POLYELECTROLYE

MULTILAYERS

PREPARATION,

CHARACTERIZATION,

INTERNAL STRUCTURE.

Main Items:

- What are polyelectrolytes?

.Definition
.Examples

- Formation of polyelectrolyte multilayers.

.Adsorption mechansim
.Thin Layers preparation

- Characterization Techniques.

.Ellipsometry
.X-ray Reflectivity

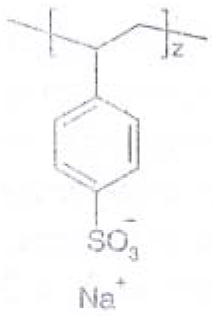
- Factors affecting formation of multilayers.

.Polyelectrolyte Concentration.
.Ionic Strength.
.Charge Density.

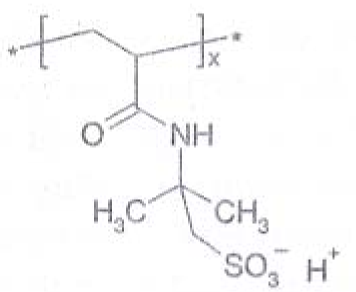
<u>Polyelectrolytes :</u>

Macromolecules " Polymer Chains" having charges distributed along the chain, these charges can be positive "<u>Polycations"</u> or negative <u>"Polyanions"</u> beside the oppositely charged "<u>Counter Ion</u>".

Examples:

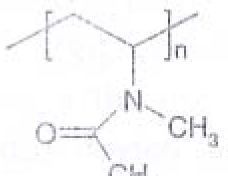


PSS

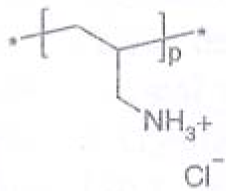


PAMPS

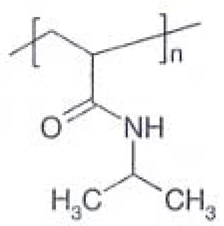
PDADMAC



PNMVA



PAH

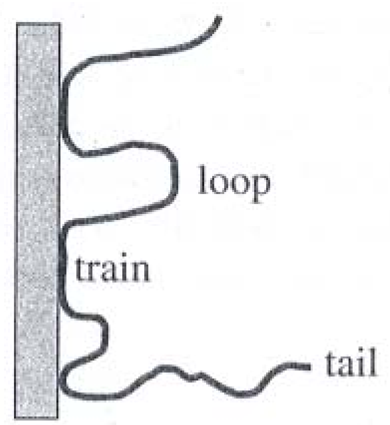


PNIPAM

CONCEPT:

Adsorption of one layer on the substrate, then the upcoming layers can adsorbe layer by layer on each other; THE DRIVING FORCE is the ELECTROSTATIC ATTRACTION between oppositely charged chains.

ADSORPTION MECHANISM:



Transport of the polymer molecule to the interface.

The primary adsorption Step.

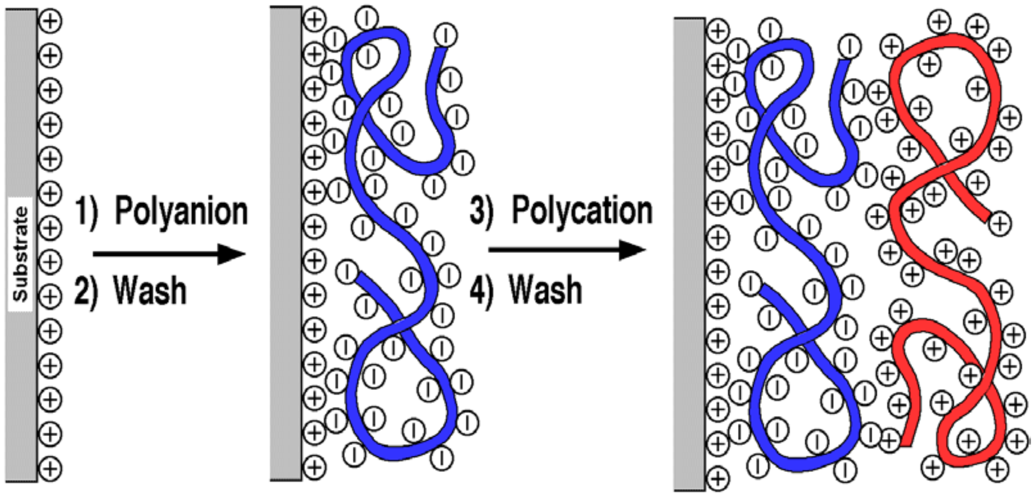
Arrangement of the adsorbed molecule.

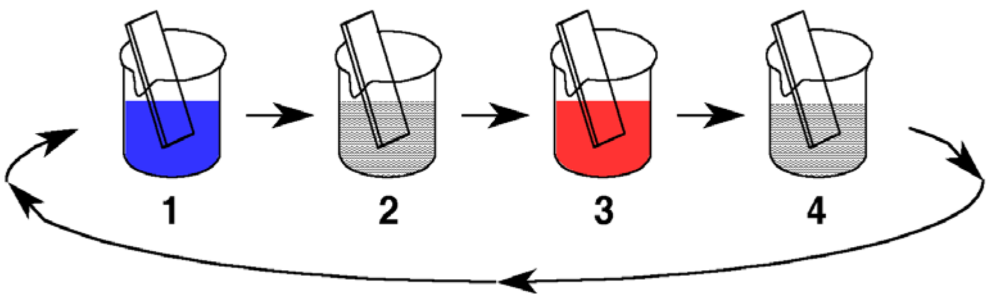
conformations were pridected by theoritical model

molecules transport is governed by *Diffusion Coeffecient* ranging from 10^{-9} to 10^{-7} Cm^2/ s

Preparation:

- First ; Cleaning the Silicon Substrates in Acidic Solution " e.g. Pirana Solution H_2SO_4: H_2O_2 in ratio 1:1" then rinsed by distilled water. This Cleaning is to get red of wax and to afford a hydrophilic surface for the the polymer chains.
- Preparation of NaCl solution of certain molarity, in which the polymer is dissolved at certain concentration.
- Then dipping the substrate for a certain time in the polyanion/polycation solution, " ideally 20 min ." followed by washing steps then the other oppositely charged polymer and again the washing steps and so on.

