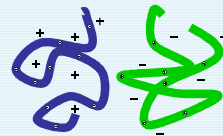


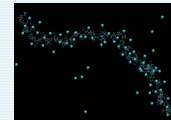
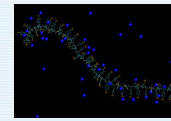
Polielektroliti u otopini i na površini

Prema IUPAC-u:

Polielektroliti - makromolekule kod koje je prisutan znatan udjel konstitucijskih (gradivnih) jedinica koje sadrže ionske i/ili lako ionizirajuće skupine.



suprotno nabijeni polielektroliti u otopini

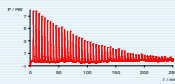


Na⁺PSS⁻

$M_n = 70\ 000\ \text{g mol}^{-1}$

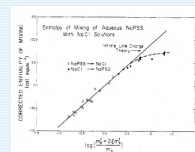


izotermalna titracijska mikrokolorimetrija (ITC)

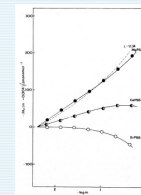


mikrokolorimetrijska titracija vodene otopine Na⁺PSS⁻ vodenom otopinom CsNO₃

izotermalna titracijska mikrokolorimetrija



G. E. Boyd, D. P. Wilson, G. S. Manning, J. Phys. Chem. 80 (1976) 808



G. Vesnaver, Z. Kranjc, C. Pohar, J. Škerjanc, J. Phys. Chem. 91 (1987) 3845

Polyelectrolyte complex characterization with isothermal titration calorimetry and colloid titration
Krzysztof Trzasko, Marcin Łasko, Robert Polowinski

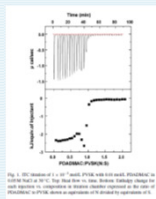


Fig. 1. ITC titration curves of 10⁻⁴ mol/L PSS with 10⁻⁴ mol/L PAA in the presence of NaCl at 25 °C. The heat flow is shown as a function of the volume of the titrant. The inset shows the titration curves for the complexation of PSS with PAA in the presence of NaCl at 25 °C.

Mixtures of cationic starch and anionic polyacrylate used for flocculation of calcium carbonate— influence of electrolytes
Regina Szymanska, Grazyna Radziszewska, Janina Chlebicka, Andrzej Brzezinski

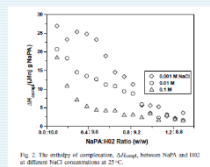
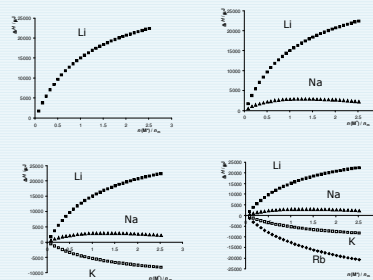
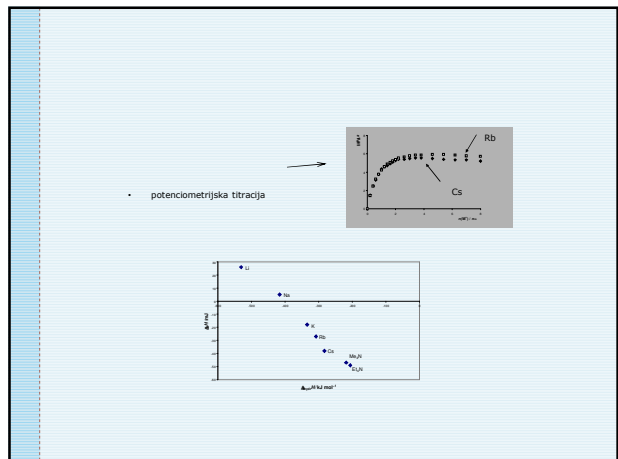
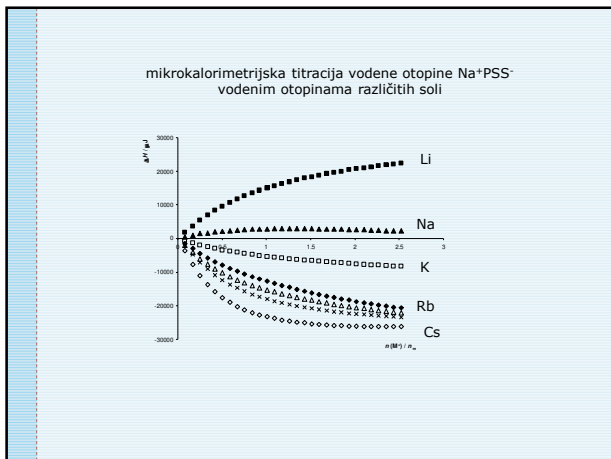


Fig. 2. The enthalpy of complexation, $\Delta H_{\text{complex}}$, between PSS and HCl at different NaCl concentrations at 25 °C.

mikrokolorimetrijska titracija vodene otopine Na⁺PSS⁻ vodenim otopinama različitih soli



