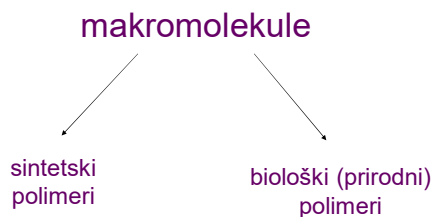
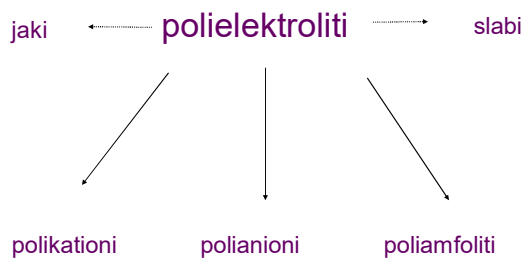
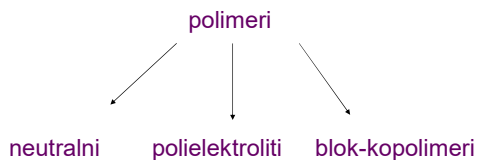


fizikalna kemija makromolekula



makromolekule



Sinteza polimera/ Polimerizacija

.Istraživanje polimera započinje s razumijevanjem metoda pomoću kojih je polimere moguće sintetizirati.

.Sinteza polimera je složen proces i može se povesti na mnoštvo različitih načina.

IUPAC definicija

polymerization: The process of converting a monomer or a mixture of monomers into a polymer.

Sinteza polimera

- 1) temeljna kemija vezanja monomernih jedinica
- 2) utjecaj mehanizma i kinetike reakcije polimerizacije na molarnu masu i raspodjelu molarne mase
- 3) utjecaj mehanizma reakcije polimerizacije na mikrostrukturu lanca

Sinteza polimera

Carothers

Tradicijska podjela polimerizacijskih reakcija:

- a) kondenzacijska
- b) adicijska

Flory

Nova podjela polimerizacijskih reakcija:

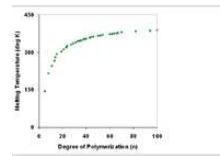
- a) stupnjevita polimerizacija (polikondenzacija)
- b) lančana polimerizacija (adicijska)

lančana polimerizacija (adicijska)

- ① Inicijacija
- ② Propagacija
- ③ Terminacija

Stupanj polimerizacije

- Za homopolimer: $DP = \frac{\text{ukupna } M_w \text{ polimera}}{M_w \text{ monomera (podjedinice)}}$



Odnos između stupnja polimerizacije i tališta za polietilen.

Molarna masa

prosjeck molarnih masa

- brojčani prosjeck molarnih masa, M_n
- maseni prosjeck molarnih masa, M_w
- viskoznozni prosjeck molarnih masa, M_v

$$\text{Indeks polidisperznosti} \quad \frac{\bar{M}_w}{\bar{M}_n}$$
$$\text{Indeks uniformnosti}$$

Metode određivanja molarne mase

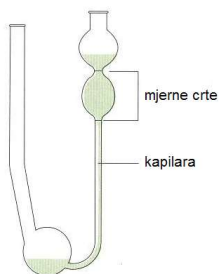
tradicionalne:

- osmotski tlak
- sedimentacija
- viskoznost

također:

- varijanta HPLC-a size exclusion chromatography (SEC) and gel permeation chromatography (GPC)
- static light scattering

viskoznost

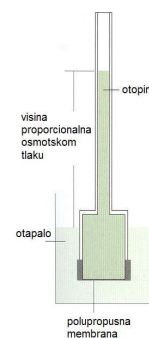


Ostwaldov viskozimetar

$$[\eta] = KM^{\alpha}$$

Mark-Houwink

osmotski tlak

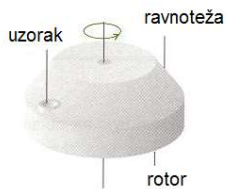


$$\Pi = c_B RT$$

$$\Pi = \frac{n_B RT}{V}$$

$$\frac{\Pi}{\gamma} = \frac{RT}{M}$$

sedimentacija



ultracentrifuga

metode određivanja veličine makromolekula

- raspršenje svjetlosti
- raspršenje röntgenskih zraka
- raspršenje neutrona
- mikroskopija

