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1. Introduction

- Substrates, polyelectrolytes
- IR spectroscopy basics, Fourier Transform, sampling techniques

2. Other IR sampling techniques

- Transmision, External reflexion, Diffuse Reflexion FTIR spectroscopy

3. ATR-IR spectroscopy

3.1. Detection, chemical composition

- PEL (multi)layers: adsorbed amount, thickness, dissociation degree, ion & protein interaction
- PEL complexes: composition/stoichometry

3.2. Conformation and orientation

- Charged polypeptides
- in-plane orientation of PEL multilayers

3.3. Interaction

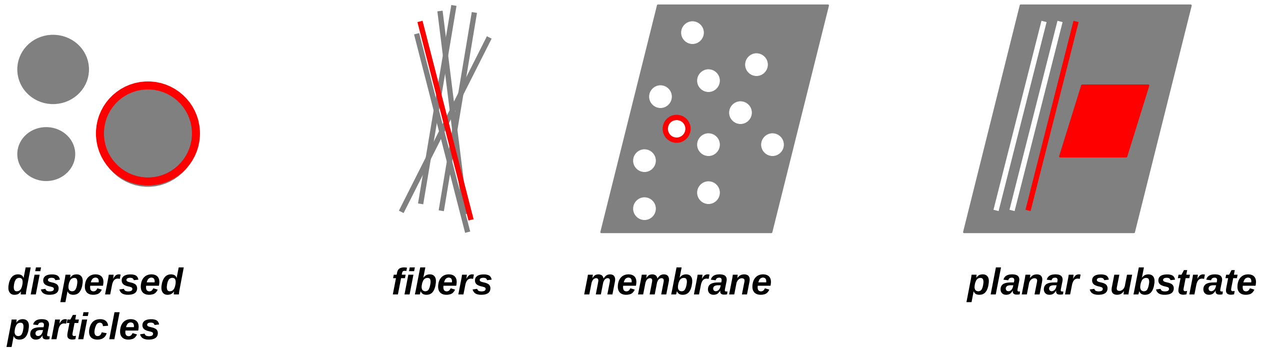
- Salt, chiral compounds, proteins
- Solvent diffusion

3.4. Combination with other techniques

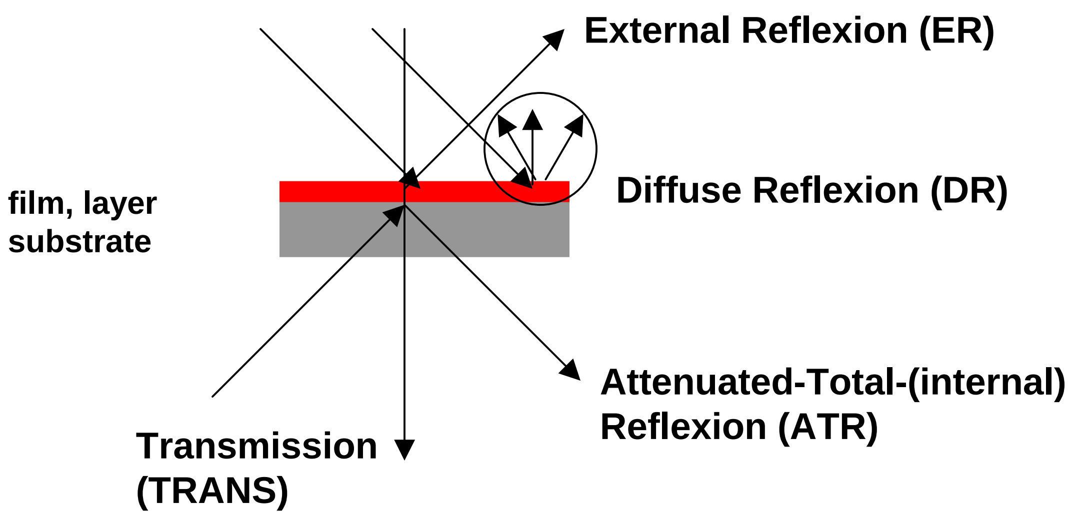
- Electrokinetics

4. Summary

1. Substrates, IR-Methods

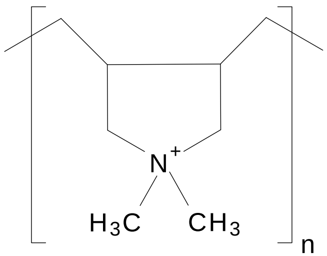


Substrate
Modification layer

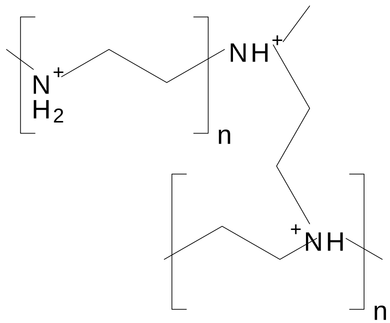


1. Polyelectrolytes

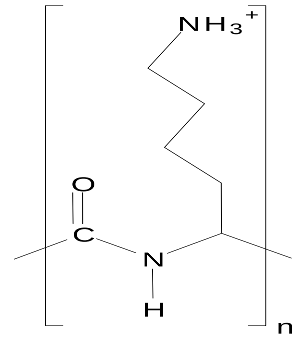
Polycations



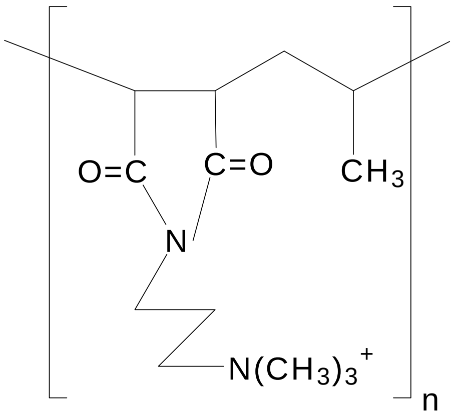
PDADMAC
(Poly(diallyldimethylammonium)
(37.000-250.000 g/mol)



PEI
Poly(ethylenimine)
(750.000 g/mol)

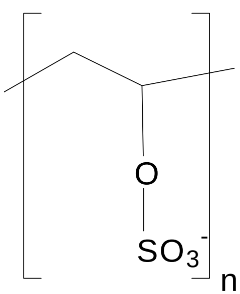


PLL
Poly(L-lysine)
(25.000 ... 309.000 g/mol)

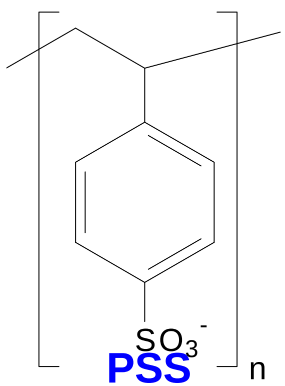


PMI-P
Poly(N-trimethylammmonium propylmaleimide-co-propylene)

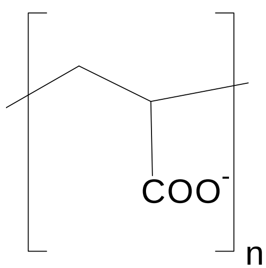
Polyanions



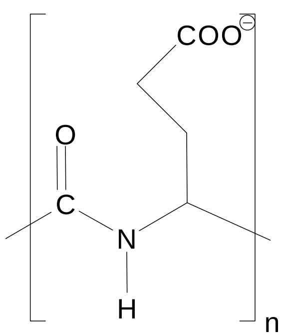
PVS
Poly(vinylsulfate)
(162.000 g/mol)



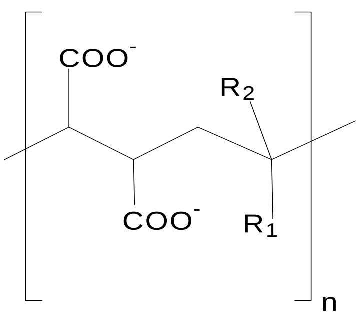
PSS
Poly(styrenesulfonate)
(70.000 g/mol)



PAC
Poly(acrylic acid)
(50.000–4.000.000 g/mol)

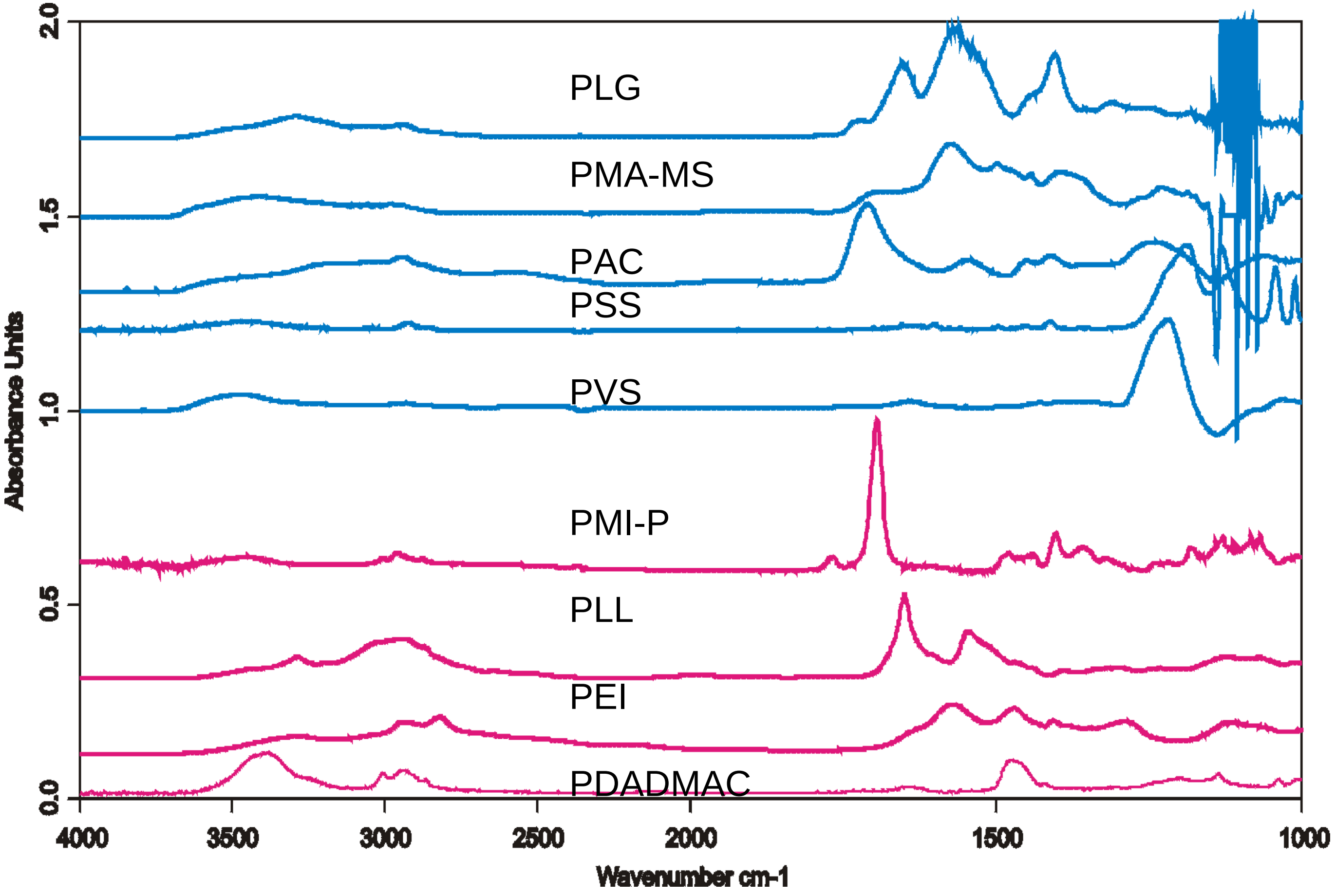


PLG
Poly(L-glutamic acid)
(70.000 g/mol)



PMA-X
Poly(maleic acid-co-olefine) (25000-50000)

1. Polyelectrolyte IR spectra

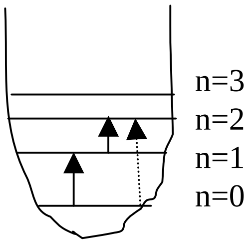


1. Basics: Vibration spectroscopy

Total energy of a molecule

$$E_{TOT} = E_{ELEC} + E_{VIB} + E_{ROT} + E_{TRANS}$$

E_{VIB}: Harmonic oscillator



$$\nu = 1/2\,\pi\,(k/\mu)^{1/2}$$

k: force constant

μ: reduced mass

Fundamental vibrations

ν(AB): A---B

assymmetric, symmetric stretch

δ(ABC): A---B---C

bending, deformation

τ(BC): A---B---C---D

torsion

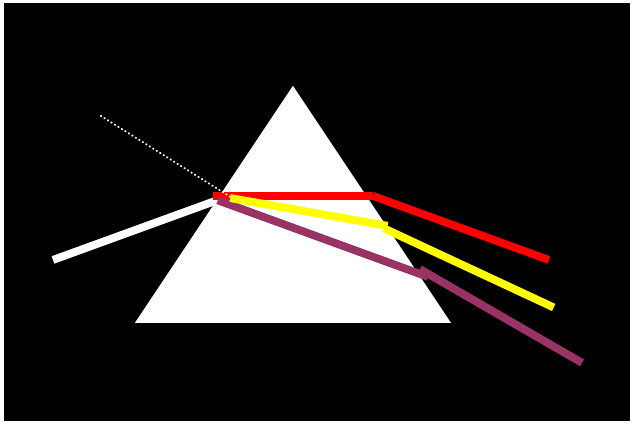
Infrared regions

	Wavenumber $\tilde{\nu}$ / [cm^{-1}]	Wavelength λ / [μm]	Frequency $\nu = c\tilde{\nu}$ / [s^{-1}]	Energy E / [J]
Near Infrared (Overtones)	10000 - 4000	1 – 2.5	3 - 1.2 * 10^{14}	1.88 – 0.76 * 10^{-19}
Mid Infrared (Fundamental)	4000 - 400	2.5 - 25	1.2 – 0.12 * 10^{14}	7.6 – 0.76 * 10^{-20}
Far Infrared (Sceletal)	400 – 40	25 - 1000	1.2 – 0.12 * 10^{13}	7.6 – 0.76 * 10^{-21}