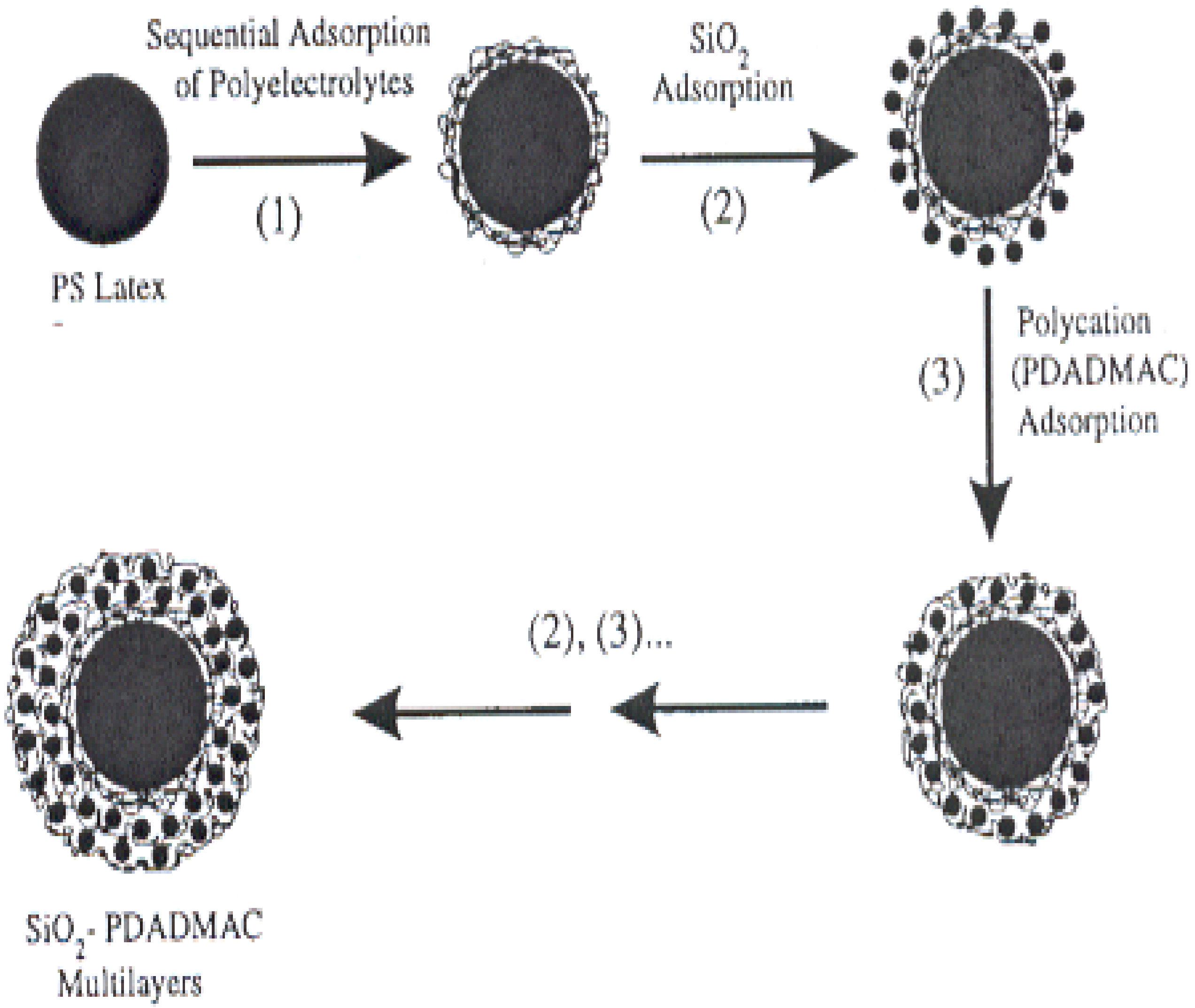




Multilayers on POLYMER LATEX:

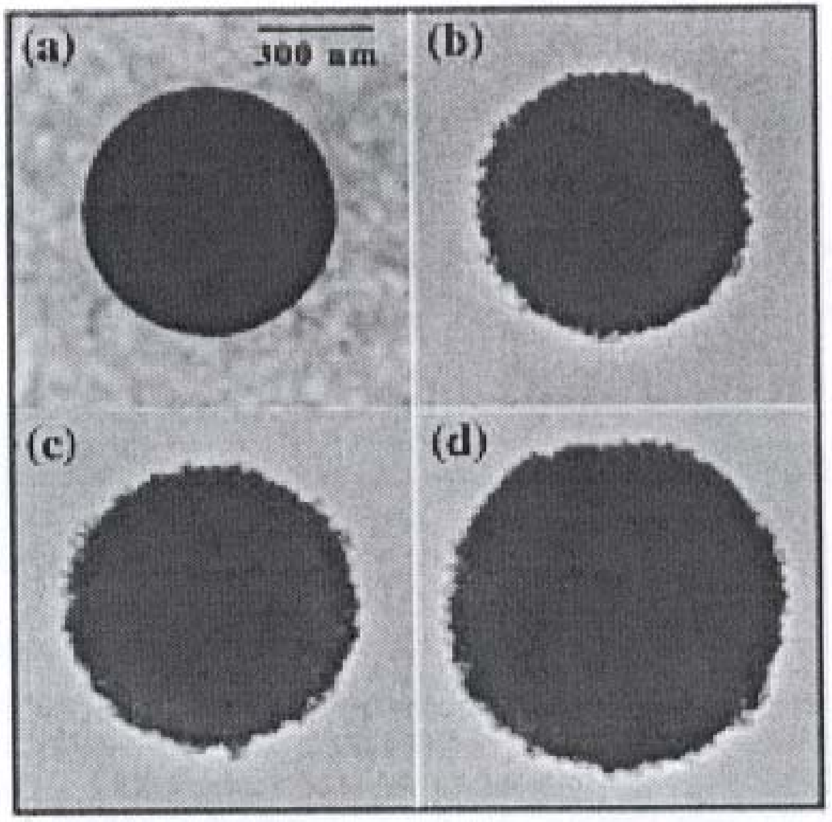
Assembly of multilayers on PS Latex .

1- Adsorption of oppositely charged polyelectrolytes (PDADMAC/ PSS/PDADMAC) or (Pr_3) in order to produce a smooth and uniformely positively charged outer surface to facilitate the adsorption of the negatively charged SiO_2.
2- Adsorption of SiO_2
3- Adsorption of PDADMAC.