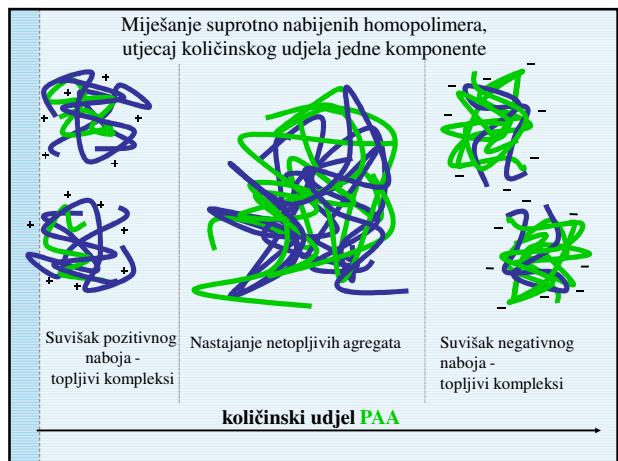
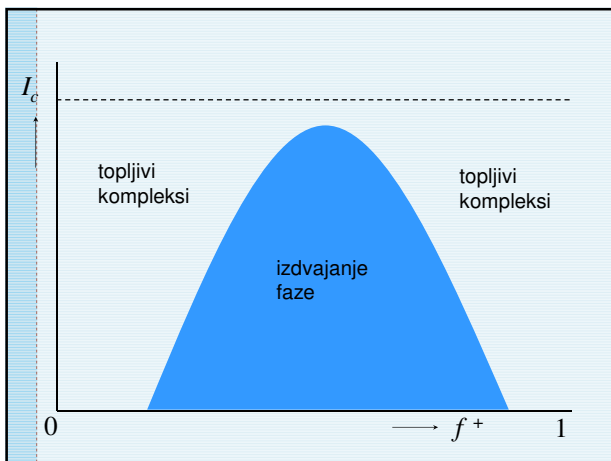
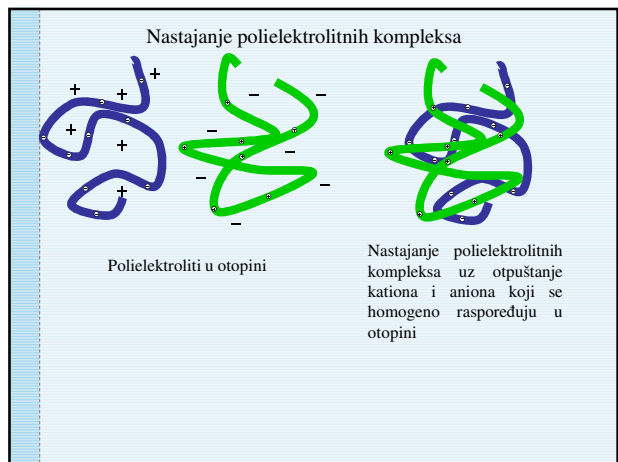


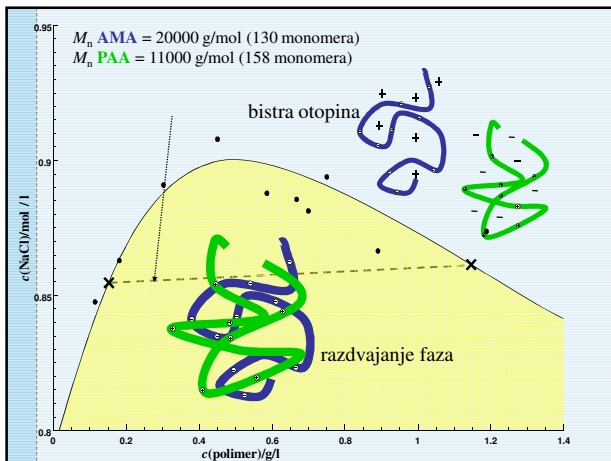
kompleksiranje polielektrolita (polikationa i polianiona) u otopini

- elektrostatske interakcije
- polielektrolitni kompleksi (*polyelectrolyte complexes*)

topljivi kompleksi
izdvajanje faze (*phase separation*)

istraživali Voorn, Bungeberg de Jong i Michaels
u *Colloid Science*, H. R. Kruyt, Ed. (Elsevier Publishing Company, Amsterdam, 1949) vol. II, pp. 335-384





Fizikalne kemije kompleksnih micela (Complex Micelles)

- miješanje blok-kopolimera različitih naboja – polyion complex micelles

A. Harada and K. Kataoka, *Science*, 283 (1999) 65.
 A. Harada and K. Kataoka, *Macromolecules*, 28 (1995) 5294.

pH, ionska jakost, omjer mješanja, duljina blokova, itd.....

P-AMA-(GMA)

Poli(di-metil-Amino-etil-MetAkrilat)-(ko-poli(Gliceril-MetAkrilat))

Različiti omjeri duljine blokova ($M_{w, total} = konst.$)

