiona na čvrstu površinu
- najčešća metoda naizmjenično uranjanje u otopinu polielektrolita
- intenzivno istraživano posljednjih petnaestak godina (preko 100 radova godišnje)
- istražuju se uglavnom jaki polielektroliti

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





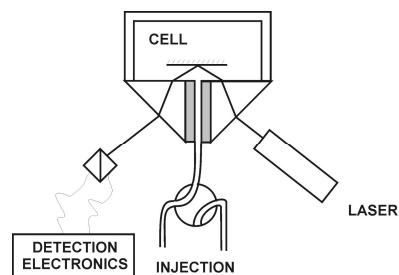
otvorena pitanja

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

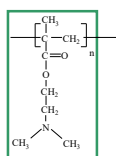
eksperimentalne metode:

- 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



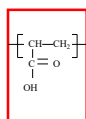
P-AMA Poli(di-metil-Amino-etil-MetAkrilat)



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

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

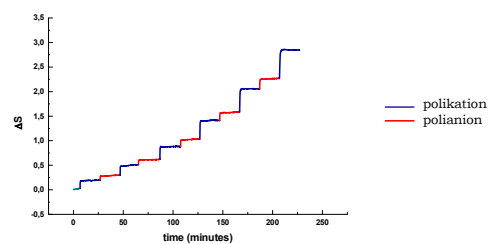
PAA Poli Akrilna kiselina (Acid)

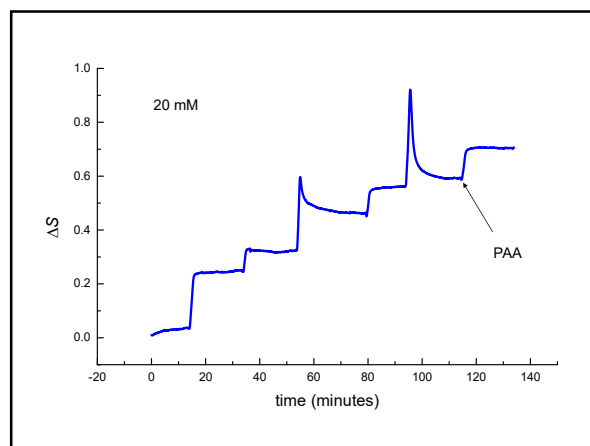
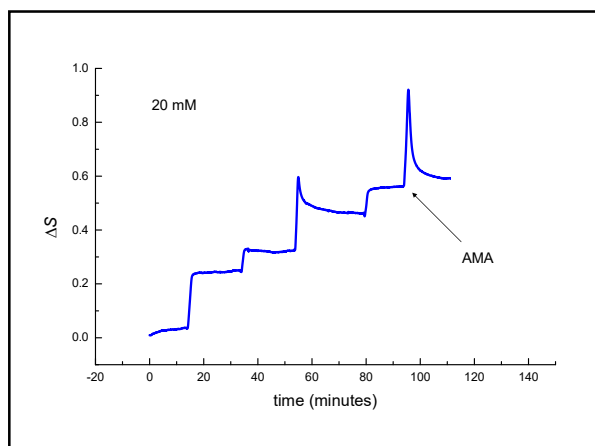
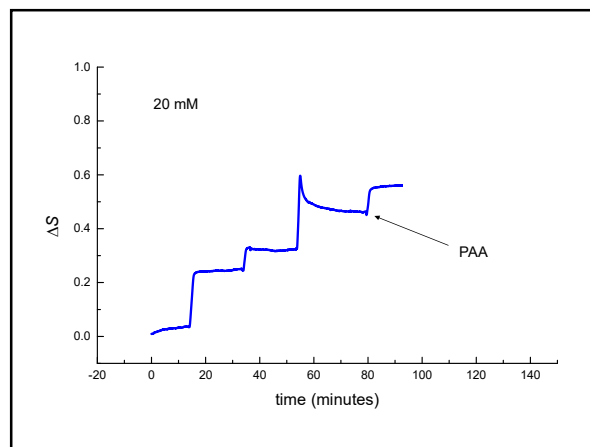
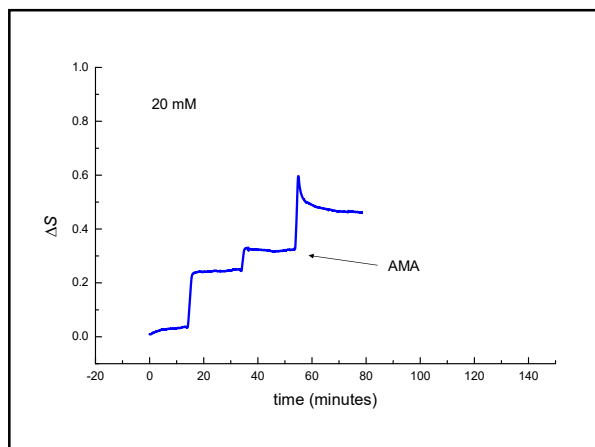
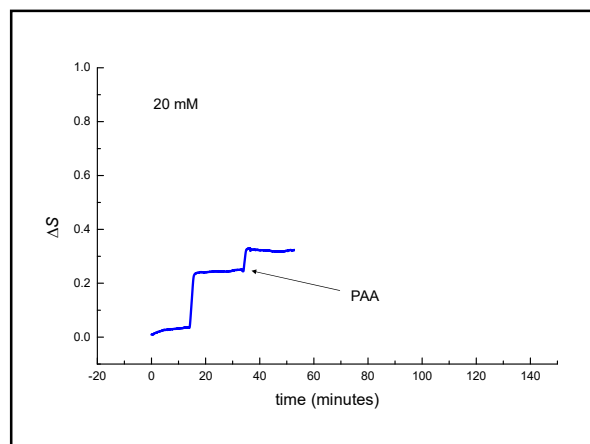
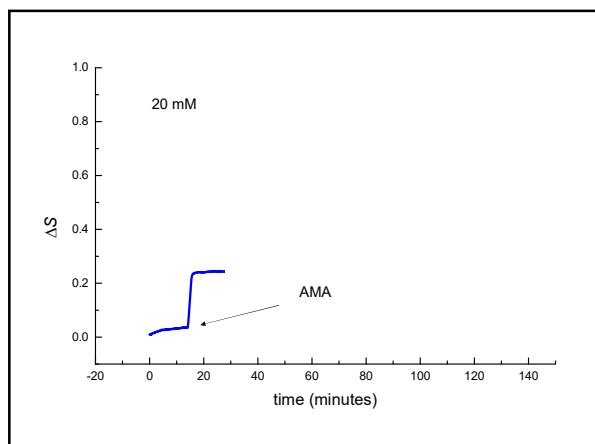