Latex growth characterization:

SFM Images:



a- Uncoated PS Latix
And PS Latices coated with [$Pr_3/(SiO_2/PDADMAC)_N$] ;
b- N = 1
c- N = 2
d- N = 4

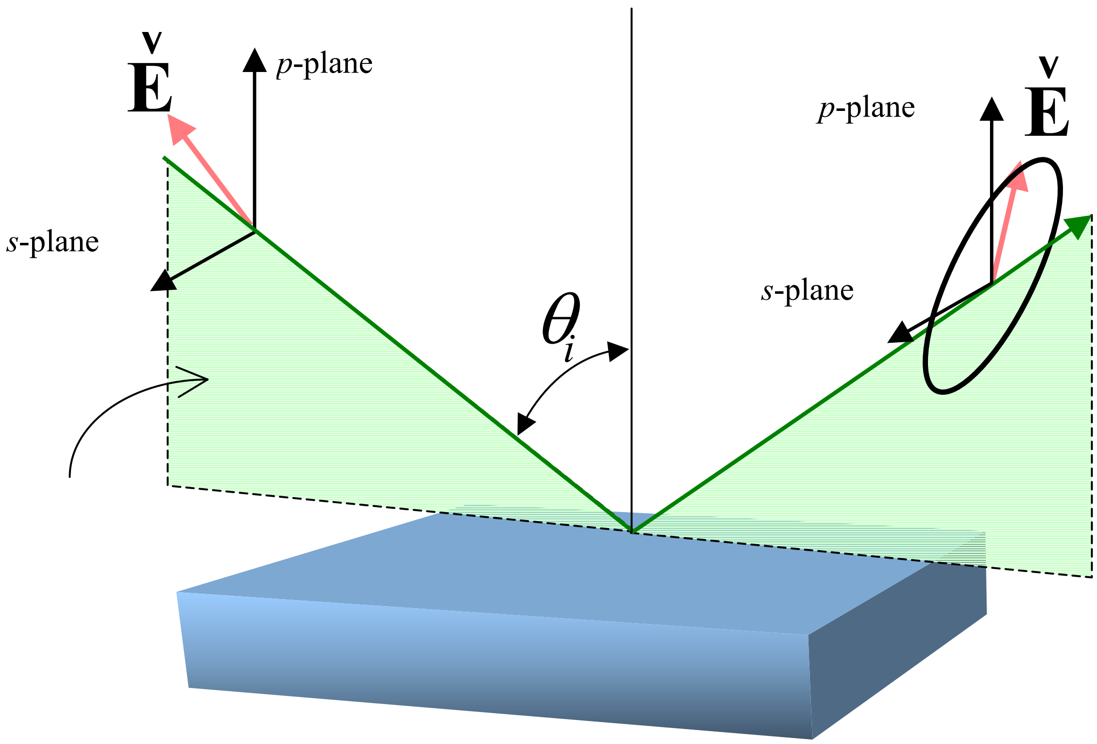
- Increased Surface roughness due to SiO_2 adsorption.

- regular growth of the SiO_2 – PDADMAC multilayers is seen.

Characterization Techniques:

- **Ellipsometry:** measures the change of polarization occurs for a monochromatic beam upon reflection at an interface between two media of two different refractive indices.

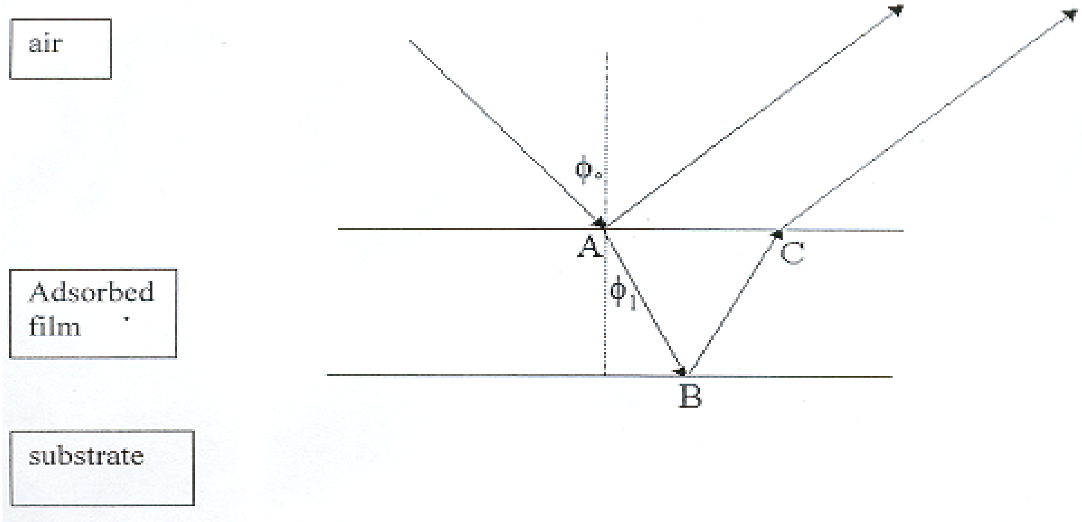
  Giving accurate values for the film thickness *d* and refractive index *n*



-The measurable quantities in Ellipsometry are

Δ the phase shift introduced by the film,
ψ is amplitude of the reflected wave.

Related to the ellipticity ρ by : $\rho = p/s = \tan\psi \exp(i\Delta)$ (1)
S and p are the Fresnel reflection coeffecient for S and P polarized light respectively.



$$\sigma_0 = \left(\frac{2\pi}{\lambda_0}\right) n_1^* d_1 \cos\phi_1$$

Where :

σ_0 is the phase lag between A and C
λ_0 is the wavelength of the incident beam
n_1^* is the refractive index of the film
d_1 is the film thickness
ϕ_1 is the refraction angle at the first interface.

$$\tan\psi\, e^{i\Delta} = \left(\frac{p_1 + p_2 e^{-i2\sigma_0}}{1 + p_1 p_2 e^{-i2\sigma_0}}\right)\left(\frac{1 + s_1 s_2 e^{-i2\sigma_0}}{s_1 + s_2 e^{-i2\sigma_0}}\right)$$

X- ray and Neutron Reflectivity:

Properties:

Properity	X-ray	Neutrons
• Rest mass	0	$1.675 * 10^{-27}$ kg
• Charge	0	0
• Spin	1	½
• Energy	$E = hc/\lambda \sim 10^4$ ev	$E = p^2/2m \sim 25$ meV
• Wavelength	1 A° for Cu k_α = 1.54 A°	~ 2 A°
• Scattering type	elastic due to high energy	elastic and can be inelastic due to low energy