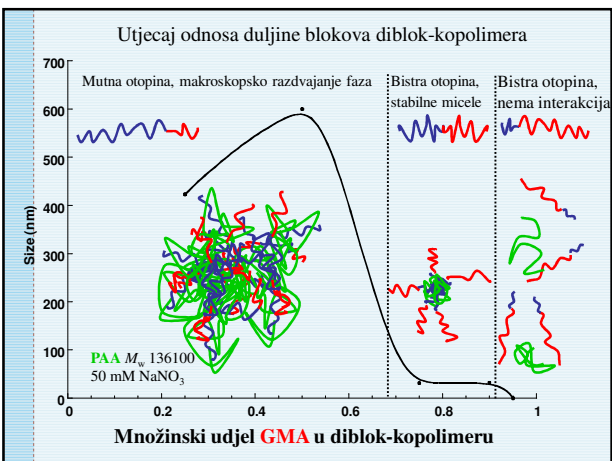
PAA
 PoliAcrylic Acid

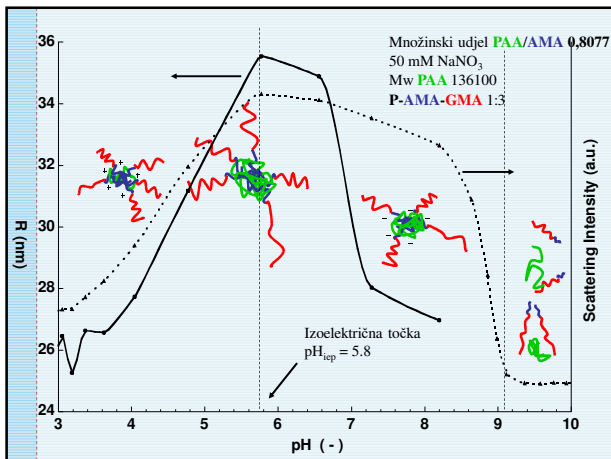
PMA
 Poly Methacrylic Acid

Različite molekulske mase

Smjesa homopolielektrolita i suprotno nabijenog diblok-kopolimera, utjecaj omjera mješanja

Množinski udjel PAA





Janusove micelle

- miješanje blok-kopolimera različitih naboja – polyion complex micelles
- amfifilni diblok (triblok) kopolimeri – Janusove micelle

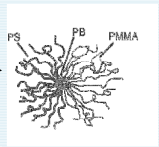
Janus



- rimski bog ulaza i vrata, početka i kraja

Janusove micelle

hidrofobna PS
polukruna
(hemicorona)



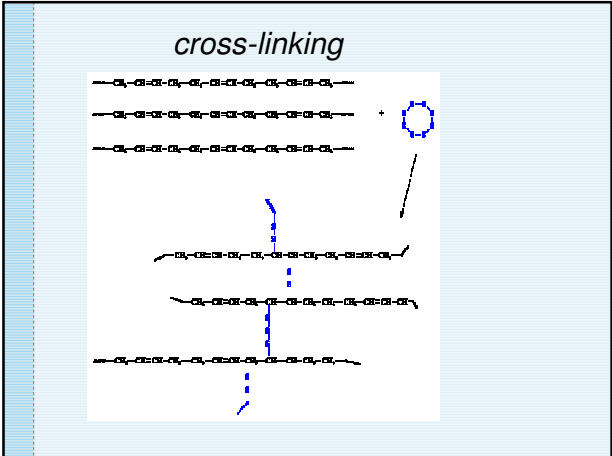
hidrofilna
PMMA
polukruna
(hemicorona)

R. Erhardt et al, *Macromolecules*, 34 (2001) 1069.
R. Erhardt et al, *J. Am. Chem. Soc.*, 125 (2003) 3260.

Janusove micelle

prekursor:
polistiren-blok-polibutadien-blok-poli(metil metakrilat)
(SBM) triblok kopolimer sintetiziran sekvencijalnom anionskom polimerizacijom

cross-linking metoda - reaktant S₂Cl₂



Janusove micle

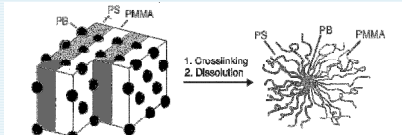


Figure 1. Schematic representation of the Janus micelles' synthesis (left hand side: sketch of SIBM is-morphology).

Janusove micle

karakterizacija:

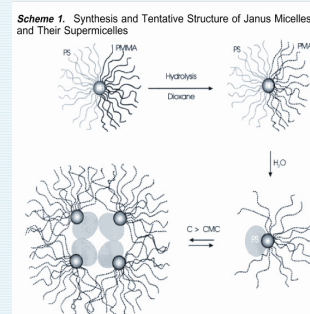
- *Transmission Electron Microscopy (TEM)*
- *Multi-Angle Laser Light Scattering Gel Permeation Chromatography (MALLS-GPC)*
- *Confocal Fluorescence Correlation Spectroscopy (FCS)*

- na svaku PB jezgu vezano 13 ± 5 lanaca
- radijus procijenjen na $11,4 \pm 0,8$ nm

Janusove micle

- u otopini tvore superstrukture orijentirane prema površini
- priprava raznih supramolekularnih objekata
- iznad kritične agregacijske koncentracije ($0,03$ g/L) nastaju u vodenoj otopini (uz NaCl) sferne superstrukture ("supermicle") od oko 30 PS-PMMA micela radijusa $40-60$ nm.

nastajanje "supermicela"



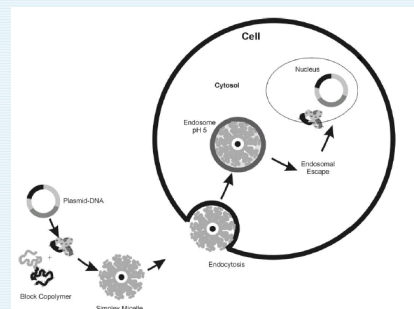
primjena

- nosači lijekova (*drug carriers*)
- ugradnja hidrofobnih anti-tumorskih lijekova u jezgru i njihova "dostava" do tumora

Block copolymer micelles for gene therapy

Transfection of plasmid DNA using diblock copolymer. DNA is released inside the cytosol and appears in the nucleus to express a desired protein.