Raspršenje svjetlosti (Light scattering)

- Dinamičko raspršenje svjetlosti
(**D**ynamic **L**ight **S**cattering, **DLS**)
- Statičko raspršenje svjetlosti
(**S**tatic **L**ight **S**cattering, **SLS**)

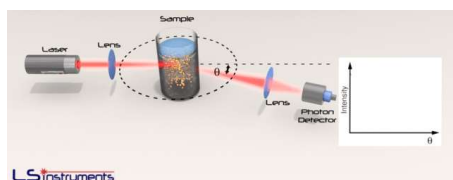
SLS

Static Light Scattering (SLS) –
mjerjenje vremenski uprosječenog intenziteta raspršenog zračenja pri različitim kutevima

Primjene:

- procjena radijusa makromolekula, tzv. radijus vrtnje (giracije) R_g
- određivanje masenog prosjeka molarne mase M_w makromolekula
- mjerenjem pri različitim koncentracijama moguće je odrediti drugi virijalni koeficijent A_2

SLS



SLS

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} \quad \frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_2c + \dots$$

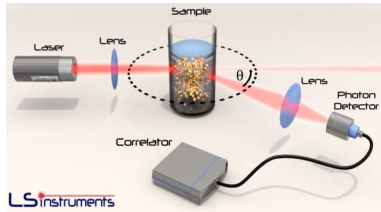
Rayleigh

$$K = \frac{2\pi^2}{\lambda_0^4 N_A} \left(n_0 \frac{dn}{dc} \right)^2$$

optička konstanta

DLS

- Dynamic light scattering (DLS)
- mjerenje vremenski ovisne fluktuacije intenziteta raspršenog zračenja
- određivanje hidrodinamičkog radijusa



DLS

$$D = \frac{k_B T}{6\pi\eta r_H}$$

Stokes-Einstein
jednadžba

Small Angle X-ray Scattering (SAXS)



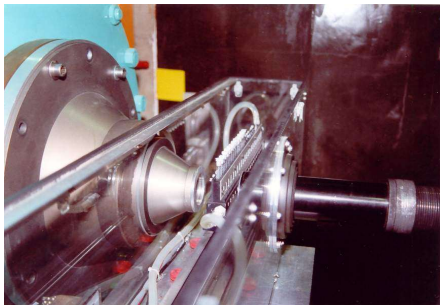
European Synchrotron
Radiation Facility (ESRF),
Grenoble, Francuska

Small Angles Neutron Scattering (SANS)



Institute ILL,
Grenoble,
France

Small Angles Neutron Scattering (SANS)



Miješanje tekućina koje tvore
idealnu smjesu

$$\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta S_{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta H_{\text{mix}} = 0$$

Makromolekularna termodinamika

- Flory – teorija rešetke (lattice theory)

$$\Delta_{\text{mix}} S = -k(n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

$$\Delta_{\text{mix}} H = kT \chi_1 n_1 \phi_2$$



Paul John Flory
(1910 – 1985)

- Hildebrand

$$\Delta_{\text{mix}} H = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

kompleksiranje polielektrolita (polikationa i polianiona) u otopini

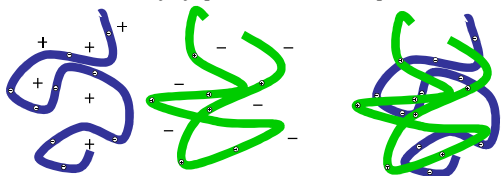
- elektrostatske interakcije
- polielektrolitni kompleksi (*polyelectrolyte complexes*)

