fizikalna kemija makromolekula

makromolekule

sintetski polimeri

biološki (prirodni) polimeri

fizikalna kemija proteina

Edwin J. Cohn

Simoni R D et al. J. Biol. Chem. 2002;277

Topljivost i kiselo-bazna svojstva proteina

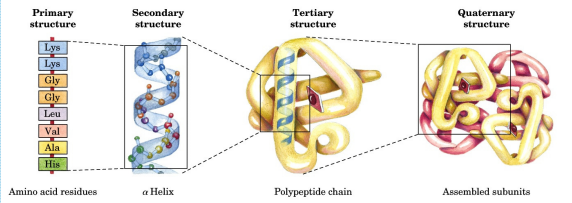
Cohn, E. J., Hendry, J. L., and Prentiss, A. M., "Studies in the Physical Chemistry of the Proteins. V. Molecular Weights of the Proteins", *J. Biol. Chem.* 63 (1925) 721-766.

Cohn, E. J., "The Properties and Functions of Plasma Proteins with consideration of the Methods for their Separation and Purification", *Chem. Rev.* 28 (1941) 395.

Klasični način opisa proteina:

- Primarna struktura - redoslijed (sekvencija) aminokiselina
- Sekundarna struktura – konformacija peptidnih lanaca
- Tercijarna struktura
- Kvaterna struktura

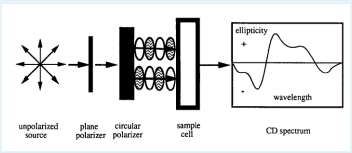
Razine strukture proteina



Spektroskopsko istraživanje sekundarne strukture proteina

- Cirkularni dikroizam (Circular dichroism, CD)
- Infracrvena (IR) i Raman spektroskopija
- Nuklearna magnetska rezonancija (NMR)

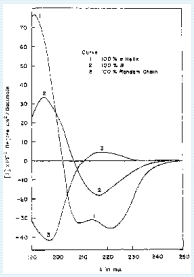
Fizikalni principi CD-a



- Kiralne ili asimetrične molekule daju CD spektar zato jer različito apsorbiraju lijevo i desno polariziranu svjetlost i zato se smatraju "optički aktivnim"

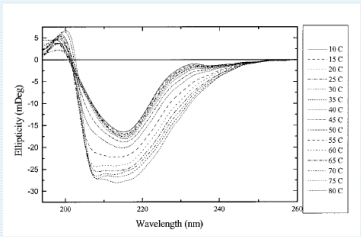
Sekundarna struktura proteina iz CD spektara

- Različita vrsta proteina daje različite CD spektre



Sekundarna struktura proteina iz CD spektara

- CD spektri su posebno korisni za određivanje temperaturne ovisnosti sekundarne strukture proteina.



Sekundarna struktura proteina iz CD spektara

ostale informacije:

- (1) interakcije protein - ligand;
- (2) termodinamika smatanja (*folding*) proteina;
- (3) promjene konformacije i agregacija proteina;
- (4) međuprodukti smatanja;
- (5) kinetika smatanja proteina.

N. J. Greenfeld, Applications of circular dichroism in protein and peptide analysis, *Trends in analytical chemistry*, vol. 18, no. 4, 1999

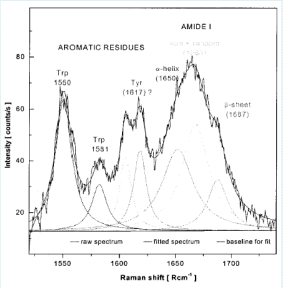
Sekundarna struktura proteina iz IR i Ramanskih spektara (vibracije!)

- amidne vrpce se najčešće koriste za istraživanje strukture proteina

Principal Amide I Frequencies Characteristic of Protein Secondary Structures

Conformation	H_2O	D_2O
α-helix	1650–1657	1647–1654
Antiparallel β-sheet	1612–1640; 1670–1690 (weak)	1628–1635
Parallel β-sheet	1626–1640	
Turn	1655–1675 1680–1696	
Unordered	1640–1651	1643

Sekundarna struktura proteina iz IR i Ramanskih spektara (vibracije!)



- Ramanski spektri daju informacije o aromatskim ostacima u području oko 1620 cm^{-1}

Sekundarna struktura proteina pomoću NMR spektroskopije

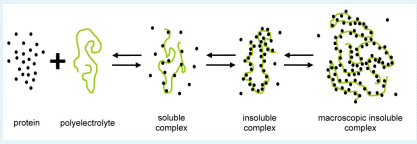
- Određivanje sekundarne strukture pomoću NMR spektroskopije ne zahtijeva potpunu trodimenzijsku strukturnu analizu kao što zahtijeva rendgenska kristalografija.
- Poznavanje kemijskih pomaka amida i protona su u principu sve što je potrebno.
- Spektroskopija NMR je najsnažnija i najtočnije metoda određivanja sekundarne strukture proteina bez trodimenzijske strukture.