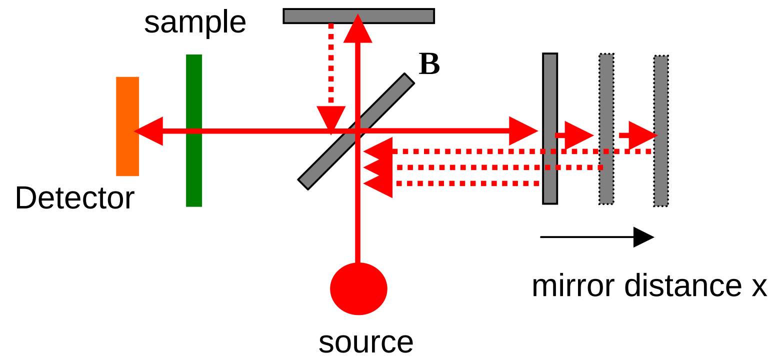
H. Günzler, H. Heise, *IR-Spektroskopie*, VCH, Weinheim (1996) & J.L. Koenig (ed.), *Spectroscopy of Polymers*, Elsevier (1999)

1. Basics: Dispersive versus FT-Spectrometer

Dispersive Spectrometer



Fourier-Transform-(FT)-Spectrometer



Monochromatic radiation (LASER)

$$I(x) = A_0 \sin(2 \pi \nu_0 x)$$

undamped sine

Polychromatic radiation (e.g. Globar)

$$I(x) = \Sigma_i A_i \sin(2 \pi \nu_i x)$$

sum of sines: interferogram

Exponentially damped sine function:

$$I(x) = A_0 \sin(2 \pi \nu_0 x) \cdot \exp(-2 \pi \gamma x)$$

↓ FT

Lorentzian function:

$$A(\nu) = A_0 \gamma^2 / [\gamma^2 + (\nu - \nu_0)]^2$$

I: intensity

x: mirror distance

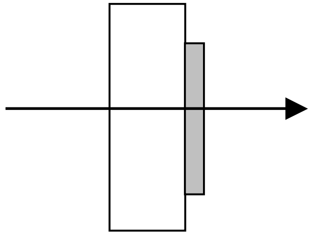
ν_0: frequency

A: absorbance

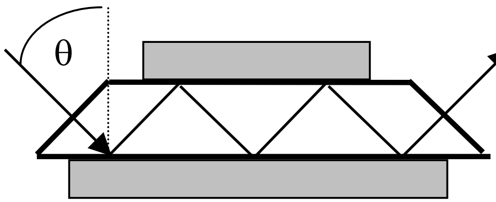
γ: half width

1. IR surface analytical methods

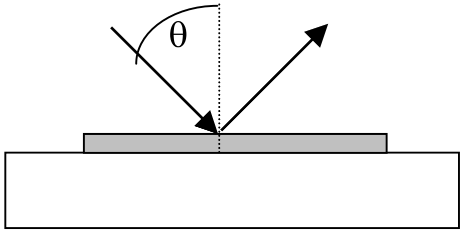
• **Transmission IR (TRANS-IR)**



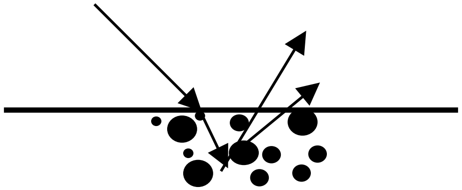
• **Internal Reflexion Spectroscopy (IRS)**
Attenuated Total Reflexion IR (ATR-IR)



• **External-Reflexion-(IR)-Spectroscopy (ERS)**
Gracing Incidence IR (GIR)
IR Reflexion Absorption Spectroscopy (IRRAS)



• **Diffuse Reflexion Spectroscopy (DRS)**
Diffuse Reflexion IR Fourier Transform (DRIFT)



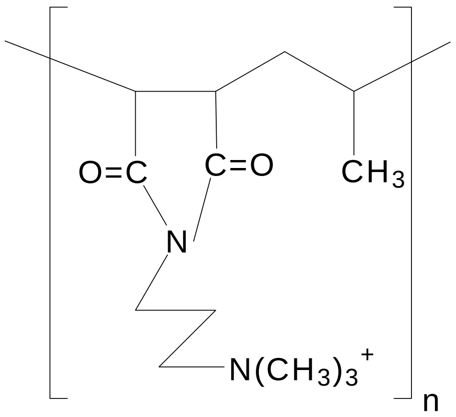
(1) Samples

- Solutions in cuvettes (NaCl, CaF_2)
- Films, layers at silicon supports

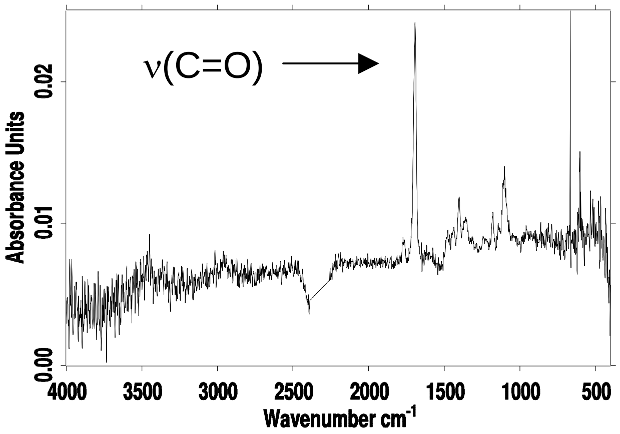
(2) Quantification of the adsorbed amount:

$$I/I_0 = A \propto M^2 E^2 \cos^2(M, E)$$
$$A = \varepsilon c d$$
$$\Gamma = c d$$

(3) Sensitivity / Detection limit (DL):



PMI-P:
Poly((N-trimethylammmonium) propylmaleimid-co-propylen)



TRANS IR of PMIP-film
(25 μg within a 42*10 mm^2 stripe on Si-IRE).

Peak intensity ν(C=O): 0.016 ± 0.001
Surf. conc: ≈ 5.952 μg/cm2
DL: ≈ 0.372 μg/cm².

(related to minimum resolvable peak intensity of 1 mA (milliabsorbance) of ν(C=O))

2. Trans-FTIR: Options, examples

(A) Detection, chemical composition

- Adsorbed amount, layer thickness
- Dissociation degree of weak polyacids

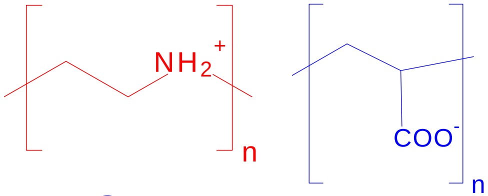
(B) Coordination

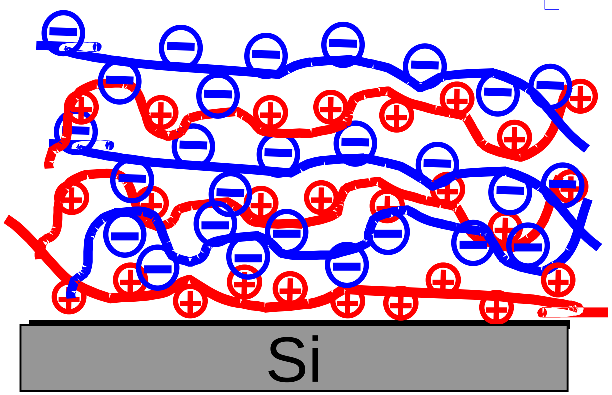
- Complexation of cations by polyacid

(C) Polymer conformation and orientation

- *in-plane* orientation of polypeptides on texturised supports

System: PEI/PAC
pH = 9 / 4





Absorbance (unpolarized light):

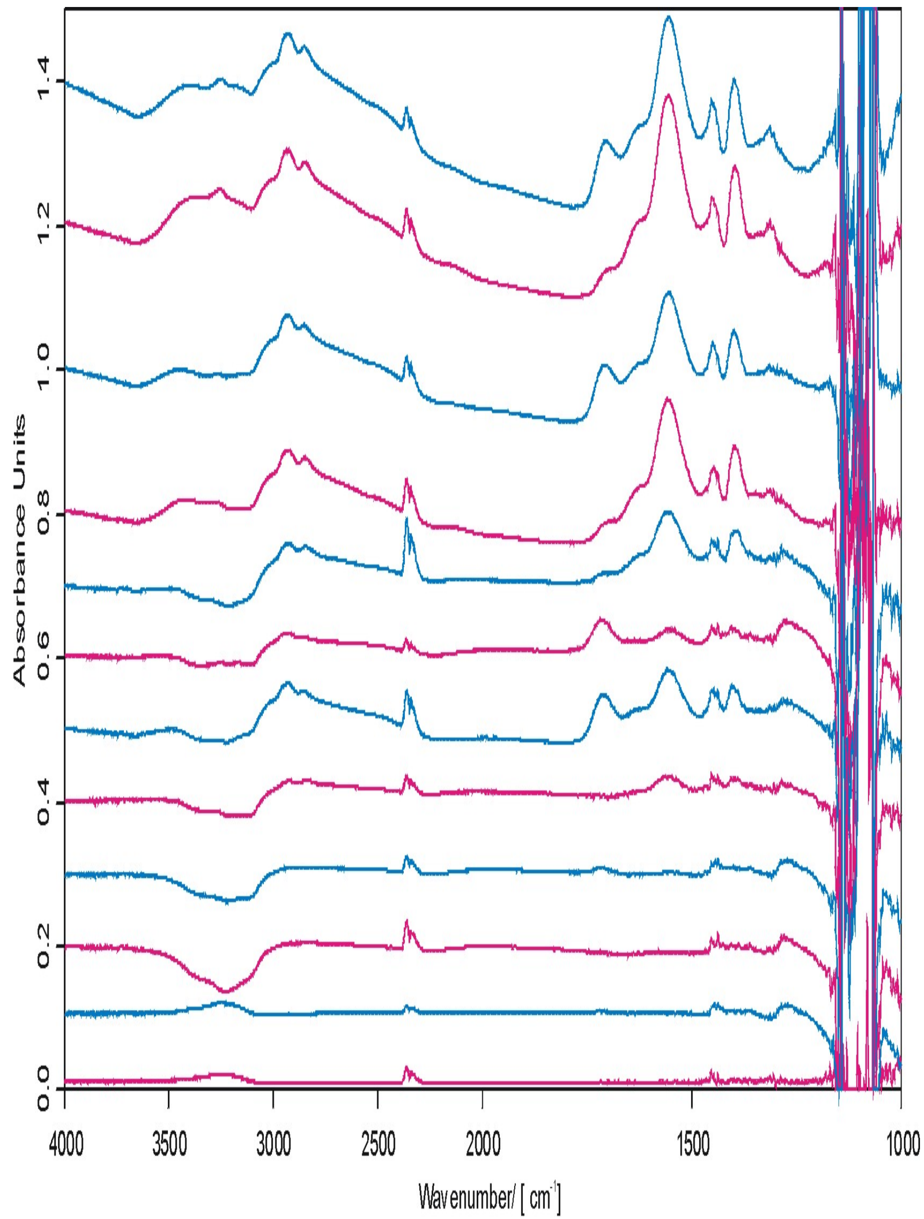
$$\mathbf{A} = -\log (I/I_0) = \varepsilon\ \mathbf{c}\ \mathbf{d}$$

A: Absorbance **e: Absorption coefficient**

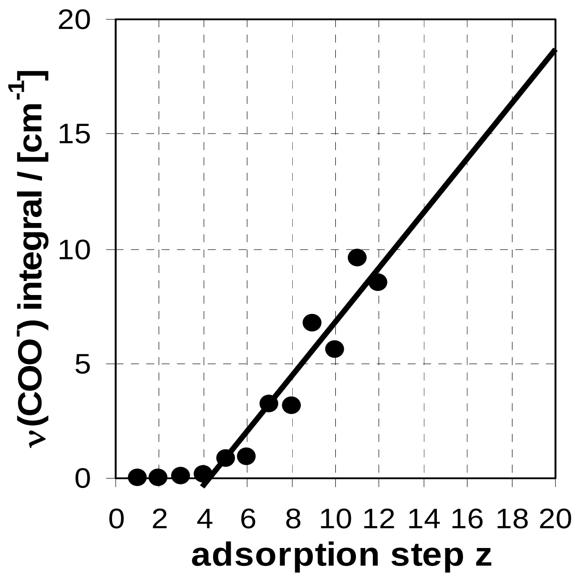
c: concentration **d: (layer) thickness**

Surface concentration:

$$\Gamma = \mathbf{c}\ d$$



Transmission-FTIR

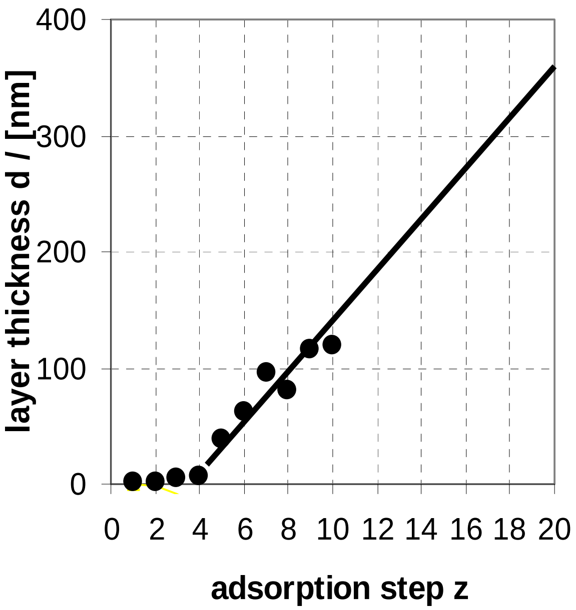


PEL adsorption:

$A(z)=A_0\,(z - z_0)$

$A_0 \approx 1.1\ cm^{-1}$
(dry state)

Ellipsometry



PEL adsorption:

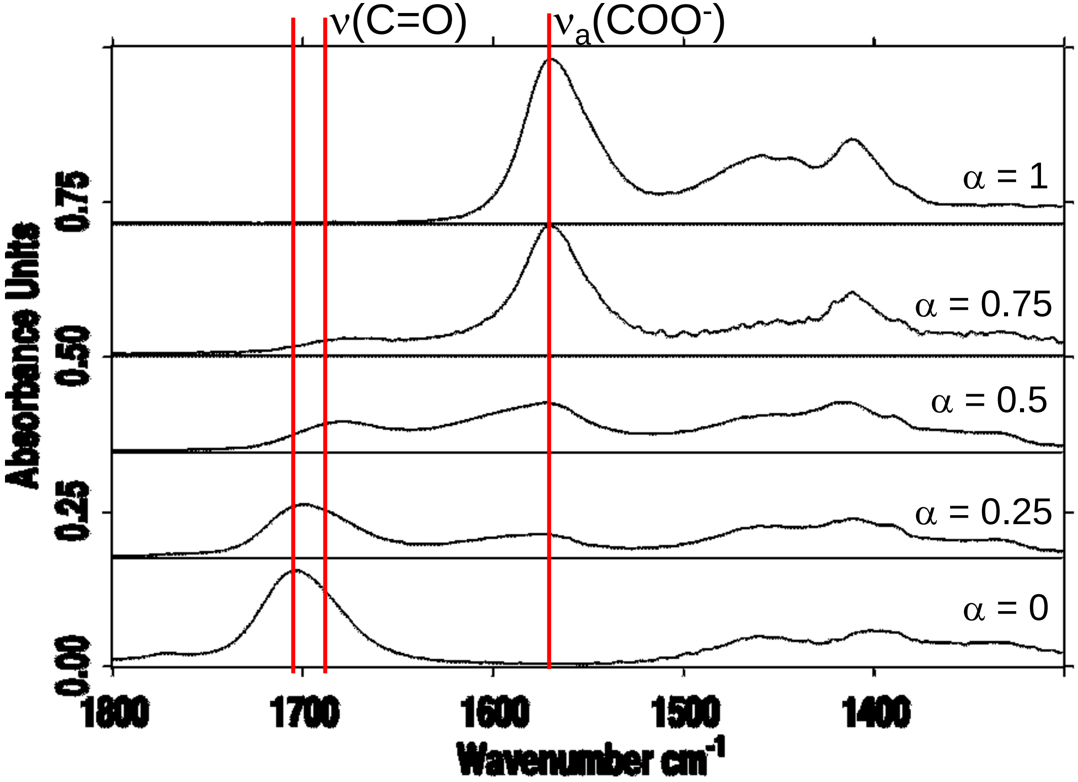
$d(z) = d_0\,(z - z_0)$

$d_0 \approx 20$ nm
(dry state)

Principle: IR spectroscopy is sensitive for:

- ν(C=O) vibration of R-COOH at 1720 - 1700 cm^{-1}
- $\nu(COO^-)$ vibration of R-COO^- at 1590 - 1550 cm^{-1} ($\nu_a(COO^-)$) and 1410 - 1350 cm^{-1} $\nu_S(COO^-)$)

➔ Dissociation degree α of weak (poly)acids: $\alpha = [COO^-] / (F \bullet [COOH] + [COO^-])$



Poly(maleic acid-co-propylene):

FTIR spectra on solutions with different dissociation degrees
α = 0, 0.25, 0.5, 0.75, 1.0 (bottom to top)

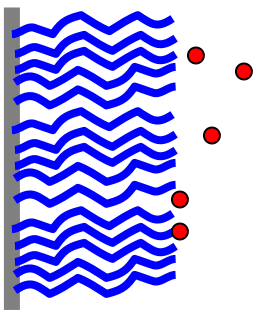
Relation α / pH:

$pH = pK + \log(\alpha / (1 - \alpha))$ or
$pH = pK + \log([COO^-] / [COOH])$

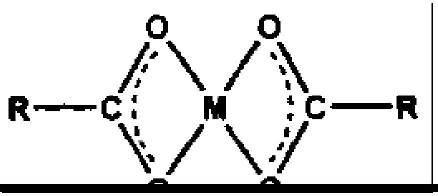
2. TRANS-IR (B): Complexation of cations by polyacids

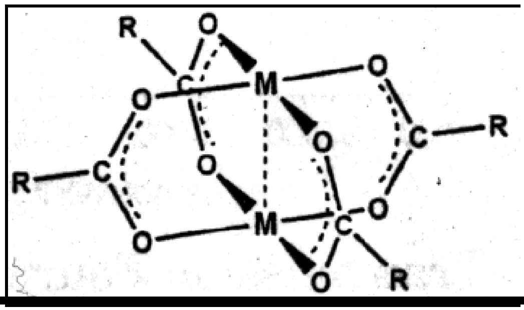
System: PMAC brush + metal ion

- McCluskey et al. and others studied poly(acrylic acid) copper ion complexes and assigned the peaks at 1559 and 1616 cm^{-1} in accordance with the data for monomeric acetate complexes.
- Poly(methacrylic acid) brushes form stable complexes with a variety of metal cations. Infrared spectra reveal different coordination geometries according to the nature of the cation. These lead to great differences in the stability of the complexes. Primarily the bridging bidentate coordination shows a greater stability than the chelating bidentate.



R-COO-M





monodentate 1567 cm^{-1}

chelating bidentate 1540-1559 cm^{-1}

bridging bidentate 1599 - 1616 cm^{-1}

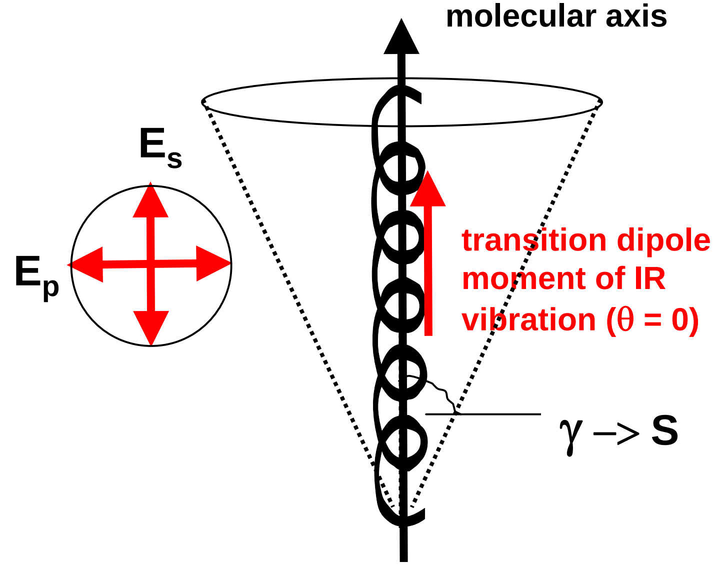
- **Results**

	monodentate	chelating bidentate	bridging bidentate
Cu^{2+}	---	xx	xxx
Al^{3+}	xxx	---	xxx
La^{3+}	---	xxx	---

R. Konradi, J. Rühe, *Macromolecules*, 37, 6957 (2004)
McCluskey, P. H.; Snyder, R.L.; Condrate, R. A.J., *SolidState Chem*. 1989, 83, 332-9.
Deacon, G. B.; Phillips, R. J. *Coord. Chem. Reu*. 1980, 33, 227-50.
Nicholson, J. W.; Wasson, E. A.; Wilson, A. D. *Br. Polym. J.* 1988,20,97-101.

(1) Samples

- stretched polymer foils
- oriented polymer films on texturised Si supports

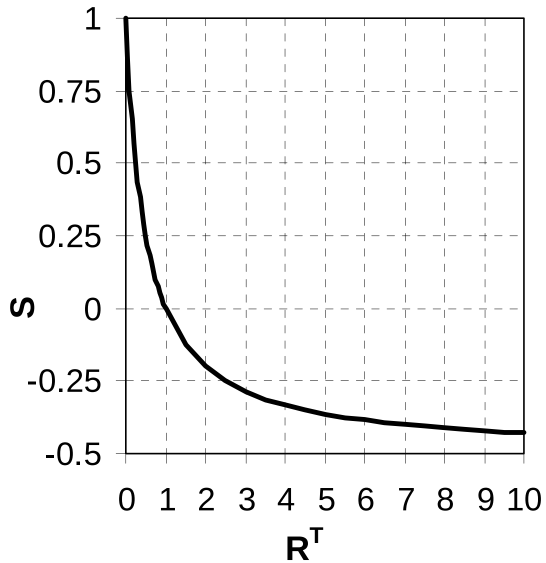


(2) Orientation analysis

$$R^T = \frac{A_p}{A_s}$$

$$S = \frac{(1-R^T)}{(2R^T+1)} \cdot \frac{2}{(3\cos^2\theta - 1)}$$

$$\gamma = \arccos\left(\sqrt{\frac{2}{3}S + \frac{1}{3}}\right)$$



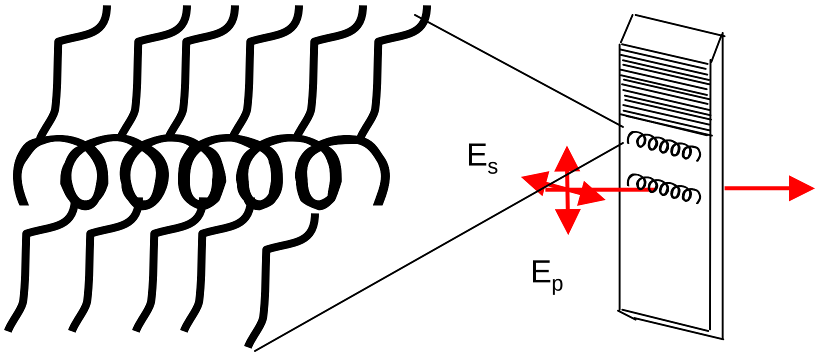
Abh. zwschen R^T und S für θ = 0.

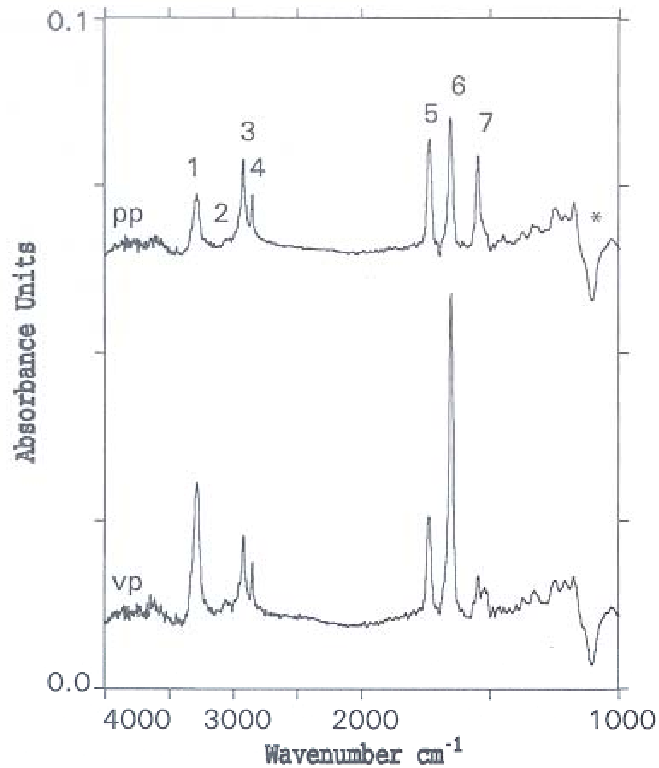
R^T:	Dichroic ratio
θ:	Angle: transition dipole moment/molecular axis
S:	Order parameter
S = 1:	Perfect parallel orientation to director field
S = 0:	No orientation
S = -1/2:	Perfect vertical orientation to director field

R. Zbinden, *IR-Spectroscopy of High Polymers*, Academic Press, NY (1964)
M. Müller, B. Keßler, K. Lunkwitz, *J. Phys. Chem. B*, 107, (2003)

Orientation of hydrophobic polypeptides on texturised supports

Poly(methylglutamate-co-octadecylglutamate)



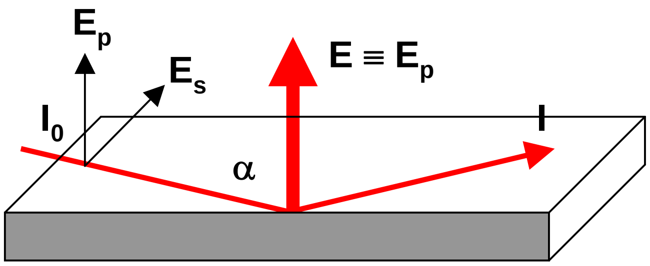


Resultate

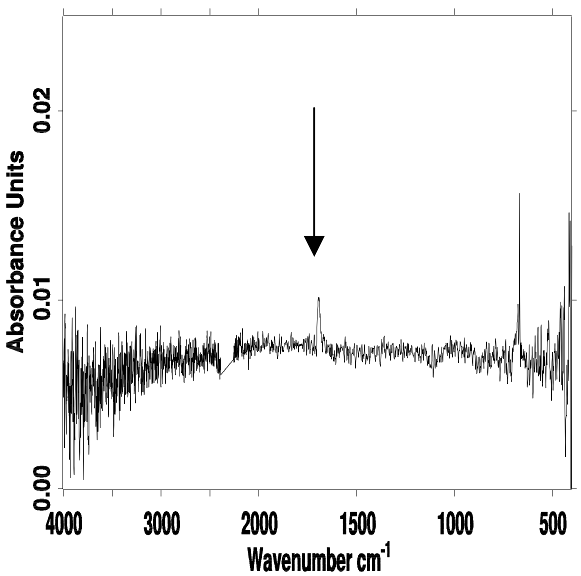
	θ	R	S	γ_0
Amid A	28°	0.43	0.5	34°
Amid I	38°	0.46	0.5	36°
Amid II	73°	1.63	0.4	41°

F.J. Schmitt and M. Müller, *Thin Solid Films*, 310, 138 (1997)

Principle



Detection limit



GIR spectrum of PMI-P layer on Si-IRE (76°).

Charakteristics

•For grazing incidence (α = 76°) a standing wave (E) is formed at the solid/liquid interface by superposition of incoming and outcoming IR radiation.