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

Nastajanje polielektrolitnih kompleksa



Polielektroliti u otopini

Nastajanje polielektrolitnih kompleksa uz otpuštanje kationa i aniona koji se homogeno raspoređuju u otopini

Miješanje suprotno nabijenih homopolimera, utjecaj količinskog udjela jedne komponente

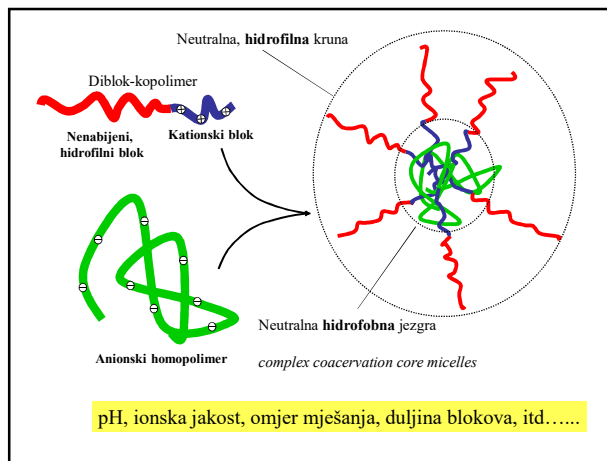
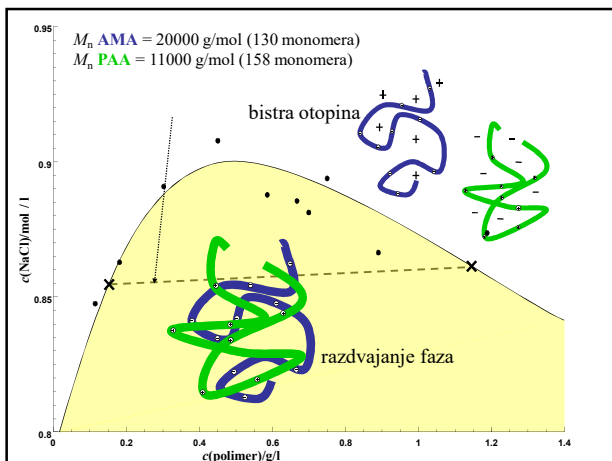


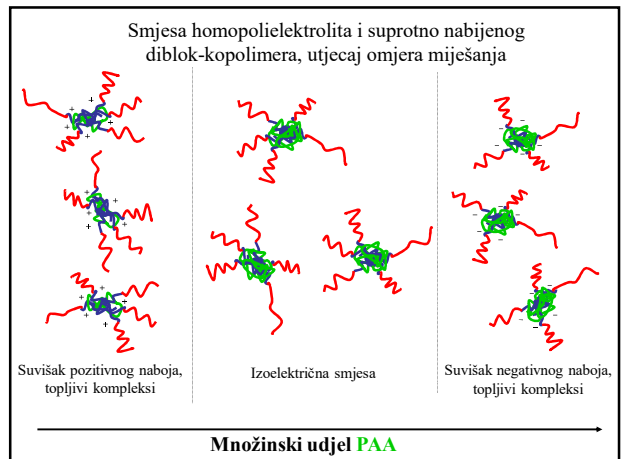
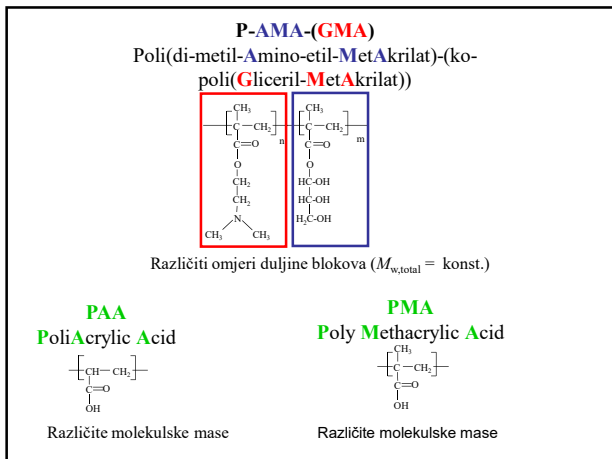
Suvišak pozitivnog naboja - topljivi kompleksi