Refractive index:

$$n = 1 - \sigma - i\,\beta$$

for X-ray : $\sigma = \lambda^2 / 2\pi \,.\, \rho_s \,.\, r_\circ$

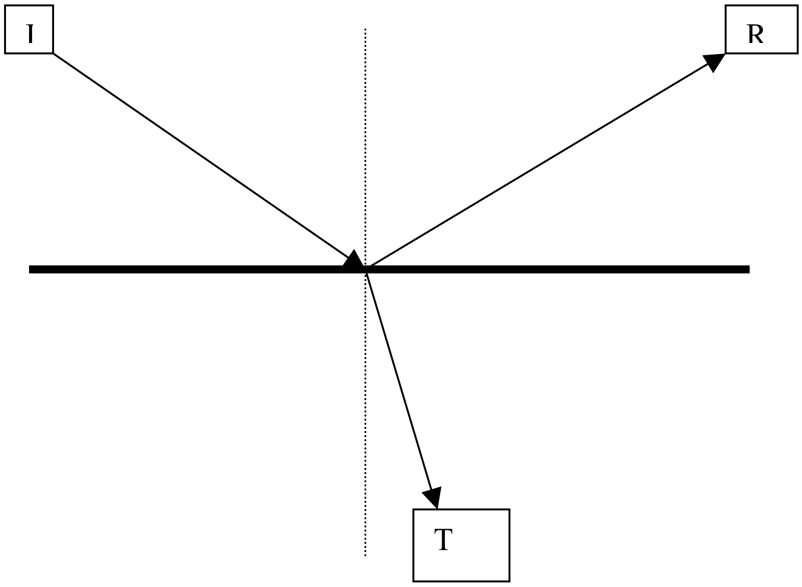
ρ_s : electron density in the film [A° $^{-3}$]

$r_\circ$: Thomson Radius , $2.82 \,.\, 10^{-5}$ [A°]

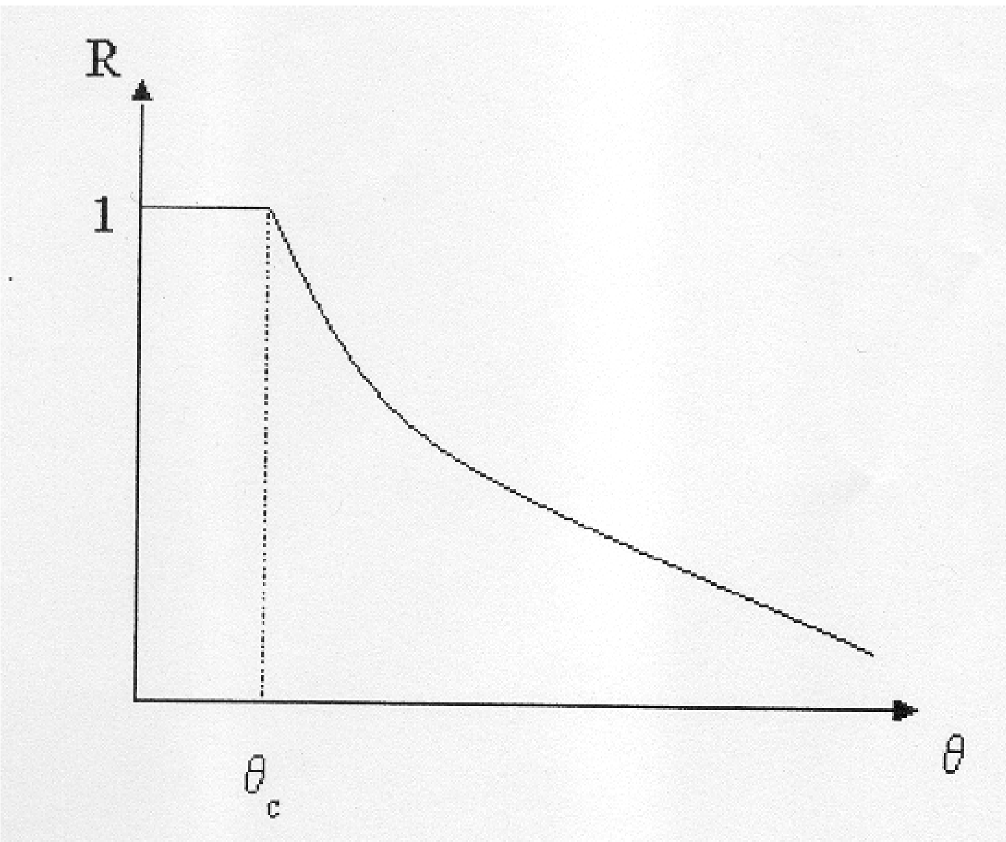
for Neutrons: $\sigma = \lambda^2 / 2\pi \,.\, N.\, B$

N : number density “number of nuclei in unit volume“ [A° $^{-3}$].
B : scattering length of neutrons [A°].

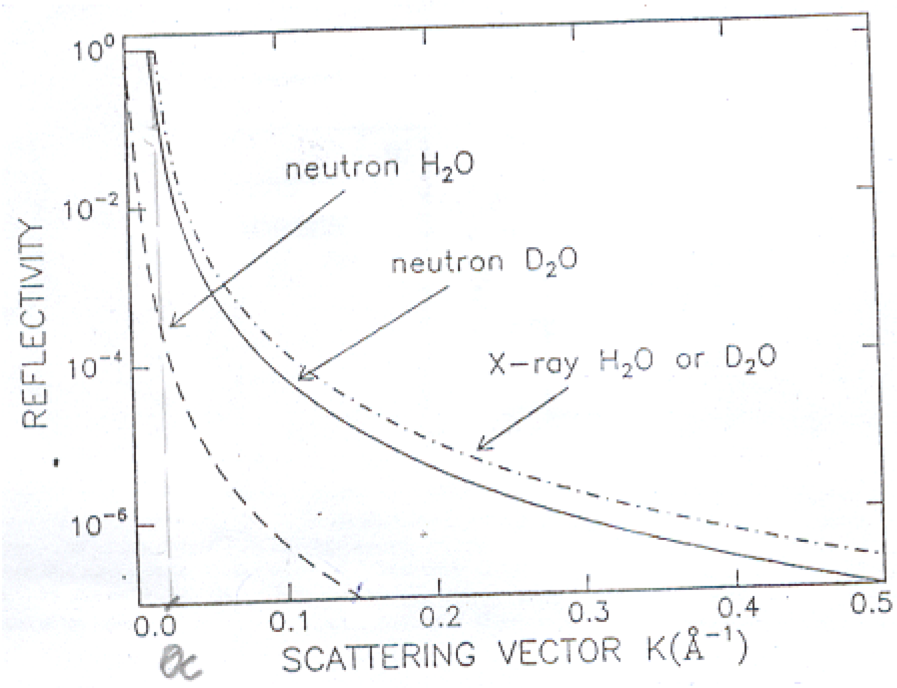
Reflection by Electrons and neutrons at surfaces:



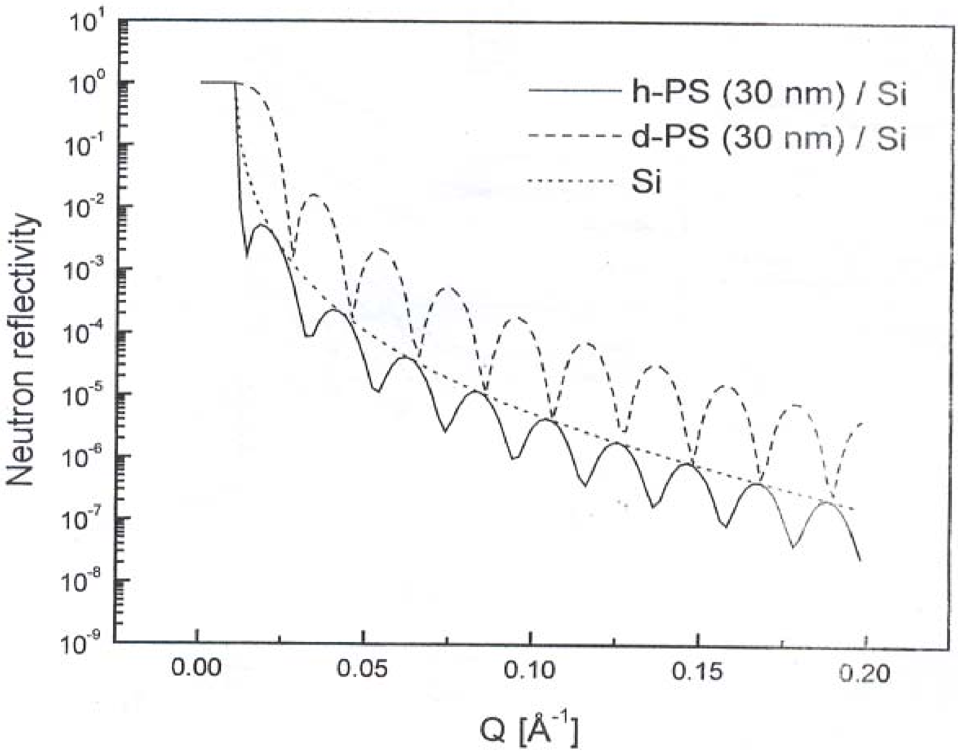
A part from the incident beam is reflected and another part is transmitted, at small incidence angles everything is reflected untill the critical angle θ_c , after which the transmission starts and reflection decaies exponentially.



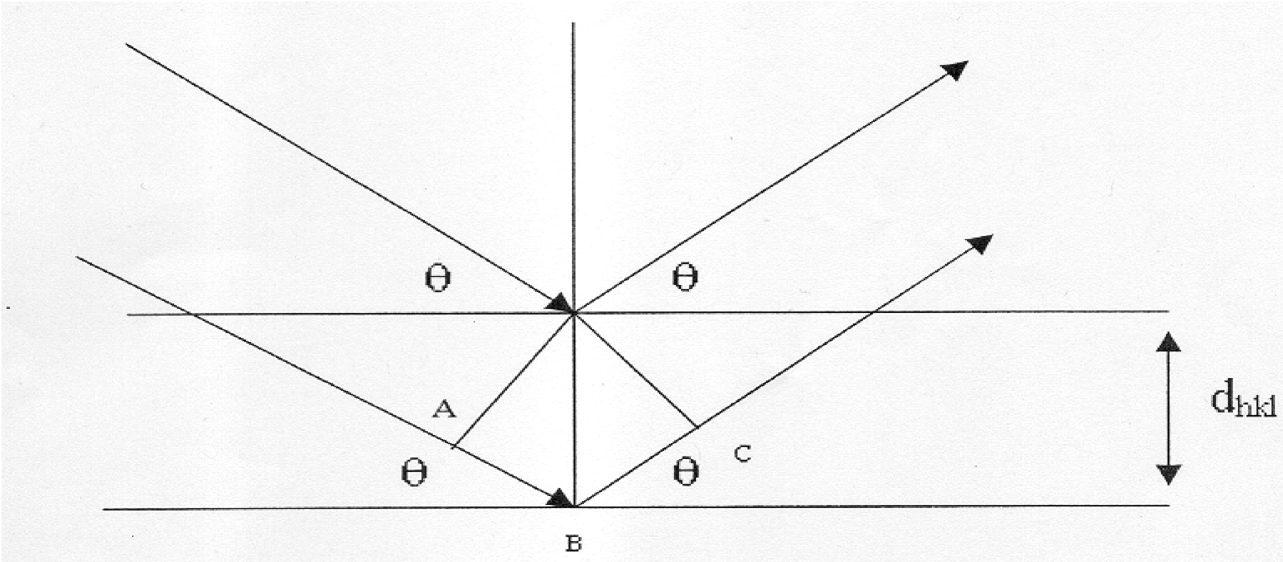
Reflectivity of Electrons and neutrons:



There is only difference between isotopes in case of neurons due to the different scattering length values, but in case of x-ray both isotopes have the same electron density.

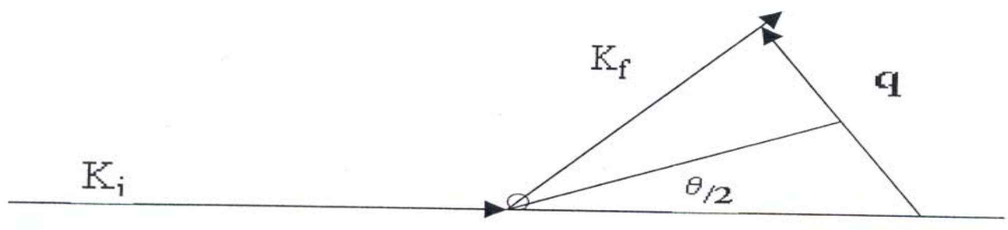


Bragg Law:



AB = d sin θ , BC = d sin θ
AB+BC = 2 d sin θ
Path length difference must equal multiple the wavelength for constructive interference

$2 d \sin\theta = n\lambda$, n = 1,2,...