Forster and M. Konrad, J. Mater. Chem., 2003

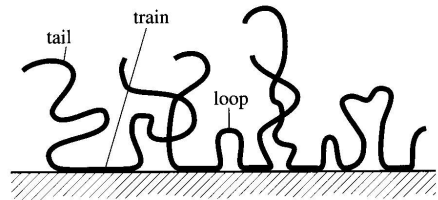


“Janus beads”

- parcijalna hidrofobna modifikacija staklenih sfernih čestica

C. Casagrande and M. Veyssié, *C. R. Acad. Sci (Paris) II* 306 (1988) 1423.

polimeri na površini; adsorpcija polimera



višesloj (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

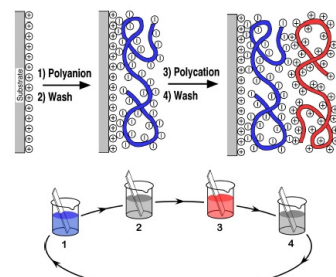
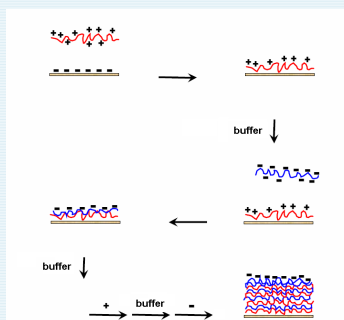


Fig. 1: Formation of PE multilayers

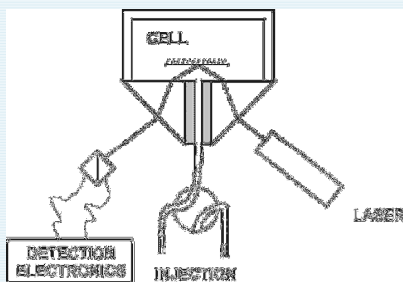
otvorena pitanja

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

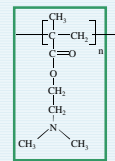
eksperimentalne metode:

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

optička reflektometrija

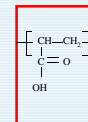


P-AMA Poly(di-methyl-Amino-ethyl-MethAcrylate)



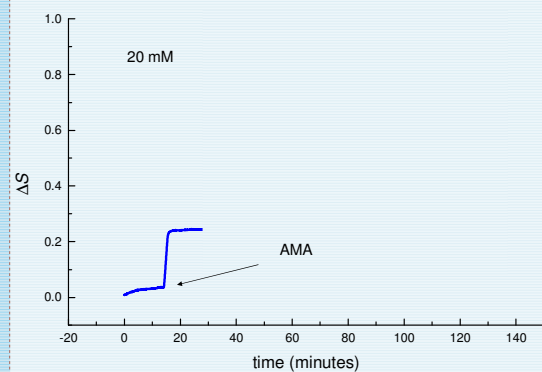
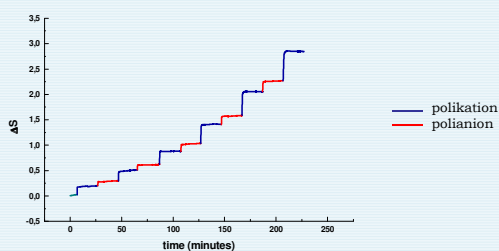
$M_w = 20 \text{ kg/mol}$
 $M_s = 157 \text{ g/mol}$