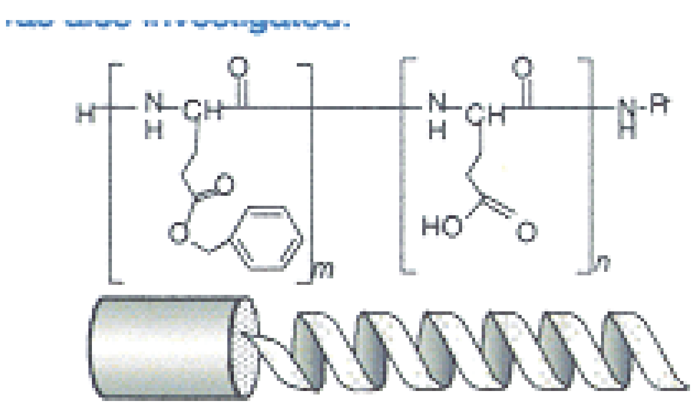
• This only holds for the p-component i.e. only E_P is active ! (phase shift δ =0°)

• The s-component is not active (phase shift δ = 180°)

Peak intensity ν(C=O):	0.003 ± 0.001
Surface conc:	5.952 µg/cm2
DL:	**≈ 2 µg/cm².**

z-axis orientation

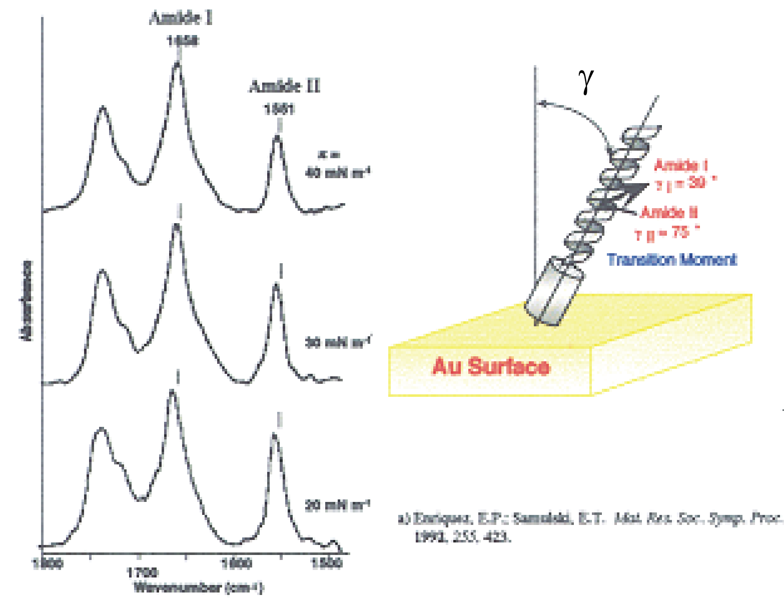
of poly(glutamic acid-co-benzylglutamate).
The polymer were deposited on gold substrates by LB technique under variation of surface pressure.



PBLG-b-PLGA (m = 17, n = 38)

from:
N. Higashi, T. Koga and M. Niwa, presented at the ACS Spring Meeting, April 1-5, San Diego (CAL) (2001)

7 RA-FTIR Spectra of PBLG-b-PLGA LB Films Transferred at Various Surface Pressures, pH 4.0, 20 ℃



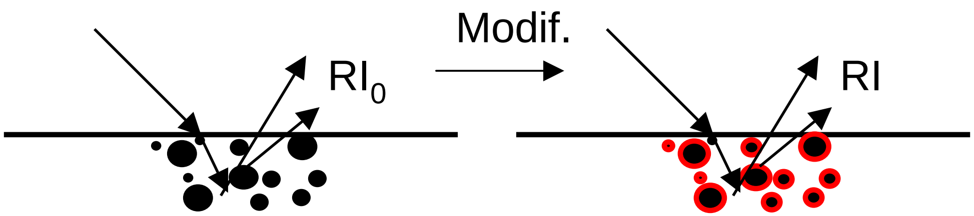
Amide I to Amide II Integrated Intensity Ratio ($D = A_I / A_{II}$) and the Average Tilt Angle of the Helix Axes from the Surface Normal γ at Various Surface Pressure

Surface Pressure (mN/m)	$D = A_I / A_{II}$	γ
20	2.4	45°
30	2.8	40°
40	3.8	33°

Orientation analysis

$$A_{AMIDE\ I}/A_{AMIDE\ II} = \varepsilon_1/\varepsilon_2\ [½\ (\sin\gamma\ \sin\theta_I)^2 + (\cos\gamma\ \cos\theta_I)^2]\ /\ [1/2\ \sin\gamma\ \sin\theta_{II})^2 + (\cos\gamma\ \cos\theta_{II})^2]$$

Principle

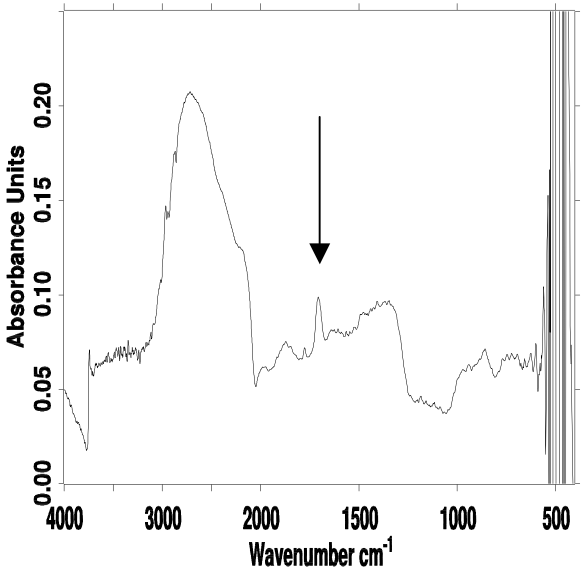


$$R(\nu) = RI(\nu) / RI_0(\nu)$$

From R the Kubelka-Munk function KM, which is an approximation for the absorbance of the scattered light, may be calculated according to:

$$KM(\nu) = [1 - R(\nu)]^2 / 2R(\nu)$$

Detection limit



DRIFT spectrum of silica modified by PMI-P (polymer/silica ratio: 1/50 w/w in 10 ml water).

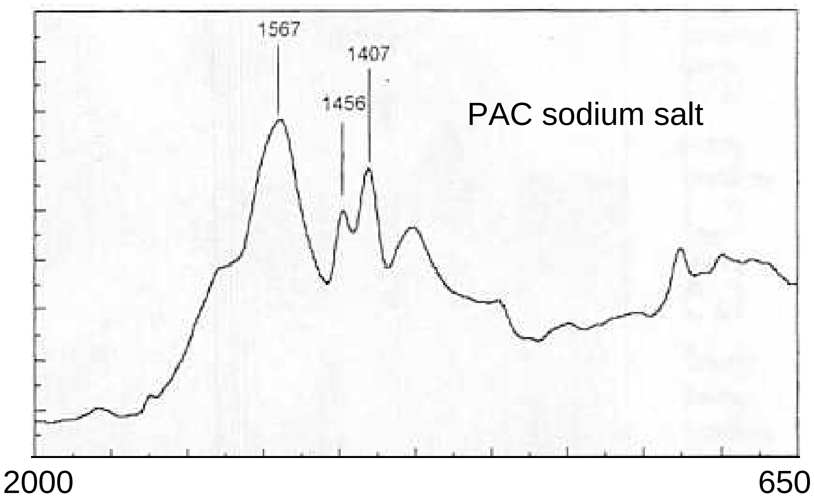
Peak intensity ν(C=O):	0.032 $\pm$ 0.001
Polymer/silica:	1/50
DL:	**1/1600**

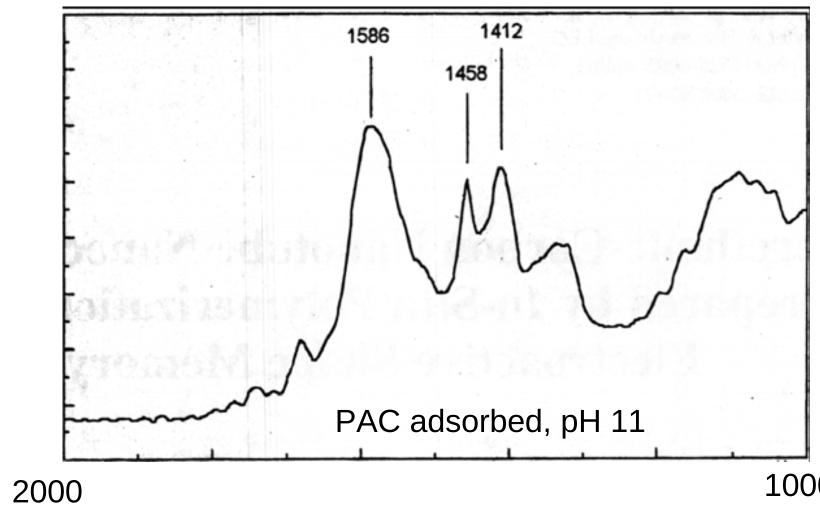
2. Diffuse Reflexion Spectroscopy: Flocculant adsorption on hematite

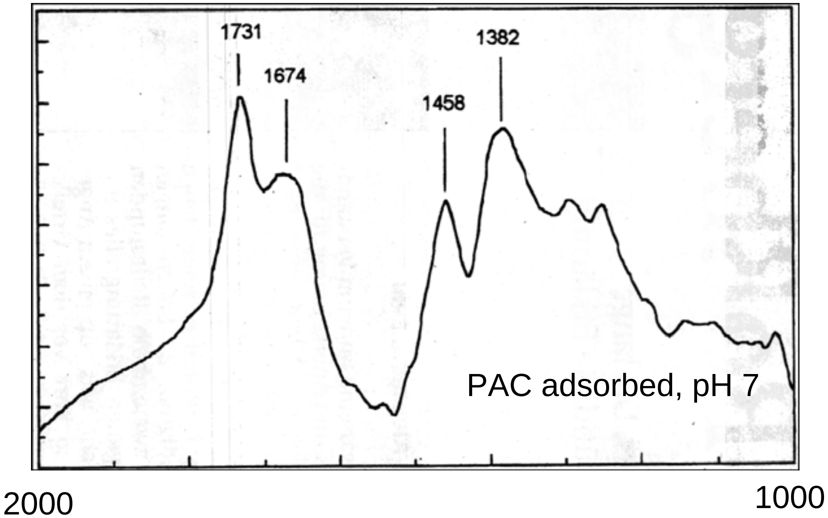
Sample: Fe_2O_3 (d_{10} – d_{90}: 0.24 – 9.5 µm)
Flocculant: **sodium polyacrylate** (14.000.000 g/mol) (PAC)

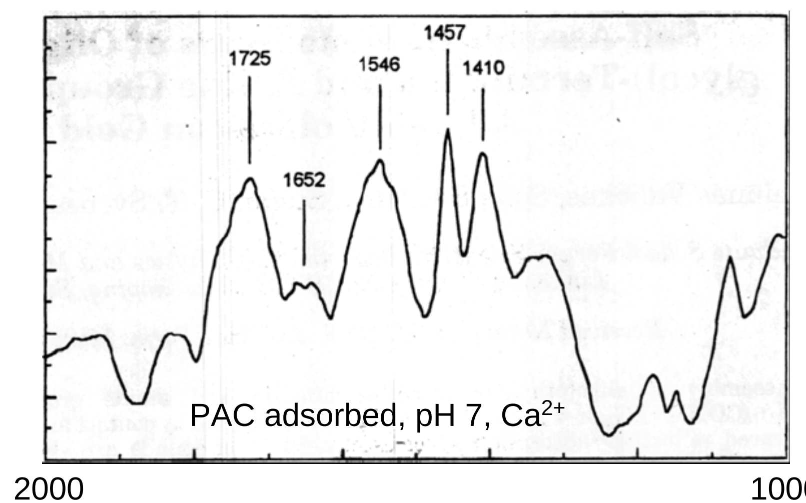
F. Jones, J.B. Farrow, W.v. Bronswijk, *Langmuir,* 14 6512 (1998)

DRIFT spectra









2. Diffuse Reflexion Spectroscopy: Flocculant adsorption on hematite

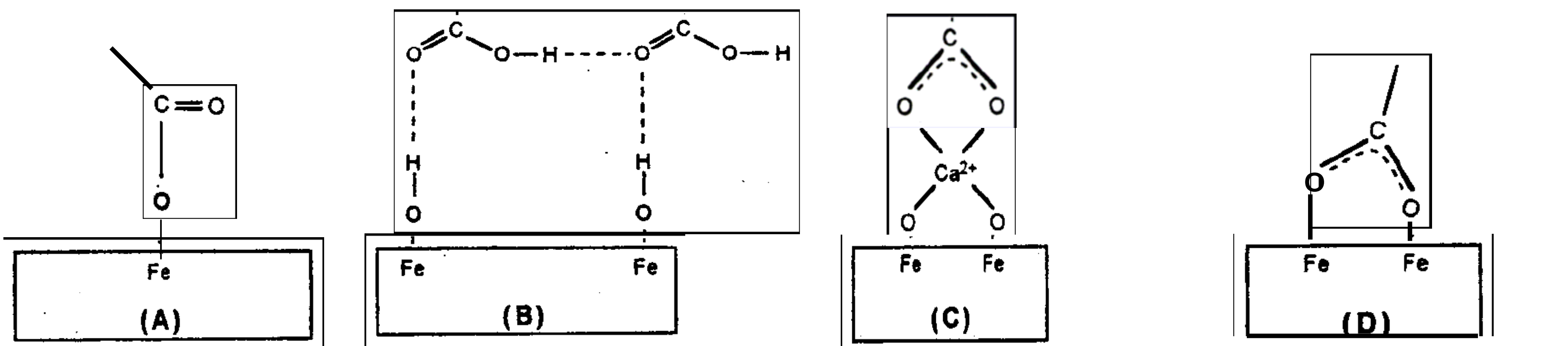
Obtained wavenumbers [cm^{-1}]:

	$\nu_a(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu$
Na^+ salt	1567	1407	160
Ca^{++} salt	1552	1411	141
pH 7	1674	1382	292
pH 11	1586	1412	174
pH 14	1599	1411	188
pH 7, Ca^{++}	1652	1410	242
	1546	1410	136
pH 14, Ca^{++}	1585	1406	179

Rules:

(1)	**If $\Delta\nu$ (adsorbed) > $\Delta\nu$ (salt) + ν(C=O) present**
->	***Monodentate***
(2)	**If $\Delta\nu$ (adsorbed) < $\Delta\nu$ (salt) + ν(C=O) abesent**
->	***BIdentate chelating***
(3)	**If $\Delta\nu$ (adsorbed) $\approx$ $\Delta\nu$ (salt) + ν(C=O) abesent**
->	***Bidentate bridging***
	if $\Delta\nu$ (adsorbed) is a little bit higher
->	***Assymmetric bridging bidentate***

Proposed binding structures PAC/hematite



Monodentate, pH 7

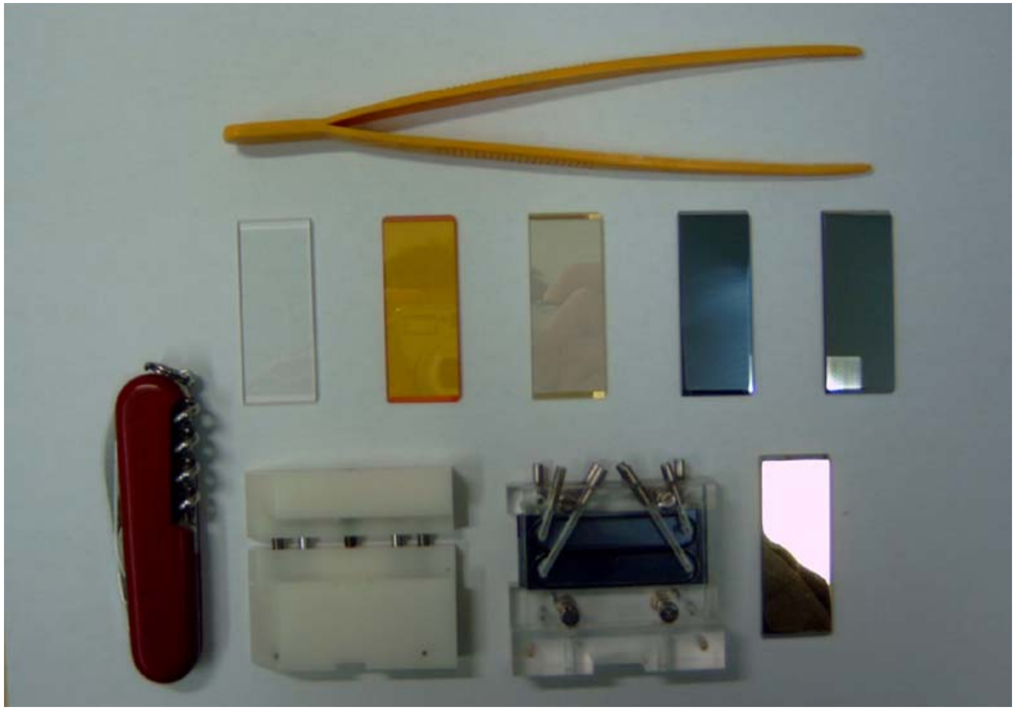
Hydrogen bonded, pH 7

Chelating bidentate via Ca^{2+}, pH 7

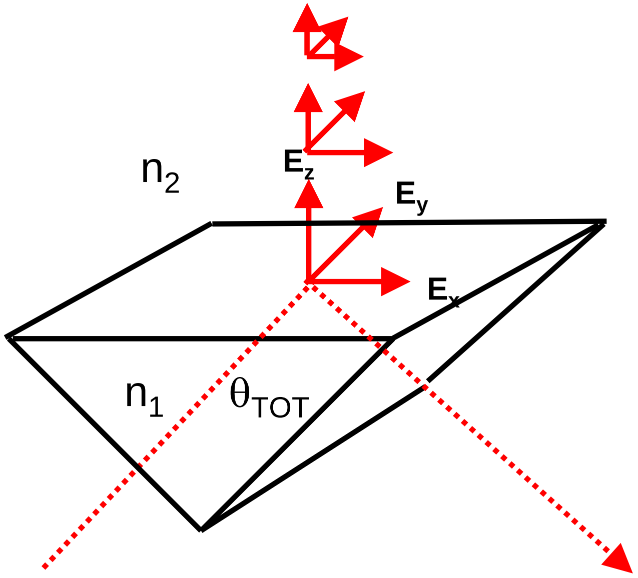
Assymm. bidentate, pH 11 to 14

F. Jones, J.B. Farrow, W.v. Bronswijk, *Langmuir,* 14 6512 (1998)

3. Attenuated total reflexion infrared (ATR-IR)



Principle



Condition for total reflexion

$\theta_{TOT} > \theta_{CRIT} = \arcsin(n_2/n_1)$

Penetration depth

$d_p = \lambda/(2\,\pi\,n_1\,[\sin^2\theta - n_{21}{}^2]^{1/2})$

Electrical field

$E_{x,y,z} = E_{0\;x,y,z}\exp(-z/d_p)$

Electrical field components

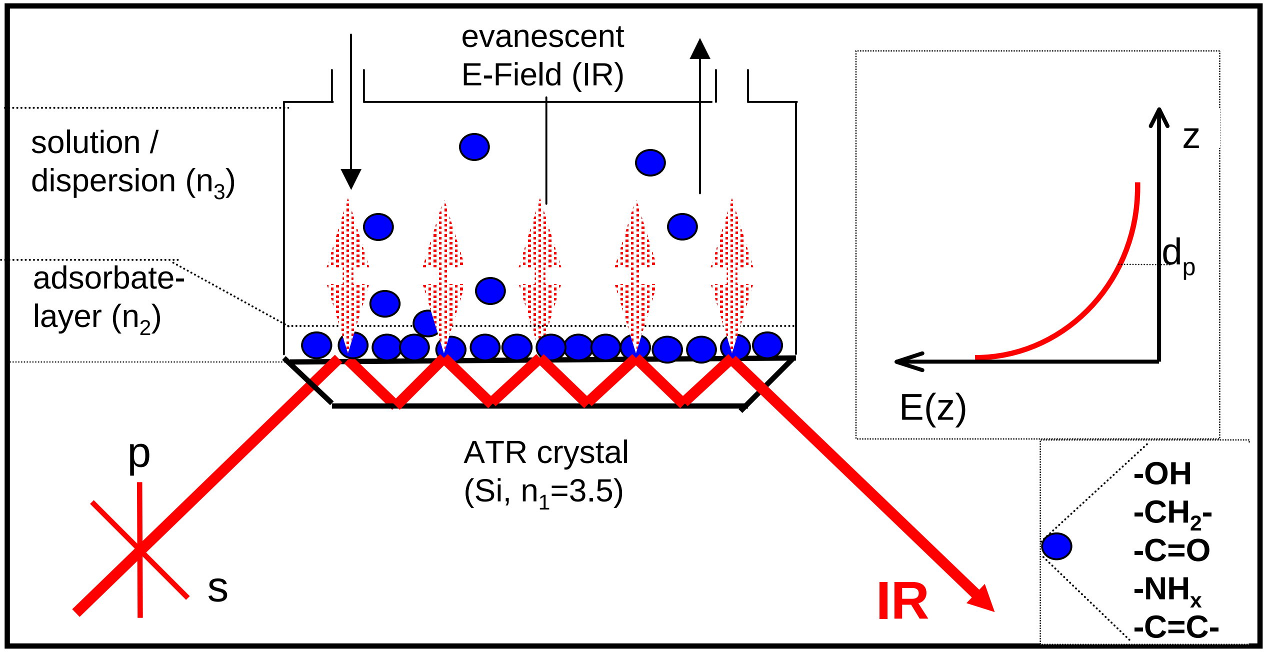
z.B. $E^r{}_{02y} = E_{02y}/E_{01\perp} = 2\cos\theta\,/\,(1 - n^2{}_{31})^{1/2}$

Characteristics

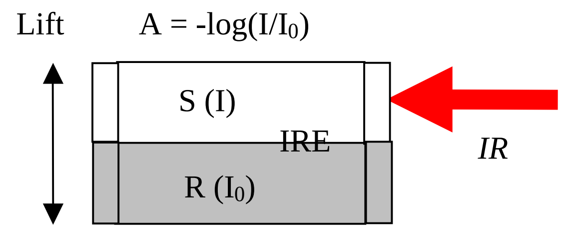
Under conditions of total reflexion a **standing wave** or **evanescent field** is established at the solid/liquid (gas) interface by superposition of incident and reflected (IR) radiation:

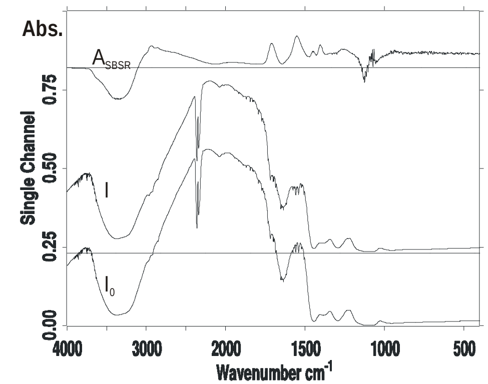
- intensity falls off exponentially in the rare medium
- 3 electrical field components in space (E_x, E_y, E_z)

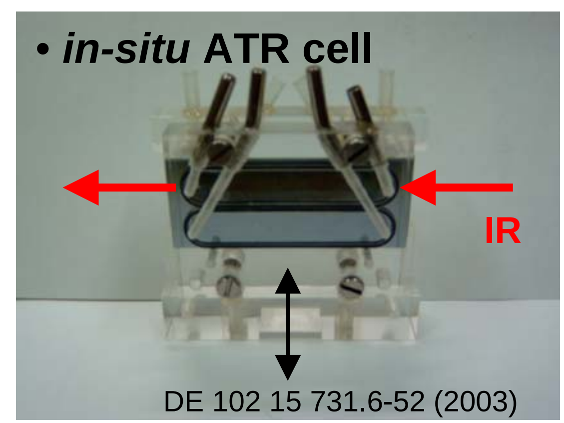
Principle



SBSR-Technik







Options

- **Detection**: Ad-, ab-, chemisorption, chemical composition, water content, dissociation degree, H-bonding at C=O groups, kinetics.
- **Conformation**: polypeptide, proteins, PEO ...
- **Orientation:** ATR dichroism of characeristic IR polymer bands

M. Müller, in ´Handbook of Polyelectrolytes´, Eds. S.K. Tripathy, J. Kumar, H.S. Nalwa, Vol. 1, ASP, 293-312 (2002)

Polarisation dependent absorbance:

$$\mathbf{A_S} = -\log (I/I_0) = \mathbf{N}\ \varepsilon\ \mathbf{c}\ \mathbf{d_{E,S}}$$

A_S: Absorbance (s-pol.) ε: Absorption coefficient c: concentration N: number of refl.

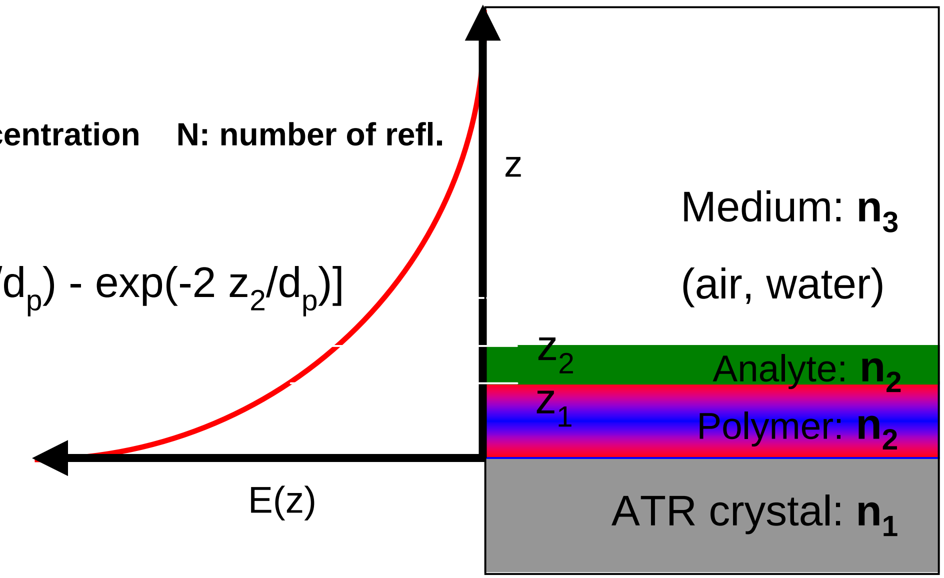
Effective thickness:

$$d_{e,y} = n_{21}\, d_p\, E_y^{\,2} / (2 \cos \theta)\ [\exp(-2\, z_1/d_p) - \exp(-2\, z_2/d_p)]$$

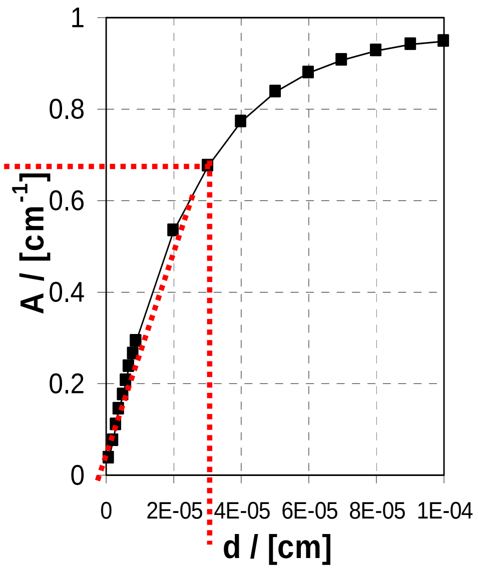
Surface concentration:

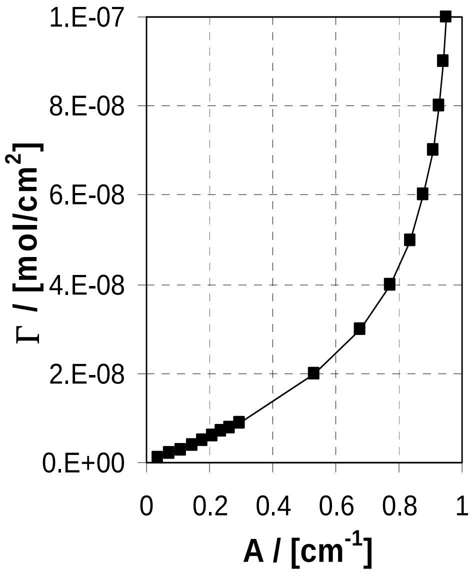
$$\Gamma = c\ d$$

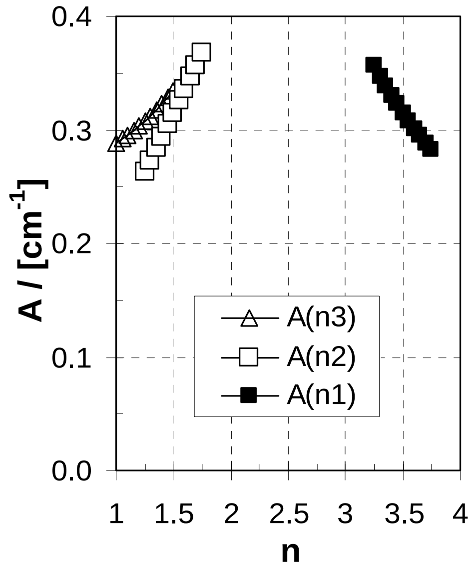
$$\Gamma_{MIN} = 200\ \text{pmol/cm}^2 \cong 20\ \text{ng/cm}^2$$



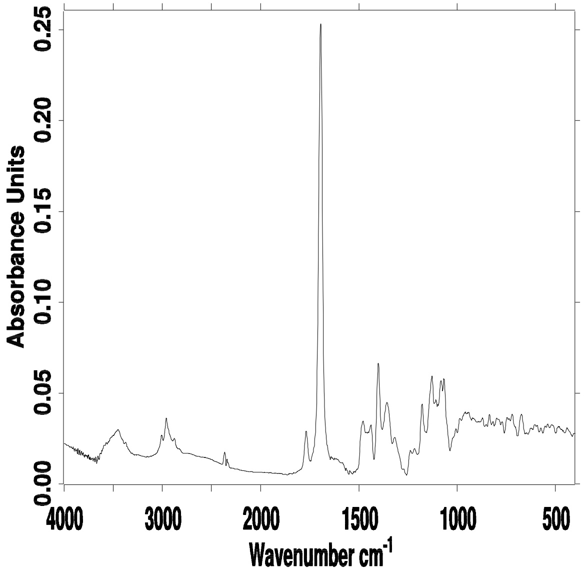
Characteristic plots







3. ATR-FTIR: Detection limit



ATR-FTIR spectrum of the PMI-P layer on the Si-IRE.

Peak intensity ν(C=O):	0.250 <u>+ 0.001</u>
Surface conc:	5.952 μg/cm^2
DL:	**0.024 μg/cm^2.**

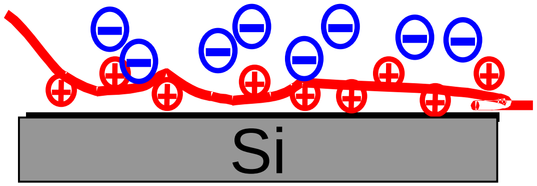
3.1. Detection, chemical composition
- (consecutive) PEL adsorption
- Dissociation degree
- Chemical composition (polyelectrolyte complexes/multilayers, blends)
- Hydrogen bonding (ν(C=O) shift, $\nu_a(COO^-)/\nu_s(COO^-)$ splitting)

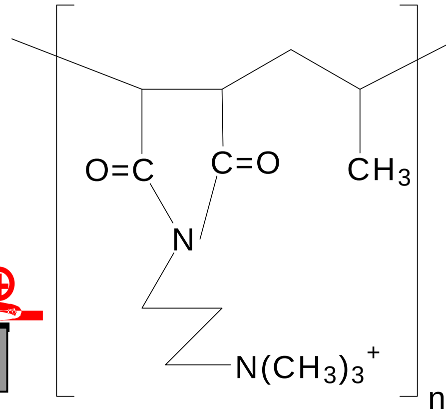
3.2. Polymer conformation and orientation
- Reversible conformation changes
- *in-plane* orientation of multilayered polypeptides on texturised substrates

3.3. Interaction
- Salt, chiral compounds
- Protein adsorption
- Diffusion in polymer films

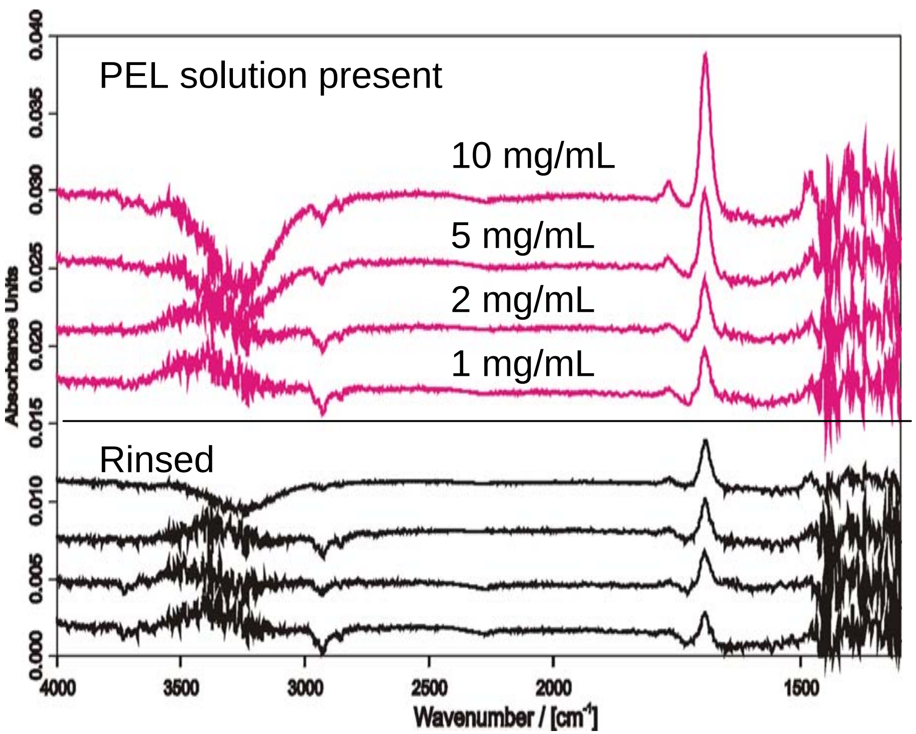
3.4. Combination with other methods
- Elektrokinetics
- Ellipsometry

System: PMIP



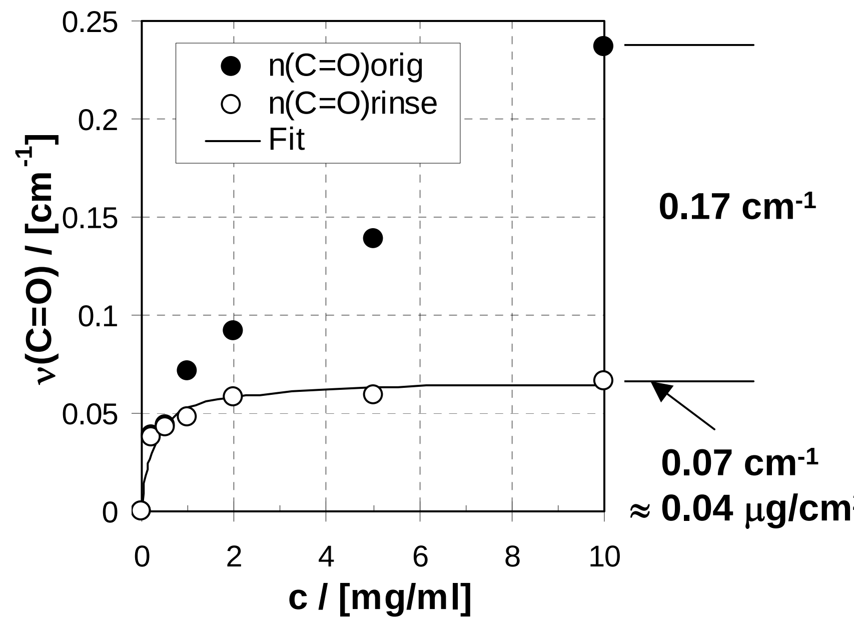


ATR-FTIR spectra



Adsorption isotherm

$$\theta = c_{PEL} / (k_{DES}/K_{ADS} + c_{PEL})$$



Estimation of the contribution from bulk c_{PEL} = 10 mg/mL ≈ 0.05 Mol/L) :

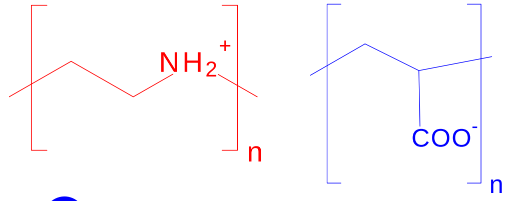
$A = N\,\varepsilon\,c\,d_E$

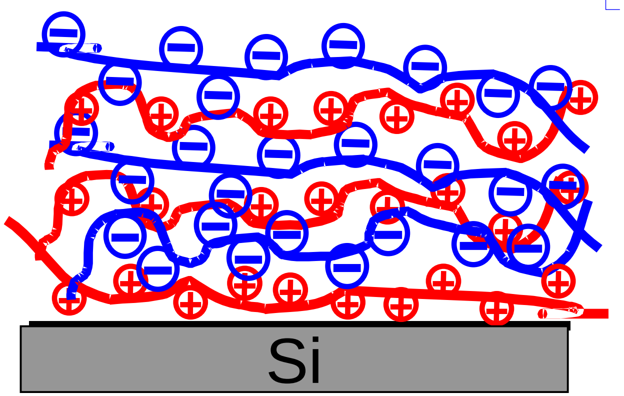
$A \approx 11 \times 1\;10^{7}\;0.05\;3\;10^{-5}$ [cm Mol^{-1} cm Mol/(1000 cm^3)]