Nastajanje netopljivih agregata

Suvišak negativnog naboja - topljivi kompleksi

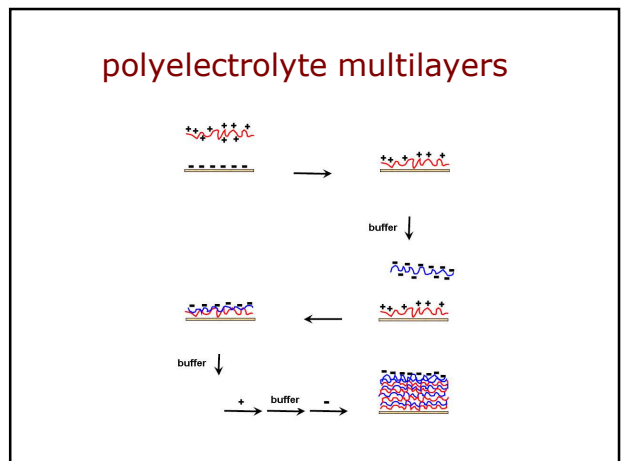
količinski udjel PAA





- 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



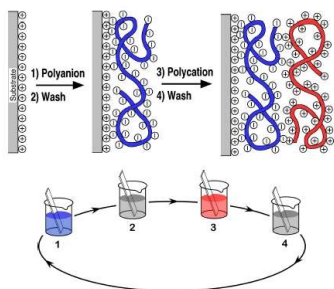


Fig. 1: Formation of PE multilayers

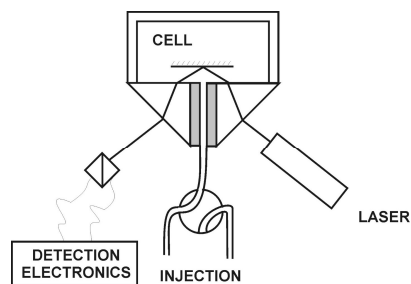
otvorena pitanja

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

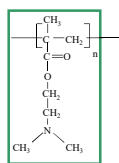
eksperimentalne metode:

- 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)

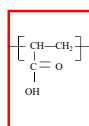


$M_w = 20 \text{ kg/mol}$

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

PAA

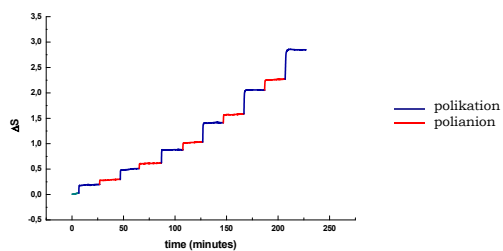
Poly Acrylic Acid

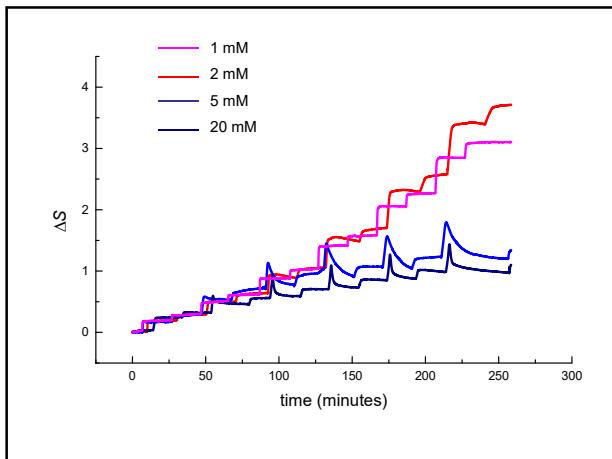


$M_w = 12.5 \text{ kg/mol}$

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

polielektrolitni višeslojevi (Polyelectrolyte Multilayers)