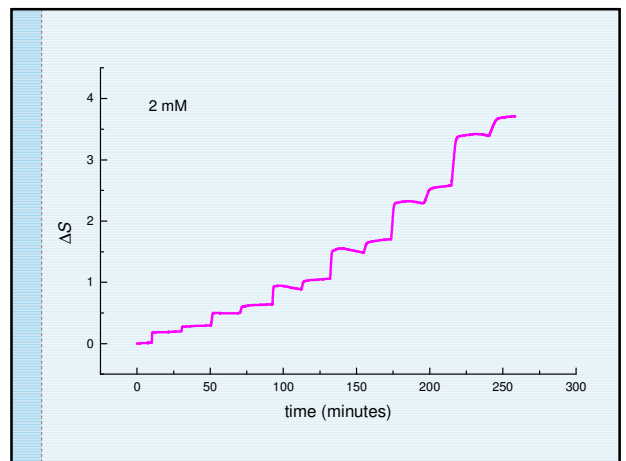
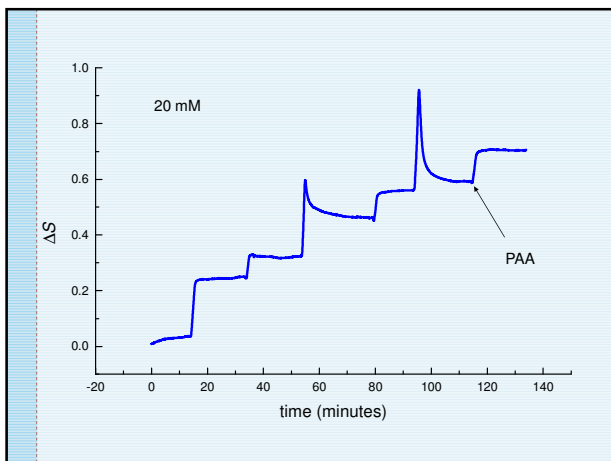
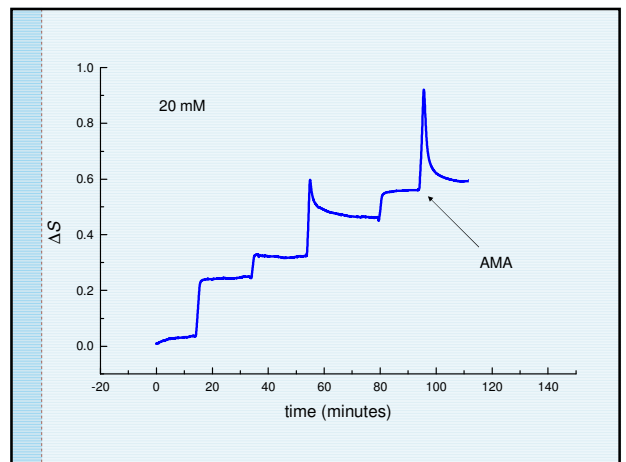
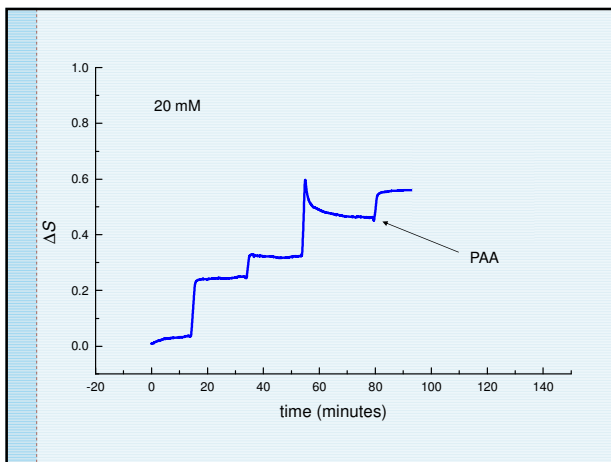
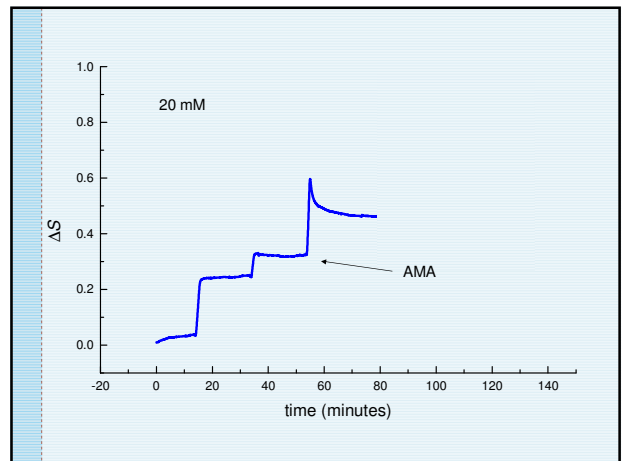
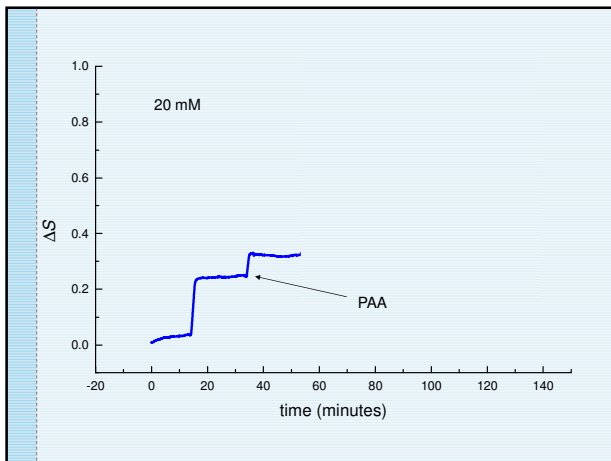
PAA Poly Acrylic Acid

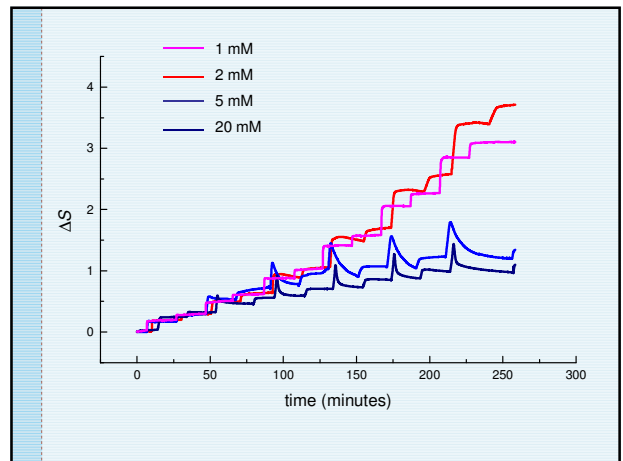
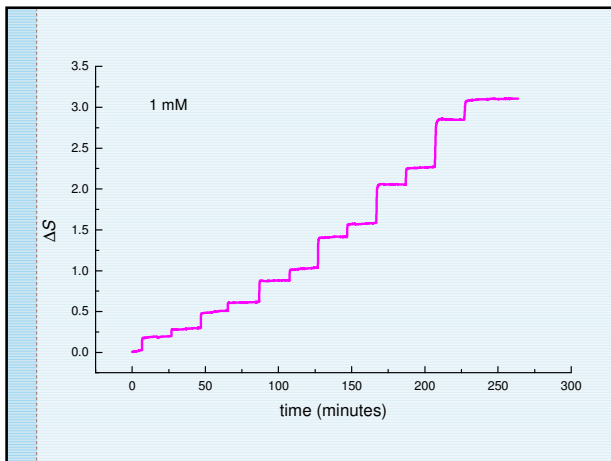