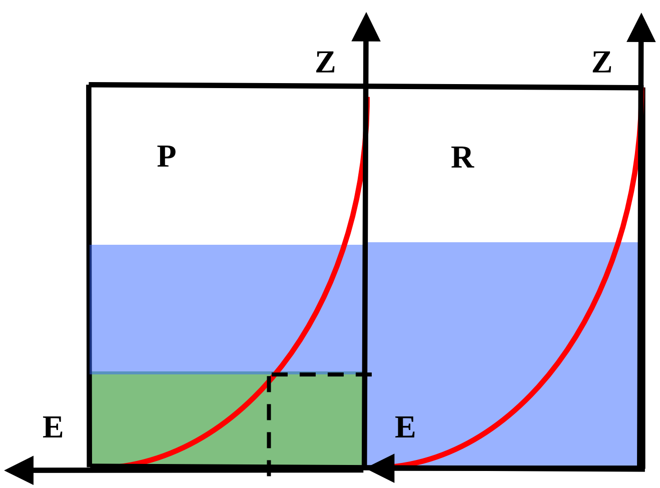
$A \approx 0.17\ cm^{-1}$

3.1. ATR-FTIR Detection: consecutive PEL adsorption

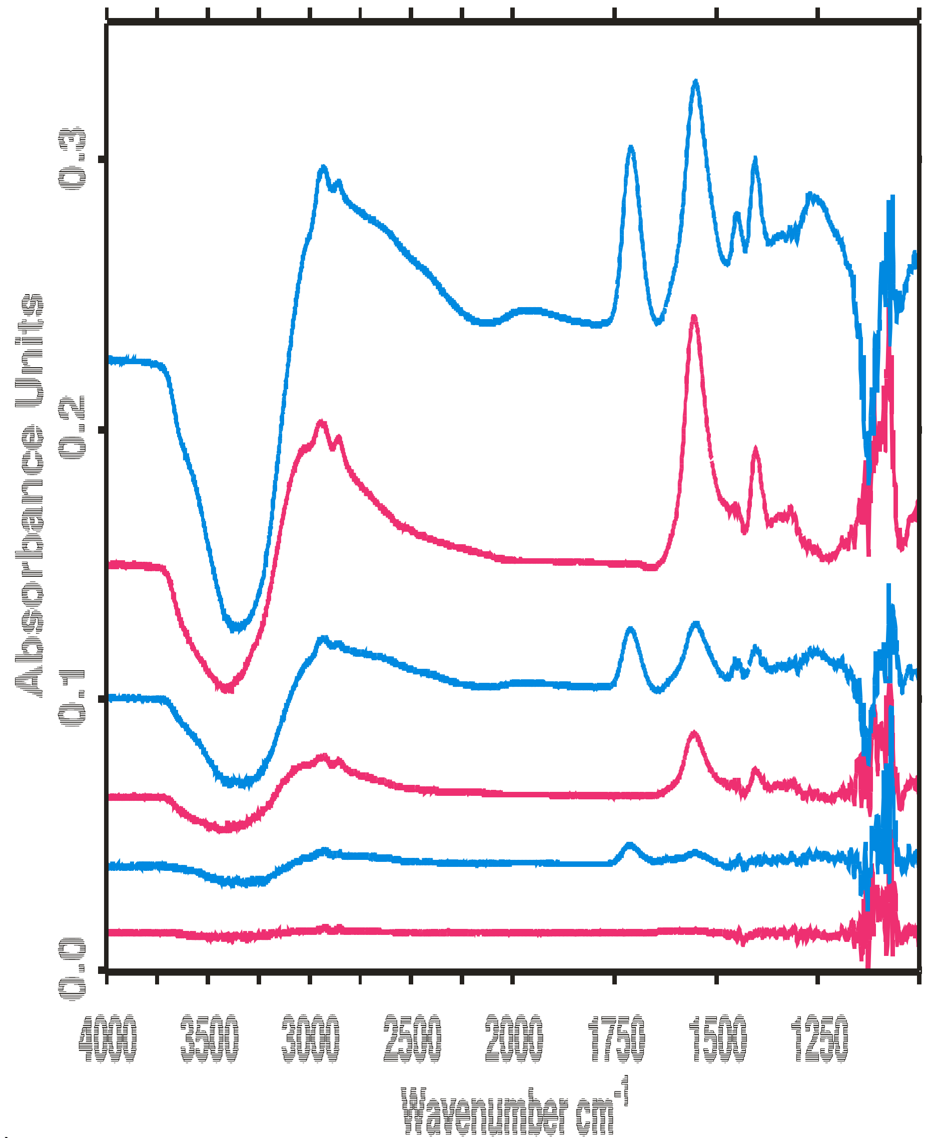
System: PEI/PAC







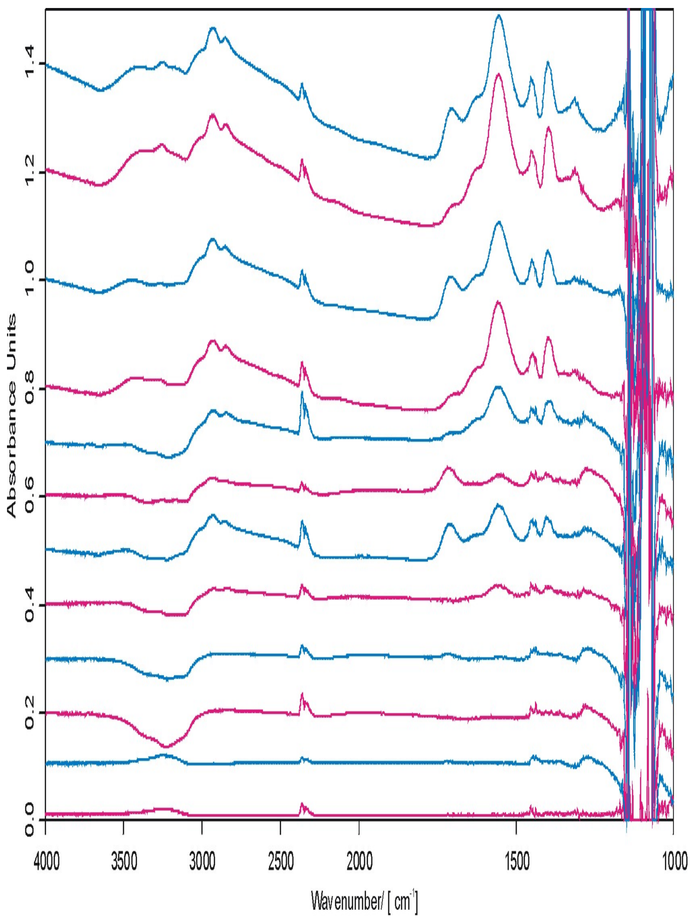
ATR-FTIR spectra

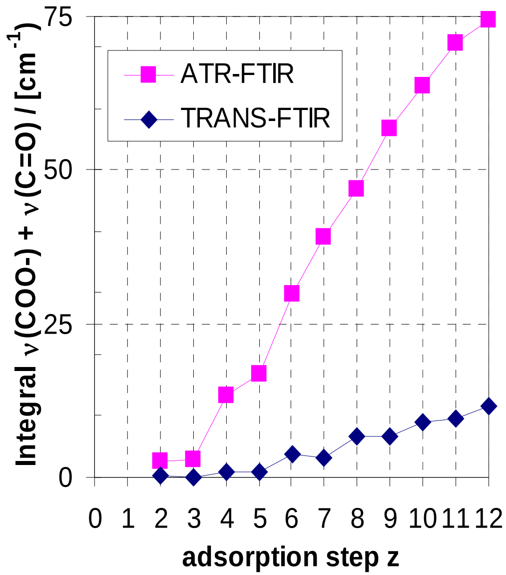


M. Müller, ATR-FTIR Spectroscopy at Polyelectrolyte Multilayer Systems, in ´*Handbook of Polyelectrolytes and Their Applications*´, Eds. S.K. Tripathy, J. Kumar, H. S. Nalwa, Vol. 1, American Scientific Publishers (ASP), 293-312 (2002)

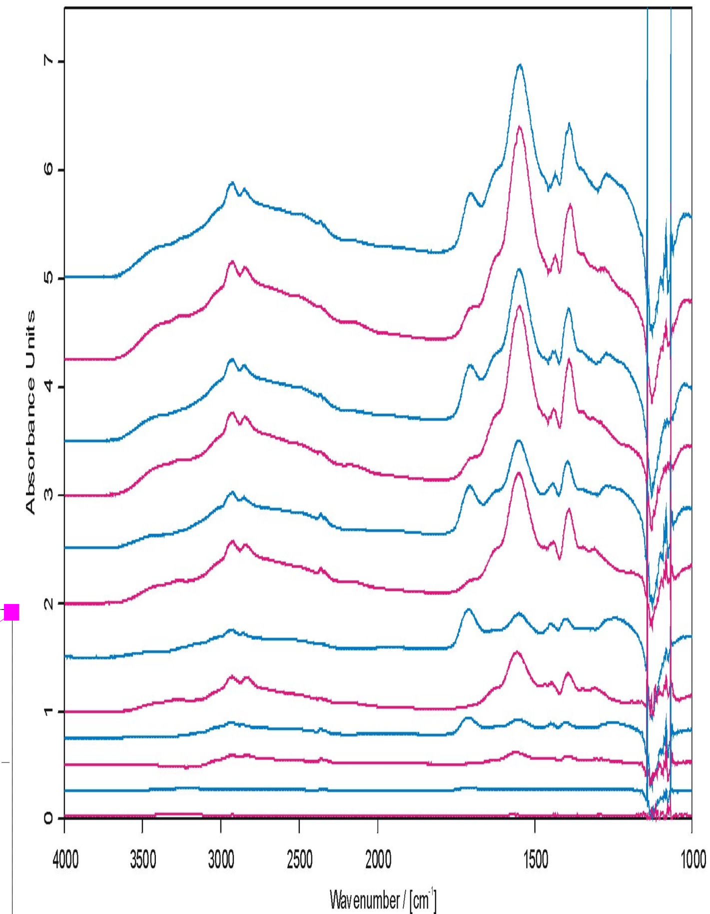
3.1. ATR-FTIR detection: consecutive PEL adsorption

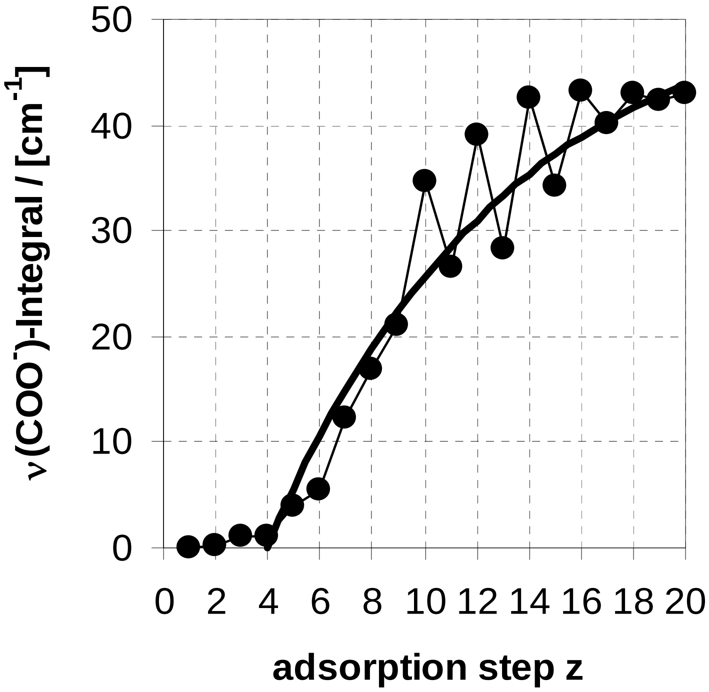
TRANS-FTIR spectra

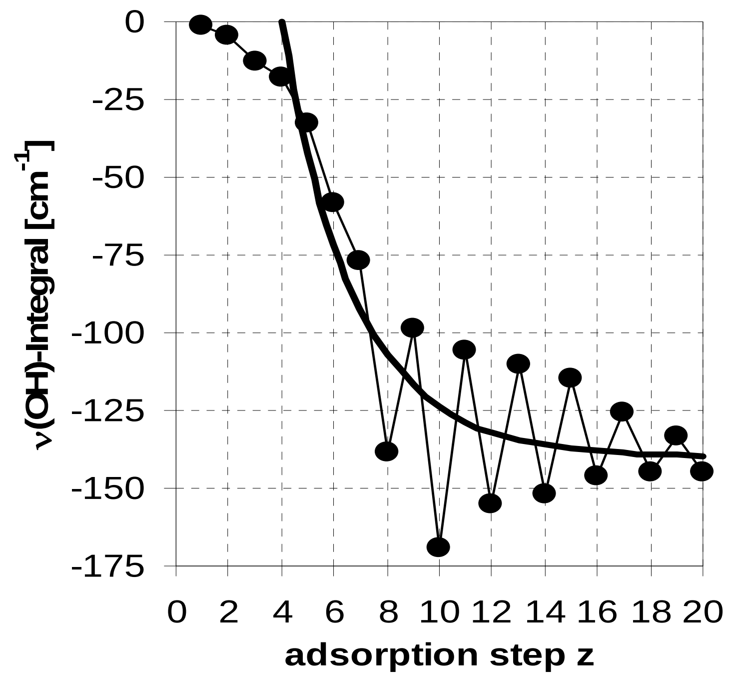




ATR-FTIR spectra





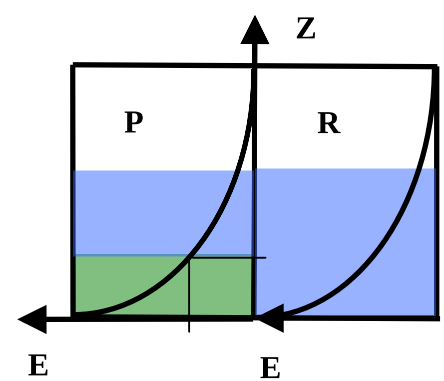


PEL adsorption

$A(z)=A_0\,[1 - \exp(-L\,(z - z_0))]$

Water desorption

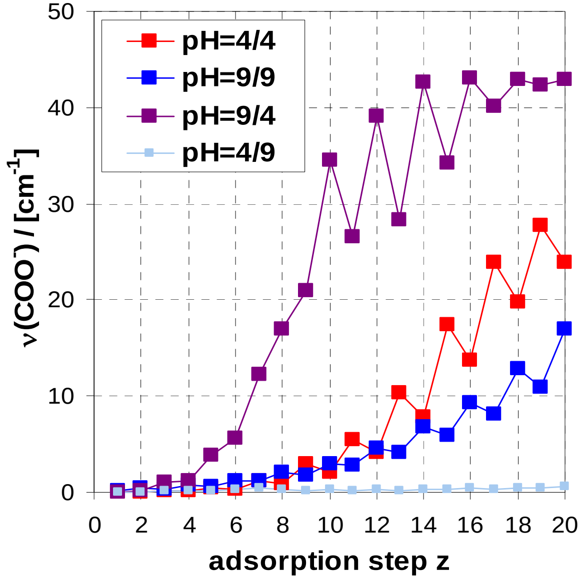
$A(z)= -A_0\,[1 - \exp(-L\,(z - z_0))]$



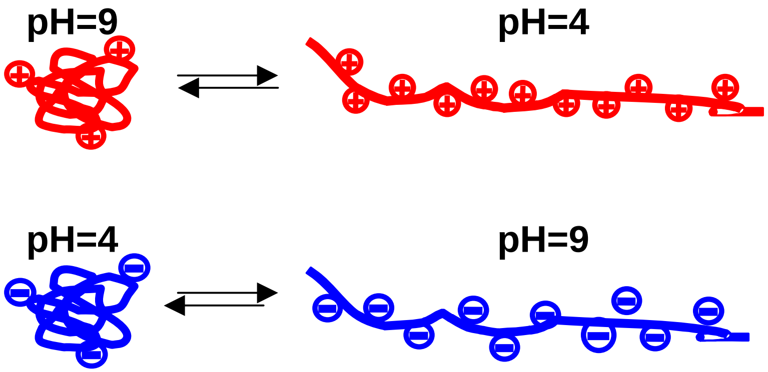
$d_0 = L/2\, d_P$
$d_0 \approx 34$ nm
(wet state)

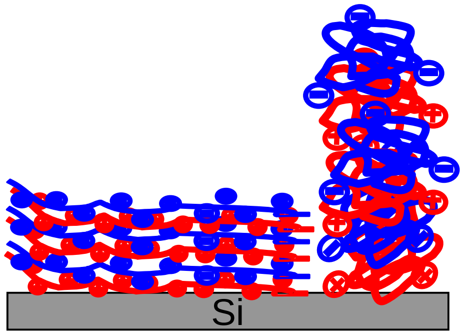
3.1. Consecutive PEL adsorption: pH dependence

System: PEI/PAC
pH = 9/4, 4/4, 9/9, 4/9



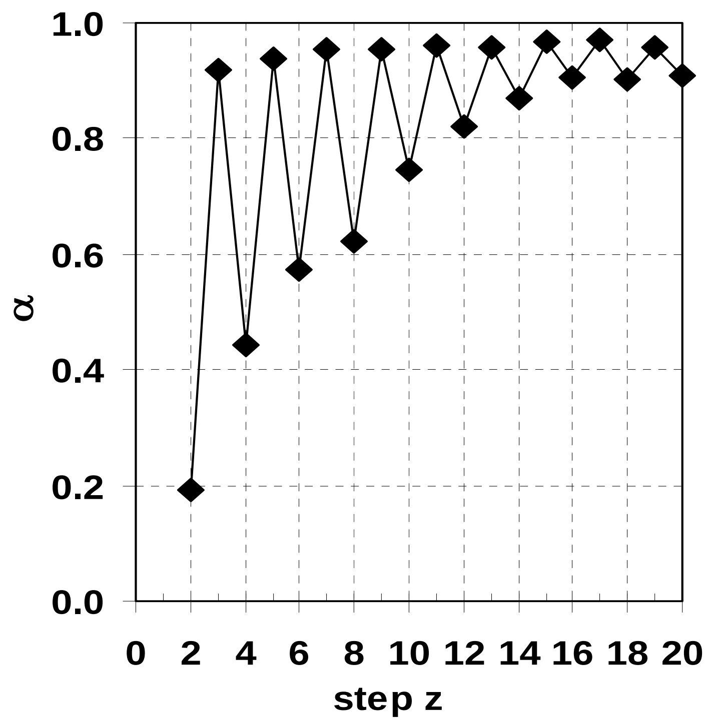
pH	9/4	4/4	9/9	4/9
L	0.148 ±0.015	0.065 ±0.011	0.015 ±0.001	0.0003
Δd_{ATR} (wet)	34 ±5 nm	15 ±4 nm	4 ±1 nm	<1nm
Δd_{AFM} (wet)	40 ±6 nm	-	-	-
$\Delta d_{AFM/ELL}$ (dry)	25 ±5 nm	–	–	–