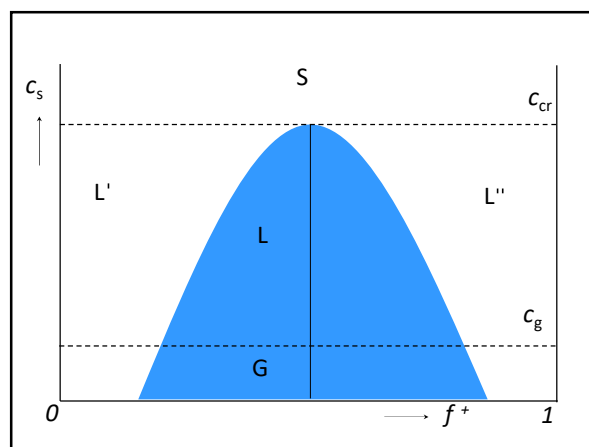
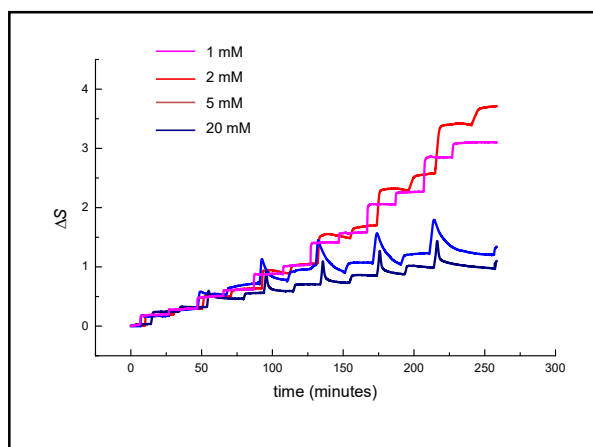
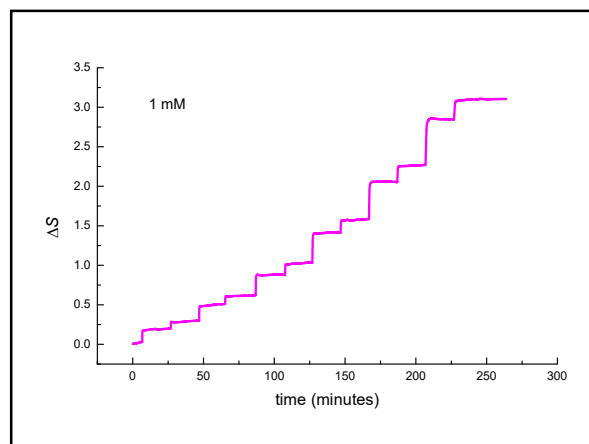
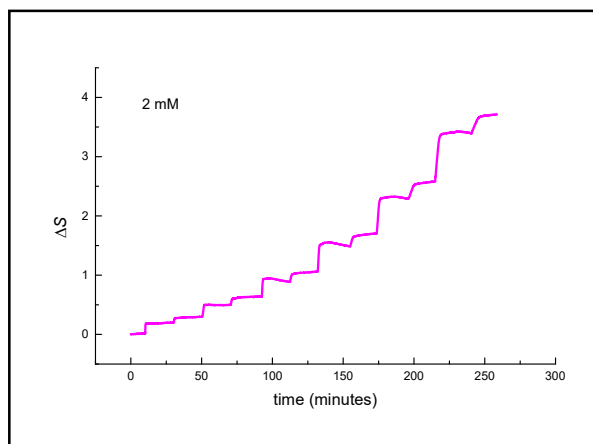
$M_w = 12.5 \text{ kg/mol}$