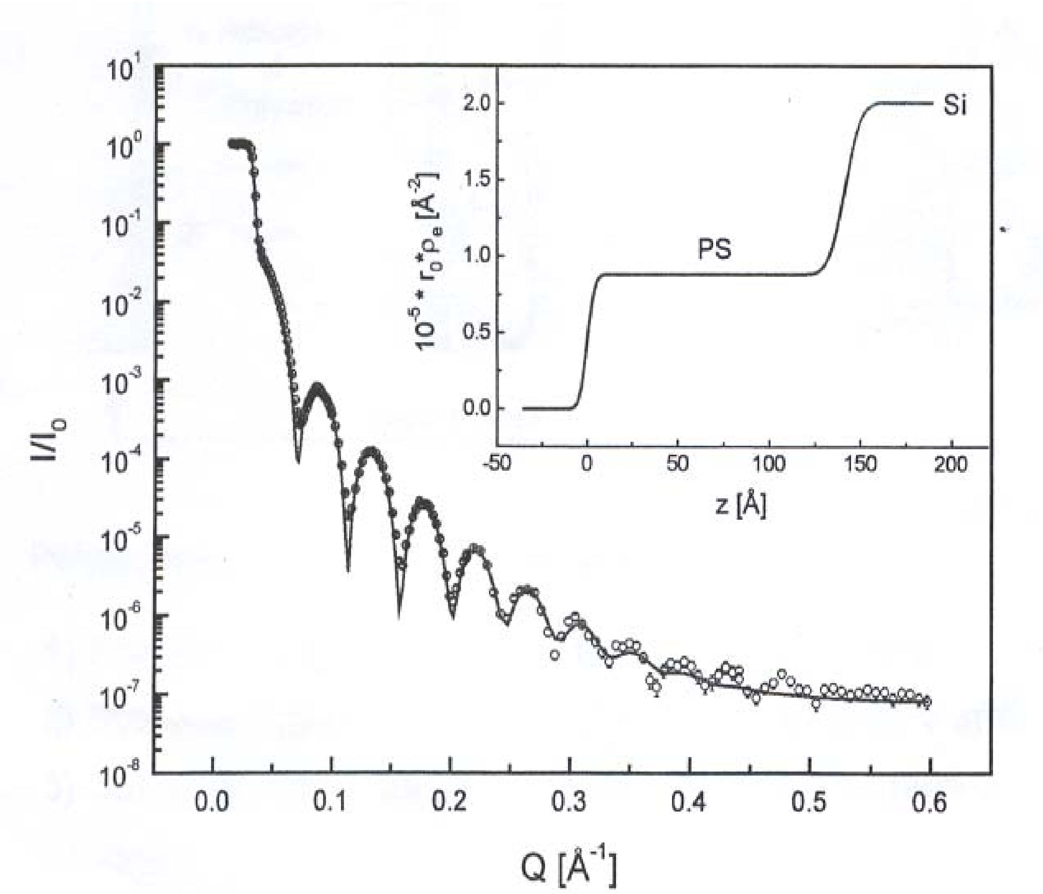


q “scattering vector“ or “ momentum transfer“

$q = 2 k \sin \theta/2$, $k = 2\pi/\lambda$
$q = 4\pi/\lambda \,.\, \sin\theta/2$

$$q = 2\pi / d$$

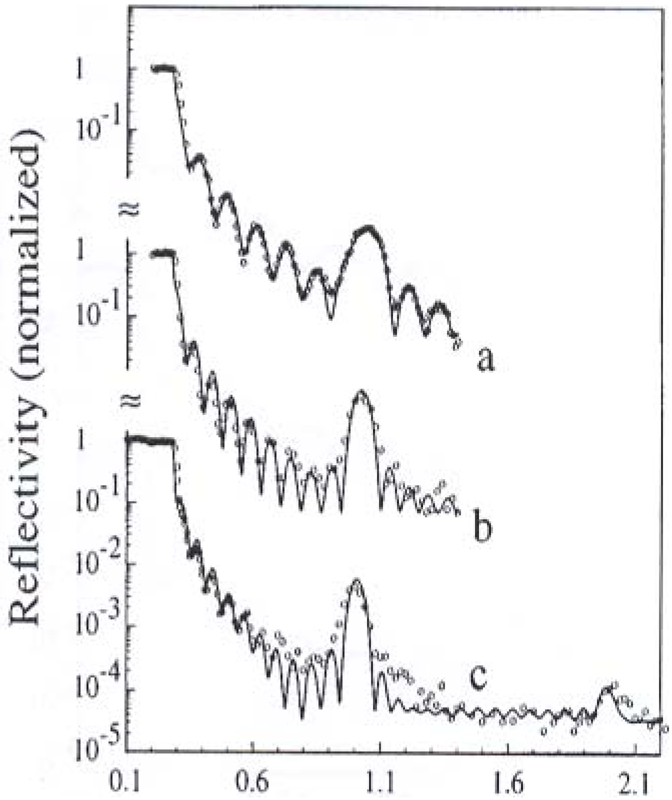
Information from Reflectivity curve:

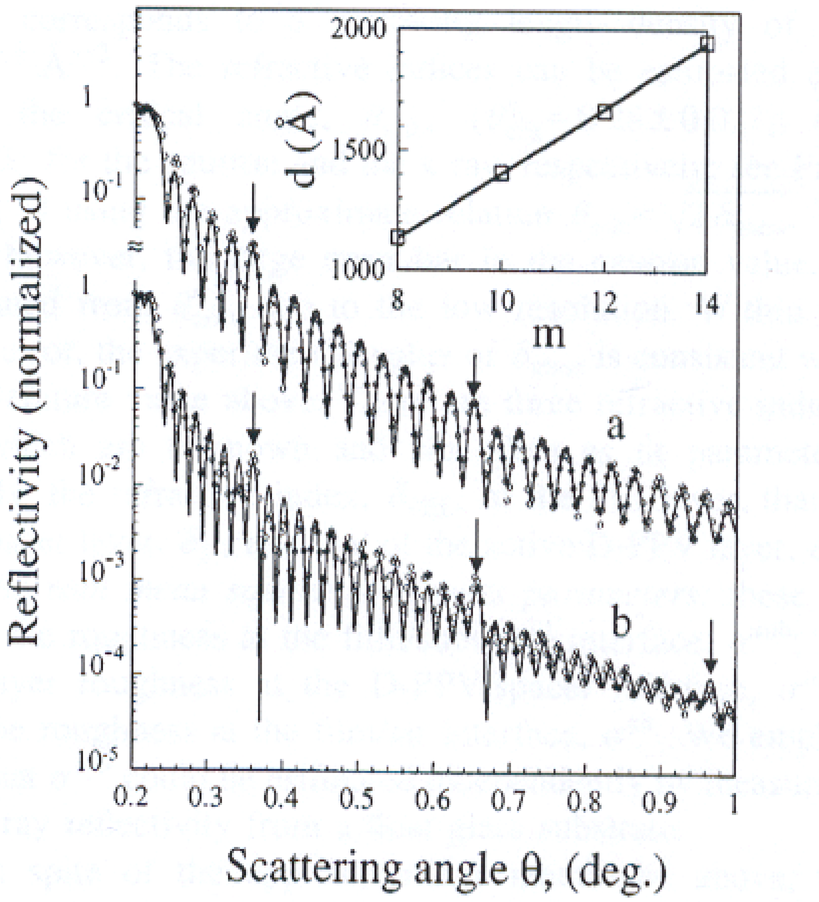


the peaks are the points of constructive interfernce.

The distance between every two peaks is Δq, giving the value of *d* "lattice constant" or in case of thin films, gives the film thickness.