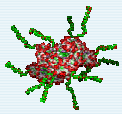
Interakcija proteina sa...

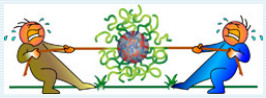
- ... polielektrolitima
- ... polisaharidima
- ... DNA
- ... itd

- Primjena!!

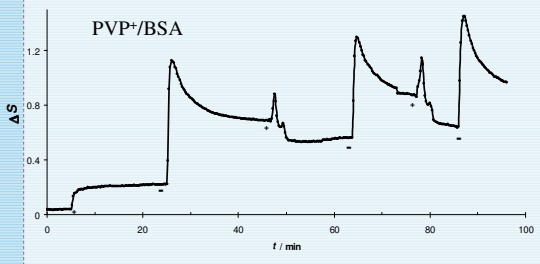
Kompleksi protein-polielektrolit



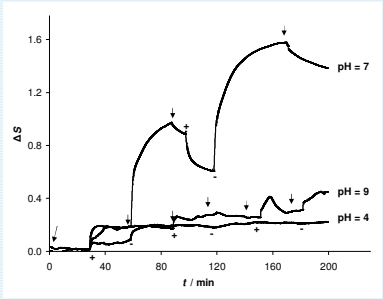




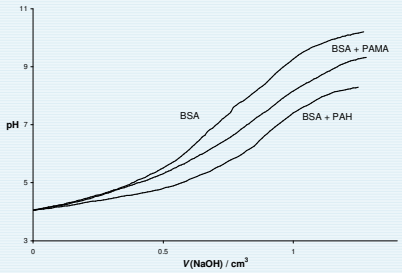
Karakterizacija polielektrolitno-proteinskih višeslojeva pomoću optičke reflektometrije



PAMA/BSA

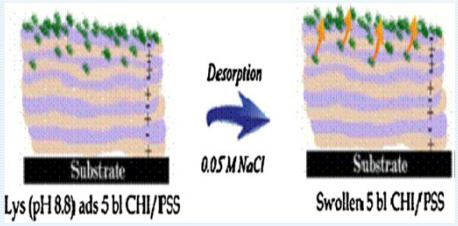


potenciometrijska titracija

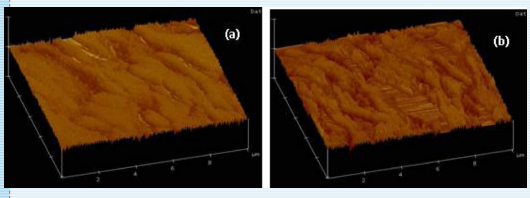


J. Mathew et al., *Fabrication of switchable protein resistant and adhesive multilayer membranes*, Colloids and Surfaces B: Biointerfaces 94 (2012) 118– 124

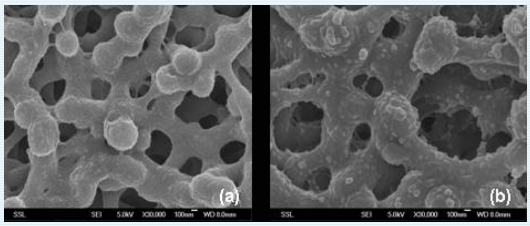
- Fabrication of protein adhesive and resistant surfaces based on chitosan/polystyrene sulfonate (CHI/PSS) multilayer membranes is presented. Adsorption behavior of bovine serum albumin (BSA) and lysozyme to CHI/PSS multilayer was studied.



Shematski prikaz adsorpcije lizozima
(a) pri pH = 8,8 (b) desorpcija, reverzna migracija na površinu.

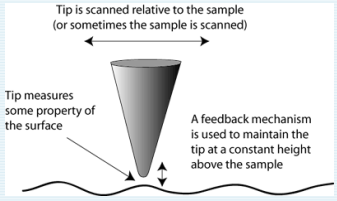


AFM iprikazi adsorpcije lizozima na CHI/PSS višesloj (10 slojeva)
(a) pH = 8,8 (b) pH = 10,6



SEM prikazi adsorpcije BSA (pH 4.8)
(a) 6 CHI/PSS slojeva (b) 14 CHI/PSS slojeva.