$M_w = 12.5 \text{ kg/mol}$
 $M_s = 72 \text{ g/mol}$

polielektrolitni višeslojevi (Polyelectrolyte Multilayers)

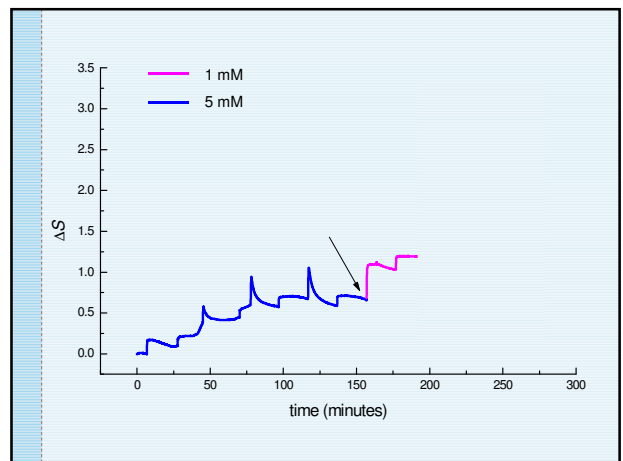
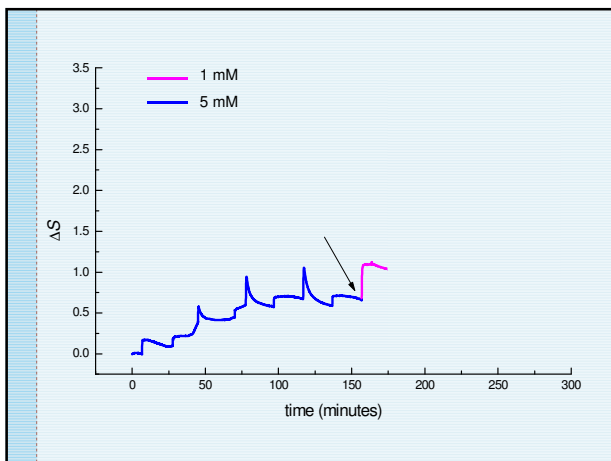
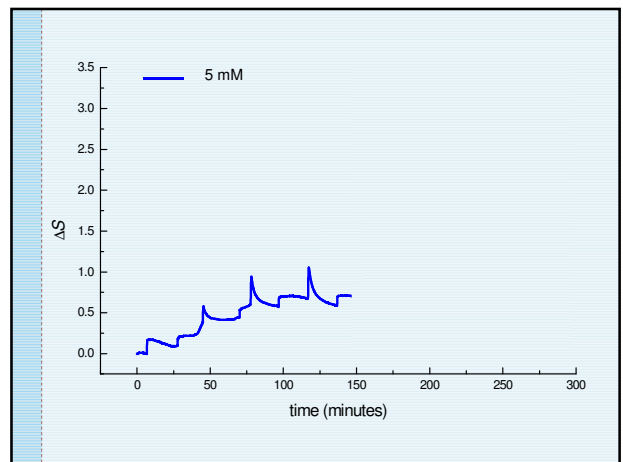