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

polielektrolitni višeslojevi (Polyelectrolyte Multilayers)

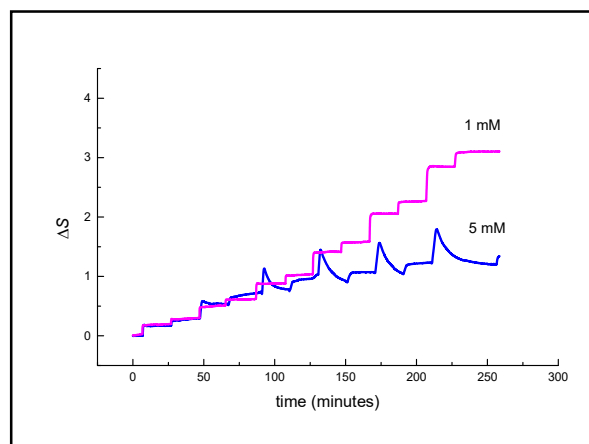






AFM mjerenja

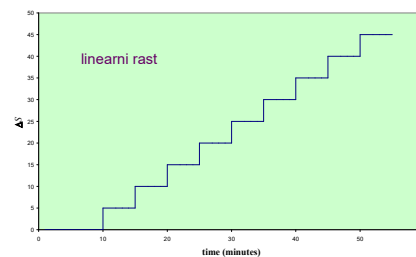
- usporedba između uzoraka pripremljenih pri 1 mM i 5 mM
- contact mode AFM



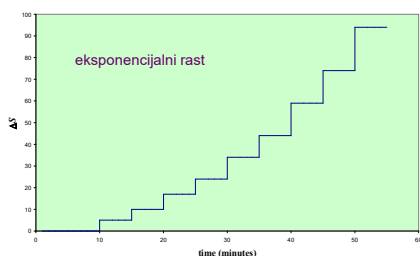
otvorena pitanja

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

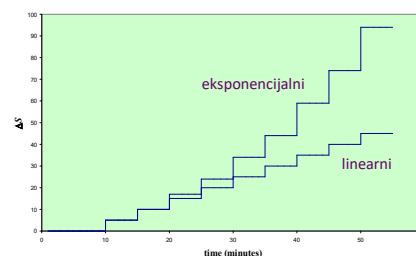
eksponencijalni vs. linearni rast



eksponencijalni vs. linearni rast



eksponencijalni vs. linearni rast

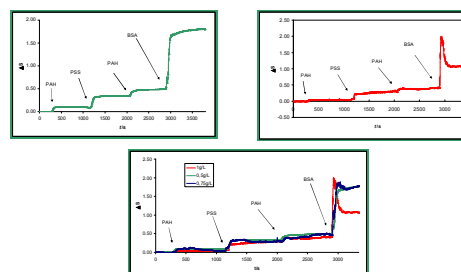


eksponencijalni vs. linearni rast

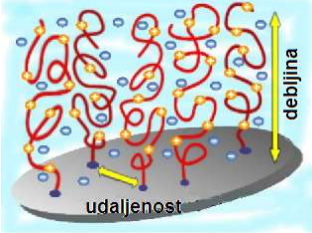
Faktori koji utječu na tip rasta:

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

adsorpcija BSA na prethodno formirani polielektrolitni višesloj



polielektrolitne "četke" (Polyelectrolyte Brushes)



polyelectrolyte multilayers - applications

Biomedicine and pharmaceutical industry

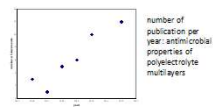
- Surface modification (thickness, charge, etc...)
- Drug delivery
- Formation of stimuli responsive systems (e.g. mechanical, temperature, pH)
- Surfaces with antibacterial properties

nature materials REVIEW ARTICLE
Published online 22 January 2013 | DOI: 10.1038/nmat3428

Emerging applications of stimuli-responsive polymer materials

Marlon A. Cohen Stuart, Willem T. S. Huck, Jan Genzer, Marissa Müller, Christopher Ober, Manfred Stamm, Günther Sukhorokov, Igel Scheller, Vladimir V. Tsukruk, Marek Urban, Franziska Winkler, Stefan Zauscher, Igor Luzinov and Sergey Minko*

Stimuli-responsive polymer materials can react to surrounding environments, rapidly transport of ions and molecules, change morphology and catalysis of chemical reactions as smart materials, as smart chemical and biological systems like sensors, actuators, medical and material devices, and drug delivery. These materials are playing an increasingly important part in a diverse range of applications, such as drug delivery, diagnostics, tissue engineering and smart optical devices, as well as catalysis, microfluidics, molecular recognition, sensing and health care. We review recent advances and challenges in the development of stimuli-responsive polymeric materials. We review several examples of stimuli-responsive materials in the biomedical field, and provide a critical analysis of emerging developments.



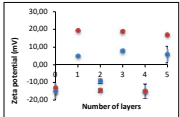
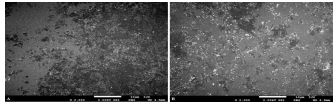
number of publications per year: antimicrobial properties of polyelectrolyte multilayers

Drastically Lowered Protein Adsorption on Microbicidal Hydrophobic/Hydrophilic Polyelectrolyte Multilayers

Sun Yan Wang,¹ Lin Han,¹ Kanna Tirumala,² Jeyna Venkatesh,^{1,2} Md Nasim Uddin,¹ Chuanxin Chen,¹ Alexander M. Kicharev,^{1,2} and Paul T. Hammond^{1,2}

¹Department of Chemical Engineering, ²Institute for Soldier Nanotechnology, ³Department of Materials Science and Engineering, ⁴Department of Chemistry, ⁵Department of Biological Engineering, ⁶Northwestern Institute of Technology, Cambridge, Massachusetts 02139, United States

adhesion of bacteria on polyelectrolyte multilayers

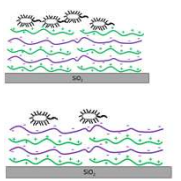
PAH/PSS multilayer

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)


Influence of Polyelectrolyte Multilayer Properties on Bacterial Adhesion Capacity

Devesh Kuvshinov,¹ Erik Probstler,² Kameron Goodell Turkay,³ Jannina Salekovic,¹ Goran Dražić,^{1,4,5} Ande Abraham,^{1,4,5} and Klaus Bohmer^{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

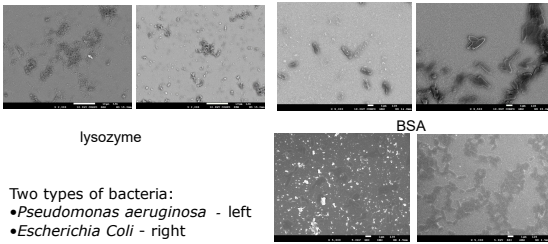


adhesion of bacteria on protein-terminating polyelectrolyte multilayers



	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
Zeta 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