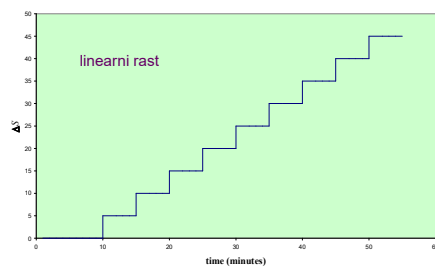




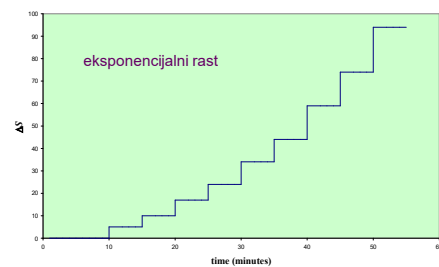
otvorena pitanja

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

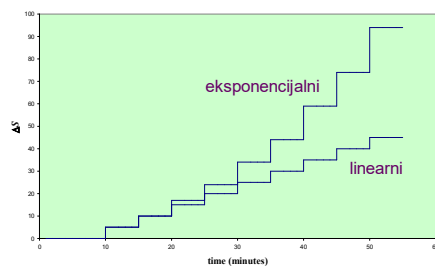
eksponencijalni vs. linearni rast



eksponencijalni vs. linearni rast



eksponencijalni vs. linearni rast

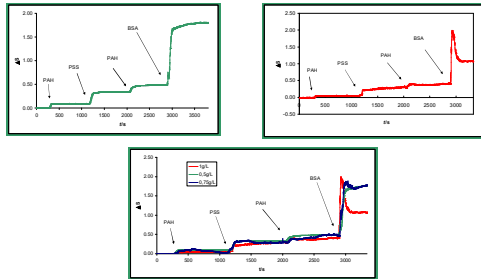


eksponencijalni vs. linearni rast

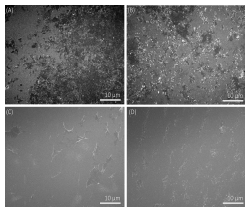
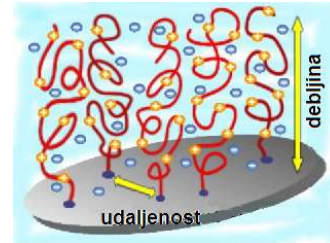
Faktori koji utječu na tip rasta:

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

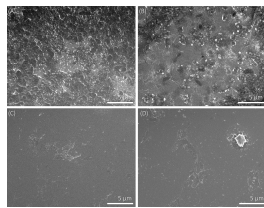
adsorpcija BSA na prethodno formirani polielektrolitni višesloj



polielektrolitne "četke" (Polyelectrolyte Brushes)



SEM images of bacteria *Pseudomonas aeruginosa* adhered on a polyelectrolyte multilayer surface at 2000x magnification.
(A) Adhered bacteria on SiO₂ plate, which is covered with five polyelectrolyte layers and the terminating layer has a positive electric charge (PAH)
(B) Adhered bacteria on SiO₂ plate, which is covered with six layers and the last adsorbed layer has a negative electric charge (PSS)



SEM images of bacteria *Pseudomonas aeruginosa* adhered on a polyelectrolyte multilayer surface at 5000x magnification.
(A) Adhered bacteria on SiO₂ plate, which is covered with five polyelectrolyte layers and the terminating layer has a positive electric charge (PAH)
(B) Adhered bacteria on SiO₂ plate, which is covered with six layers and the last adsorbed layer has a negative electric charge (PSS)

primjena

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

šuplje sfere