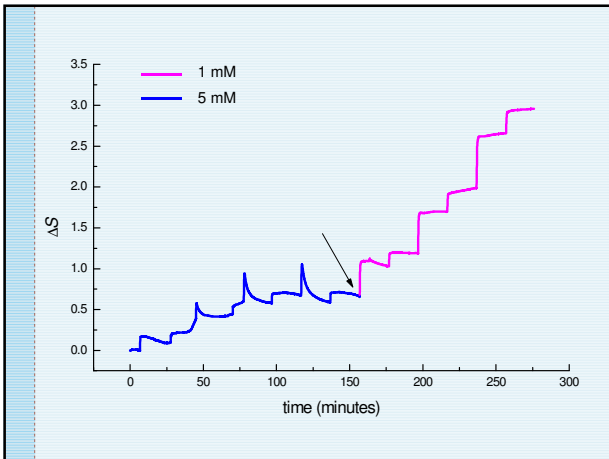




utjecaj ionske jakosti

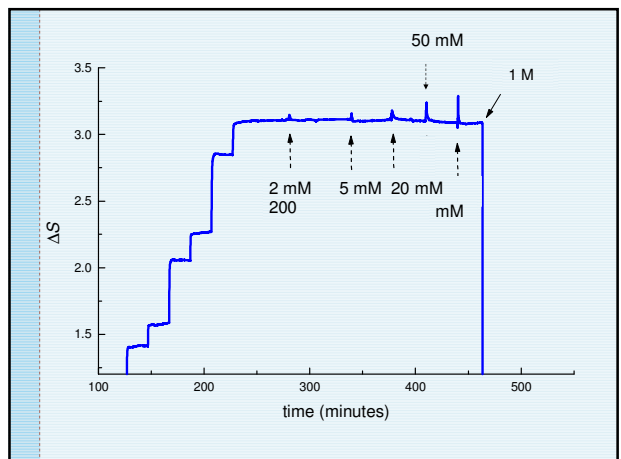
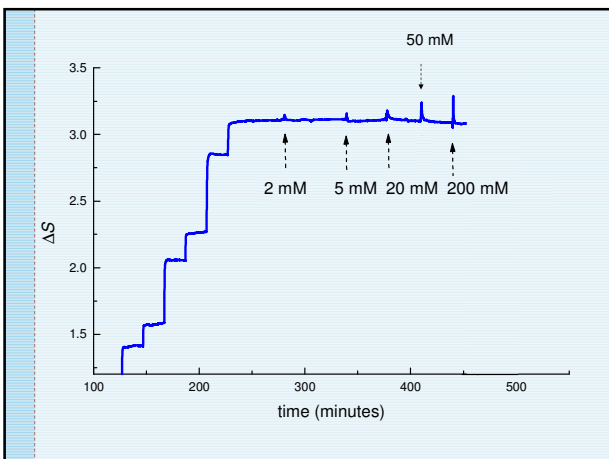
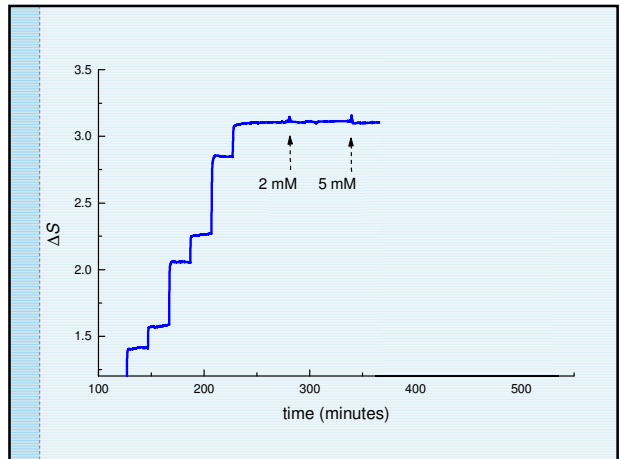
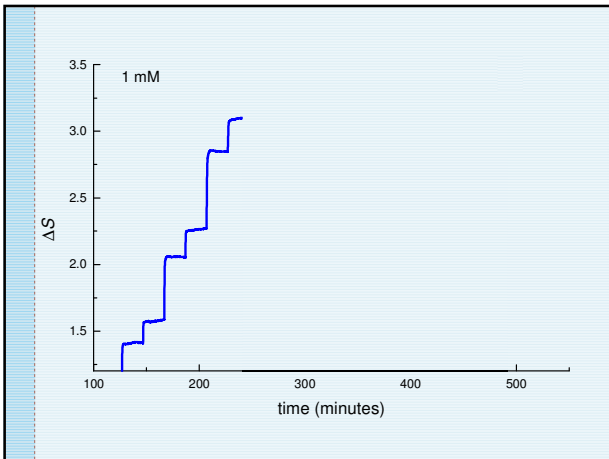
- dva slučaja
- a) niska ionska jakost (e.g. 1 mM, 2 mM) – nastaju višeslojevi
- b) visoka ionska jakost (e.g. 5 mM, 20 mM) – ne nastaju višeslojevi
- što se događa ako se ionska jakost varira tijekom eksperimenta?

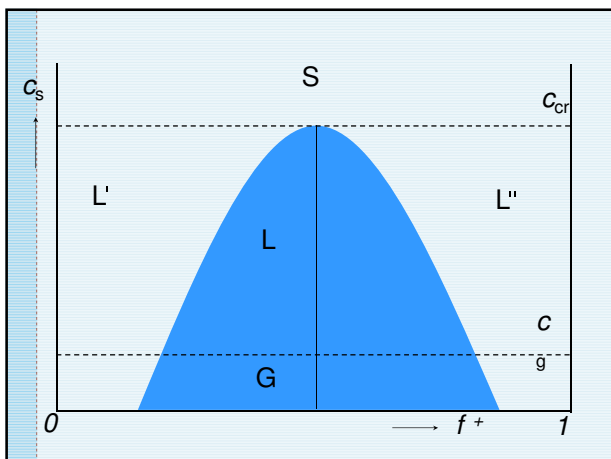




utjecaj ionske jakosti

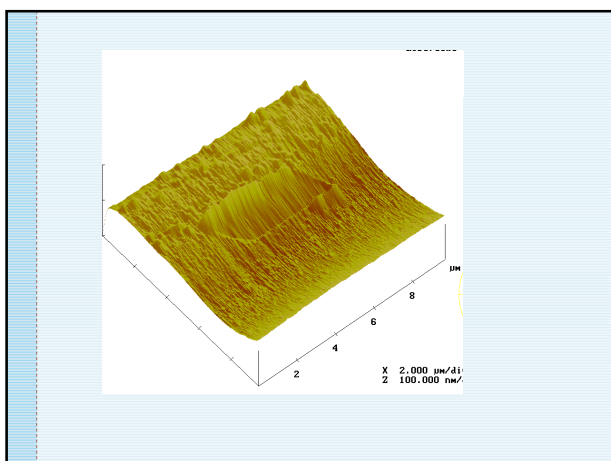
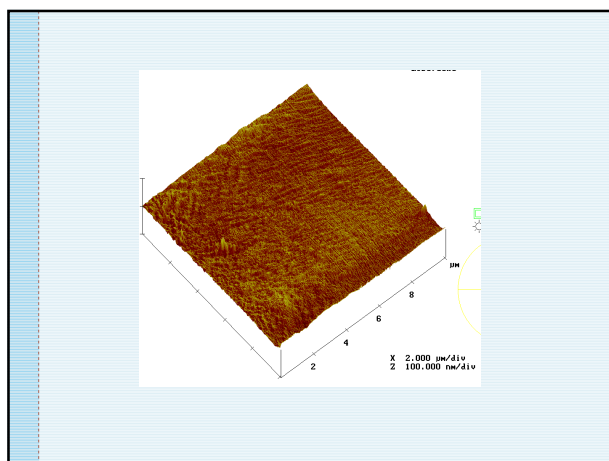
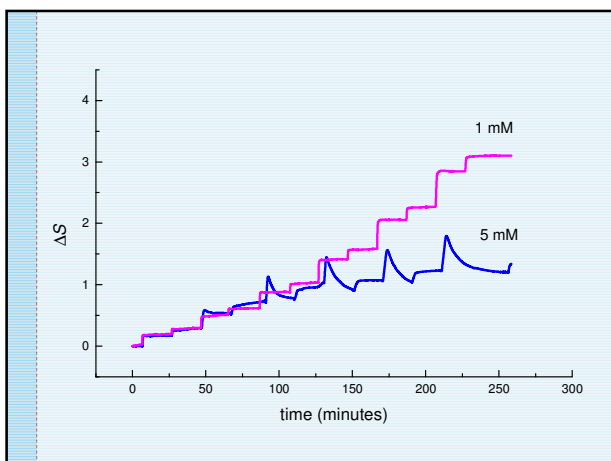
- je li elektrolit odgovoran za destrukciju višeslojeva?