"Scanning Probe Microscopy" techniques



Atomic Force Microscopy (AFM)

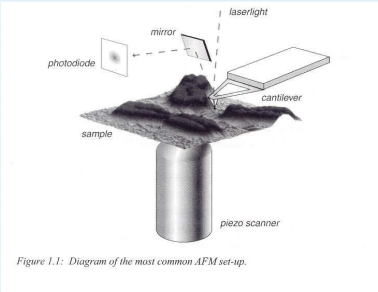
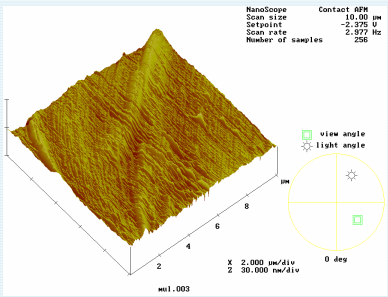


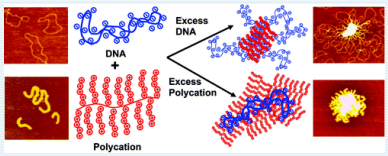
Figure 1.1: Diagram of the most common AFM set-up.

Contact mode
Tapping mode

Atomic Force Microscopy (AFM)



Polyelectrolyte – DNA complexes

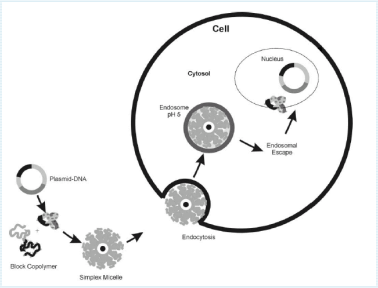


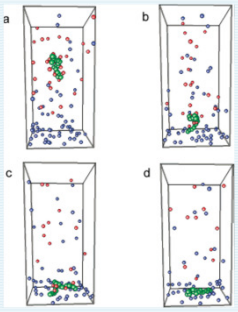
D. Störkle, S. Duschner, N. Heimann, M. Maskos, and M. Schmidt, Complex Formation of DNA with Oppositely Charged Polyelectrolytes of Different Chain Topology: Cylindrical Brushes and Dendrimers, *Macromolecules*, 2007, 40 (22), pp 7998–8006.

Block copolymer micelles for gene therapy

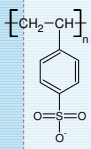
Transfection of plasmid DNA using diblock copolymer. DNA is released inside the cytosol and appears in the nucleus to express a desired protein.

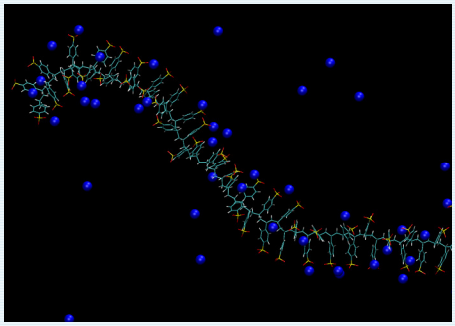
Forster and M. Konrad, J. Mater. Chem., 2003



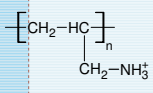


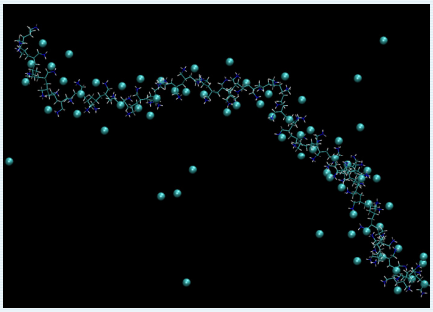
Sample configurations of a simulation of the adsorption of a 20 monomer PE chain on a charged surface, yielding a surface monomer density of 2 monomers/nm^2. The bulk electrolyte concentration was 0.010 M. Green: polyelectrolyte monomers. Red: negative ions. Blue: positive ions.





Molecular dynamics simulation of the structure of sodium poly(styrenesulfonate) (t = 5 ns)





Molecular dynamics simulation of the structure of poly(allylammonium perchlorate) (t = 5 ns)

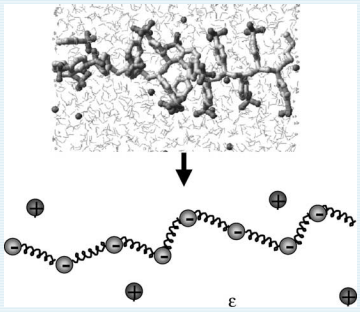


Illustration of the mapping procedure of sodium polystyrene sulfonate (NaPSS) in water. The repeat units of NaPSS are replaced by spherical monomers connected by springs and the solvent molecules are represented by a continuum with dielectric constant e. Counterions are represented by spherical beads.

konfiguracije lanca