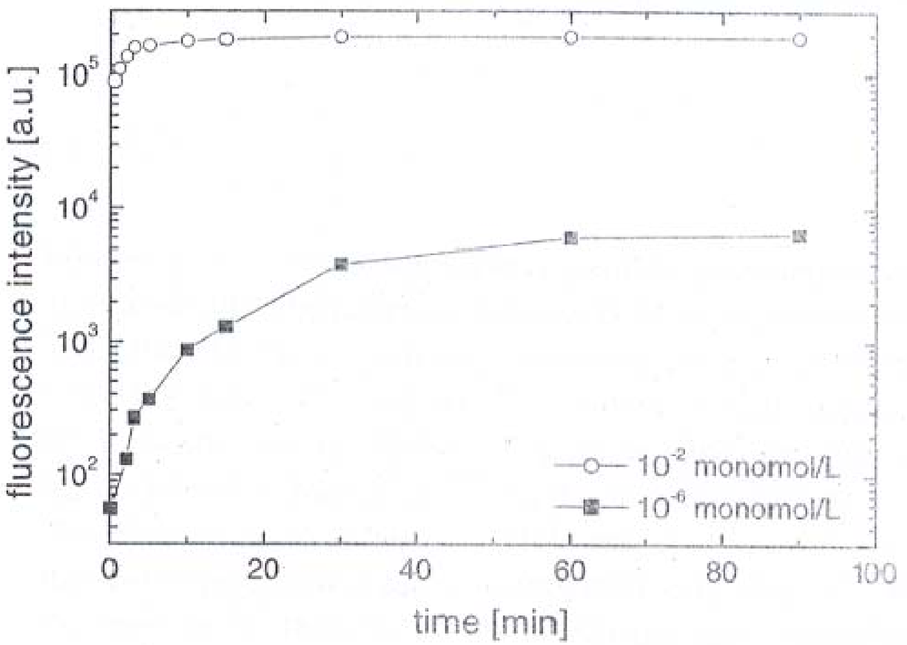
Legand is the Refractive index profile


Reflectivity (normalized)
1
10^-1
1
10^-1
1
10^-1
10^-2
10^-3
10^-4
10^-5
a
b
c
0.1
0.6
1.1
1.6
2.1

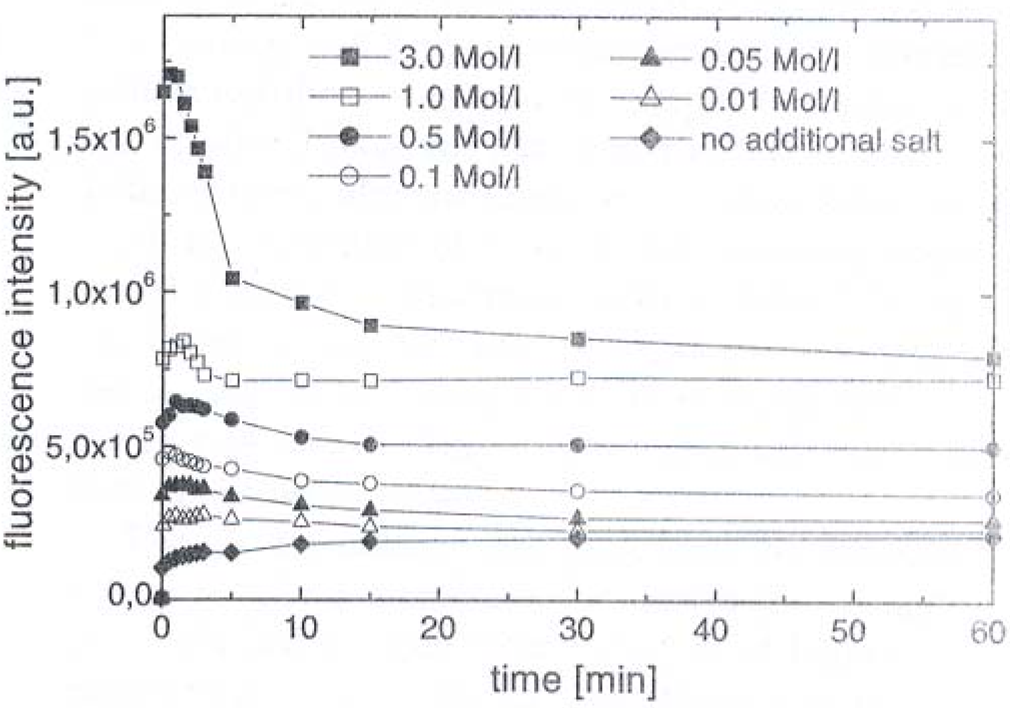

Reflectivity (normalized)
1
10^-1
1
10^-1
10^-2
10^-3
10^-4
10^-5
a
b
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Scattering angle θ, (deg.)
d (Å)
2000
1500
1000
8
10
12
14
m

Multilayers Internal structure:

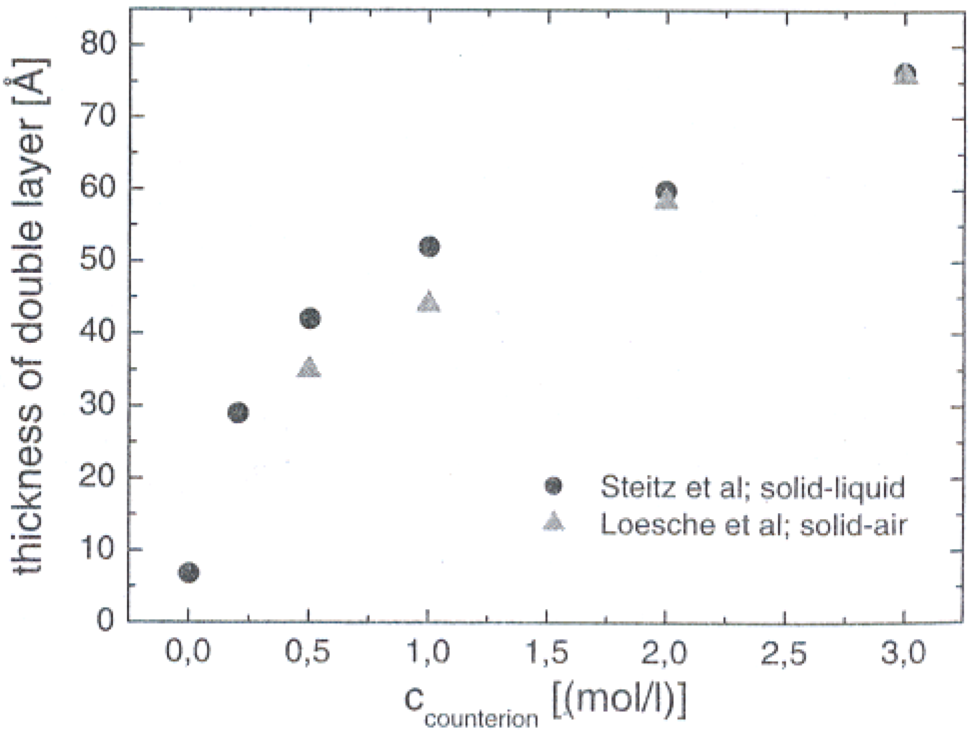
- POLYELECTROLYTE CONCENTRATION:



-Influence of IONIC STRENGTH:



Factors affecting FILM THICKNESS:

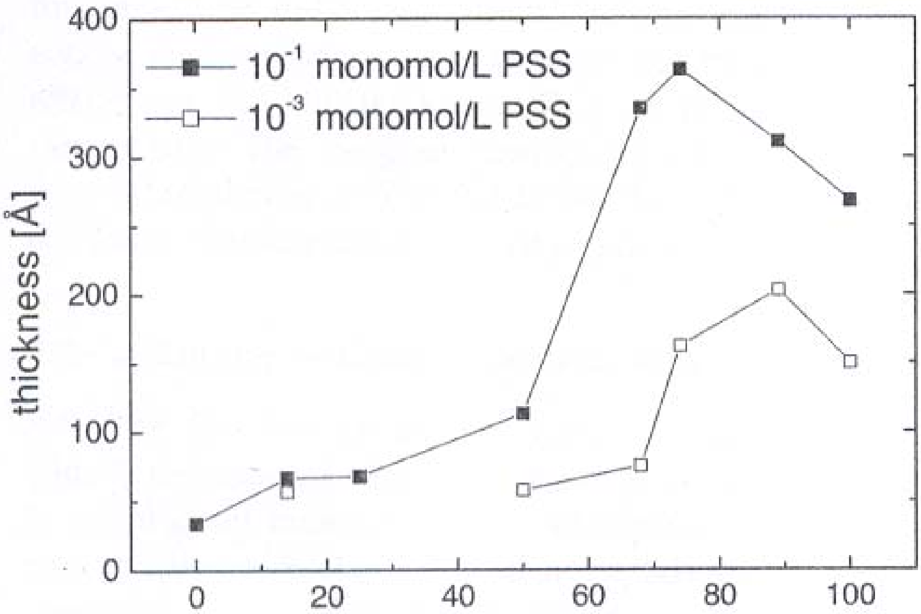


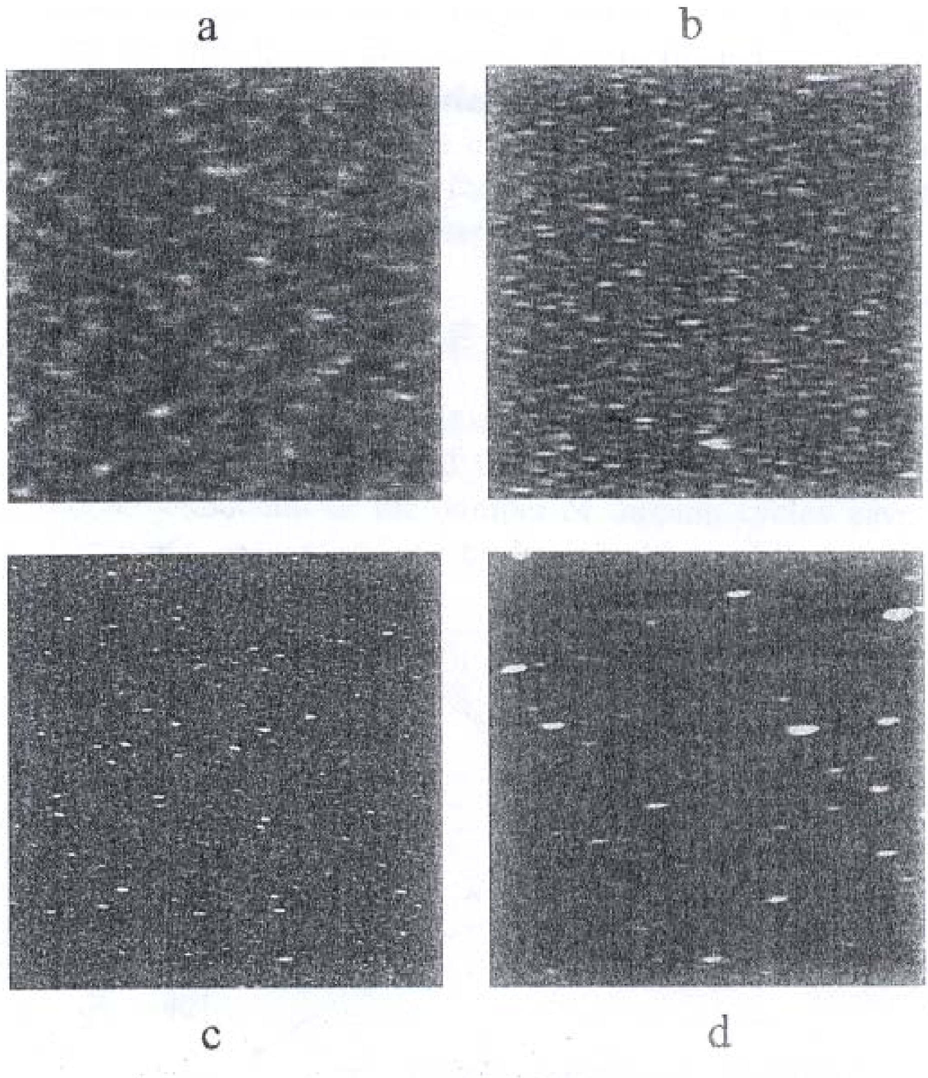
-HIGHER POLYELECTROLYTE CONCENTRATIONS GIVES HIGHER FLUORESCENCE INTENSITY.

- HIGHER SALT CONCENTRATIONS ALSO GIVES HIGH FLUORESCENCE INTENSITIES; *AT LOW IONIC STRENGTH THE CHARGES ALONG A CHAIN REPEL EACH OTHER YIELDING MORE STRECHED CHAINS " HIGHER RADIUS OF GYRATION" . AT HIGH IONIC STRENGTH THE CHARGES ALONG THE CHAIN ARE SCREENED YIELDING MORE COILED CHAINS " DECREASE IN RADIUS OF GYRATION" AND MORE FLEXIBLE CHAINS"DECREASE IN PERSISTANCE LENGTH".*

- THICKNESS INCREASES BY INCREASING THE SALT CONCENTRATION AS THE POLYMER CHAINS ARE MORE ENTANGLED.

Charge Density





REFERENCES:

- Handbook of polyelectrolyte and their applications ‚chapter 14 " internal structure of multilayers" by Regine v. klitzing and Roland steitz.

- Langmuir, Vol. 17, No.15, 2001

- J. Appl. Physi., vol.83, No. 2, 15 january 1998

- SCIENCE. VOL. 277 . 29 August 1997

- Lectures by Roland Steitz at Physical chemistry Dept. TU Berlin.