AFM mjerenja

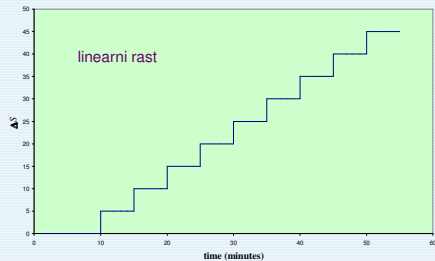
- usporedba između uzoraka pripremljenih pri mM i 5 mM
- contact mode AFM



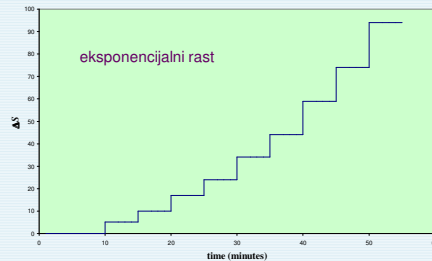
otvorena pitanja

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

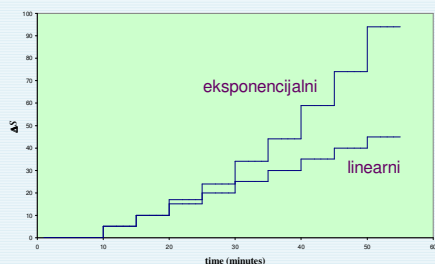
eksponecijalni vs. linearni rast



eksponecijalni vs. linearni rast



eksponecijalni vs. linearni rast

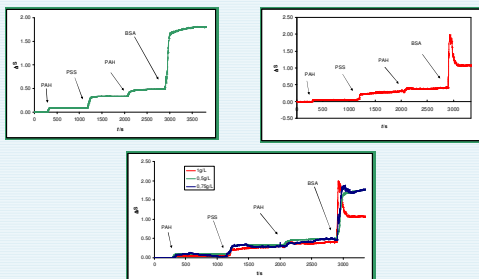


eksponecijalni vs. linearni rast

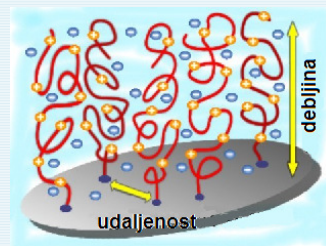
Faktori koji utječu na tip rasta:

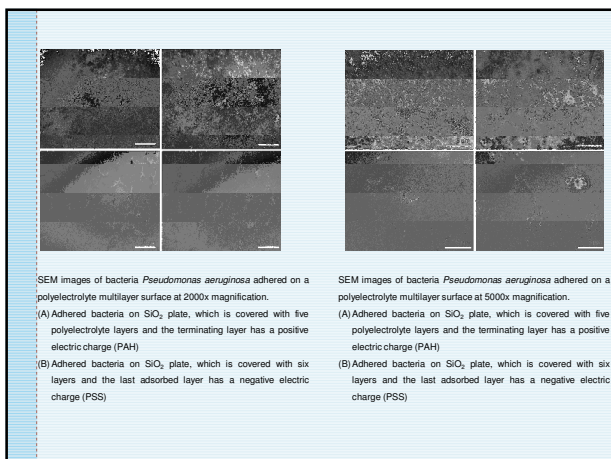
- kemijska priroda polielektrolitnog para
- vrsta dodanog elektrolita
- ionska jakost
- temperatura
- metoda pripreve

adsorpcija BSA na prethodno formirani polielektrolitni višesloj



polielektrolitne "četke" (Polyelectrolyte Brushes)





PARTICLE COATING

PEMs can even be formed on colloidal particles as templates instead of planar substrates. In this case, the excess polyelectrolyte has to be removed by centrifugation or ultrafiltration.

The development of PEM-coating procedures for particles is a major achievement, since it allows to prepare dispersions with a large surface area. In such samples, PEMs can be studied by volume techniques which require a sufficient amount of compound, such as for example NMR or DSC.

After coating of colloidal particles the template itself can be removed employing suitable chemical procedures (for example a dissolution or degradation in acidic conditions). Provided that the PEM shell is stable against that treatment, a hollow polymeric capsule is remaining. Such hollow containers are interesting objects for applications such as encapsulation and the controlled release of active compounds.

primjena

- modifikacija površine
- inkapsulacija (encapsulation)
- šuplje sfere (hollow spheres)
- drug delivery