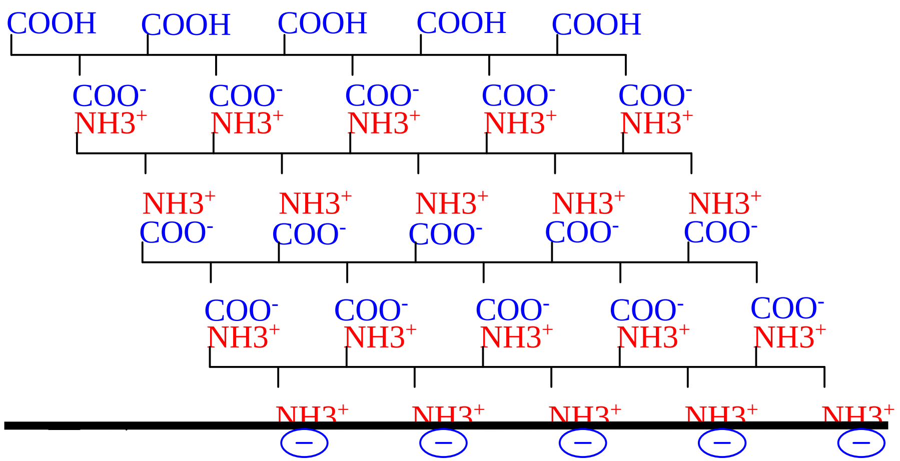


M.M. et al., *J. Adhesion*, 80(6), 521 (2004)

3.1. Consecutive PEL adsorption: dissociation degree



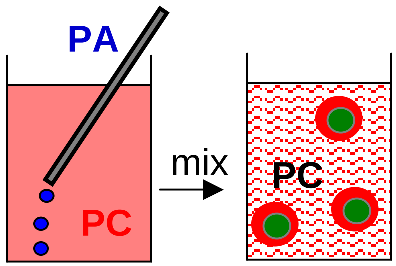
Simplified PEM model

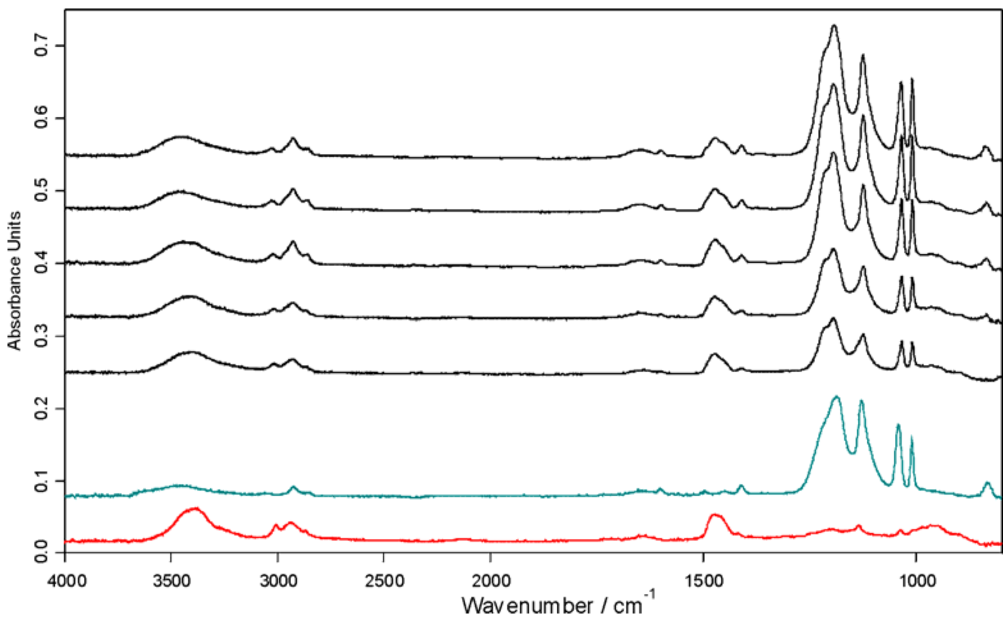


Dissociation degree:

$\alpha_{IR} = A_{\nu(COO^-)} / (A_{\nu(COO^-)} + 1.74\, A_{\nu(C=O)})$

System: PDADMAC/PSS, c = 0.01 M





Integration (INT) or Factor Analyis (FA)

$$A_{PEC} = a * A_{Polyanion} + b * A_{Polycation}$$

n-/n+: experimental mixing ratio (SHOULD)
a/b: effective stoichometric ratio (IS)

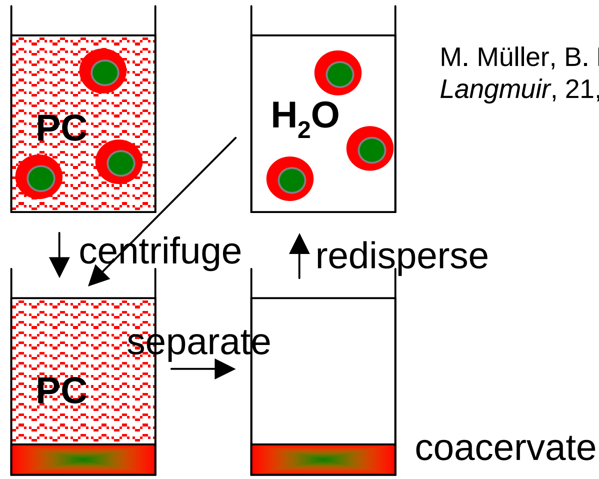
	Integration (I)	FA (II)
$A_{Polyanion}$:	1510-1430 cm-1	1510-990 cm-1
$A_{Polycation}$:	1280-1060 cm-1	1510-990 cm-1

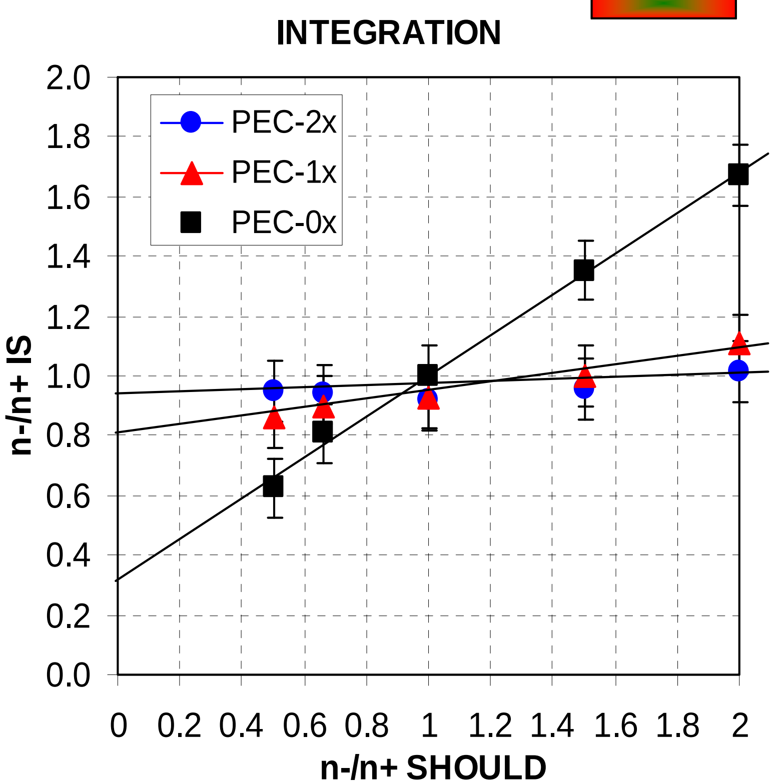
Results

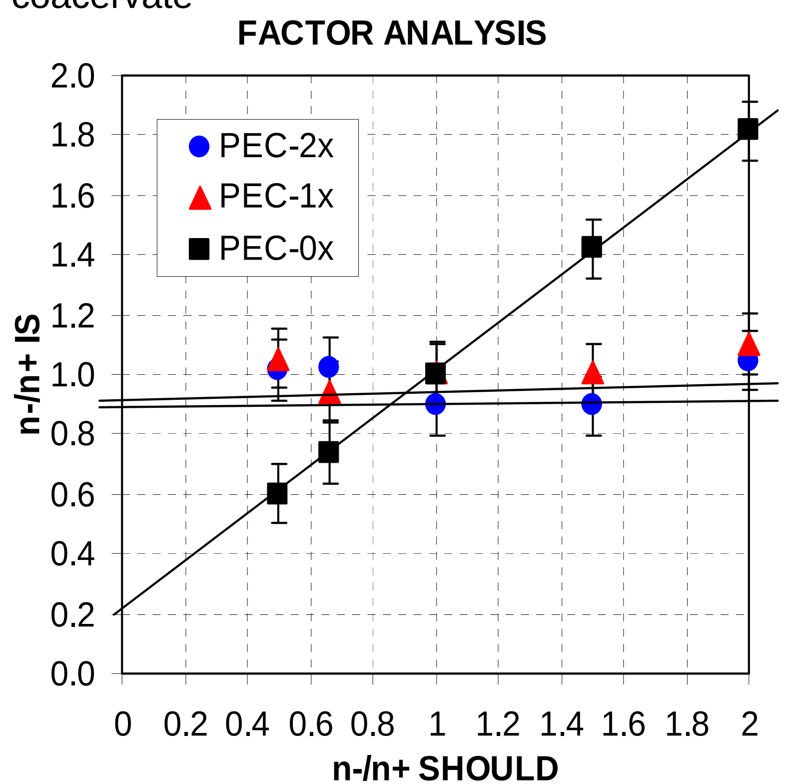
SHOULD n-/n+	IS (INT) n-/n+ (I)	IS (FA) n-/n+ (II)
0.50	0.63	0.60
0.66	0.81	0.74
1.00	1.00	1.00
1.50	1.35	1.42
2.00	1.67	1.81

3.1. Composition/Stoichometry of centrifuged polyelectrolyte complexes

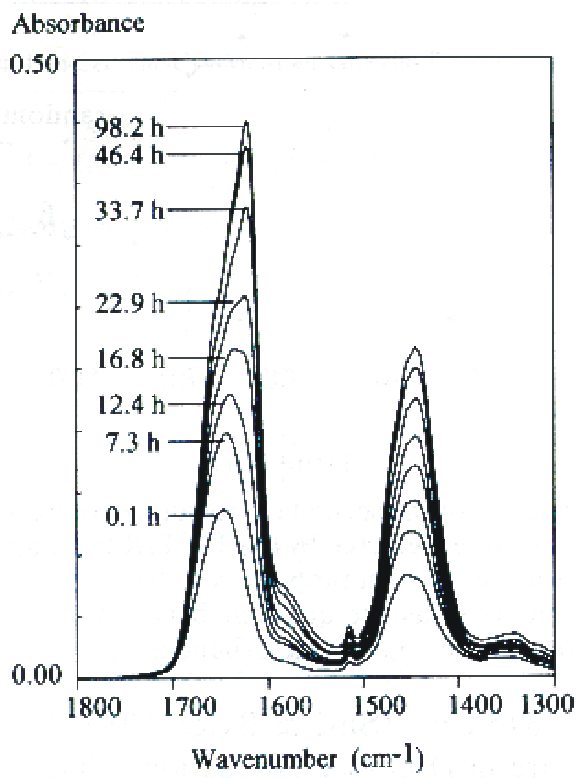
M. Müller, B. Keßler, S. Richter, *Langmuir*, 21, 7044 (2005)



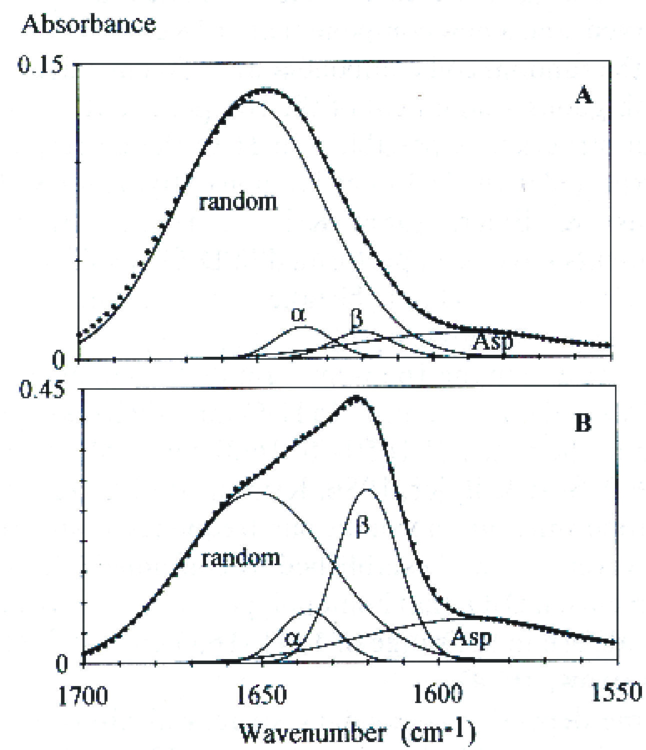




• **Validation of peptide drug: human calcitonin (osteoporose)**



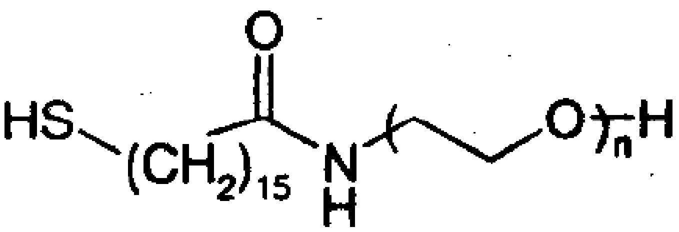
Adsorption of human calcitonin (hCT, former CIBA) at Ge model surface.

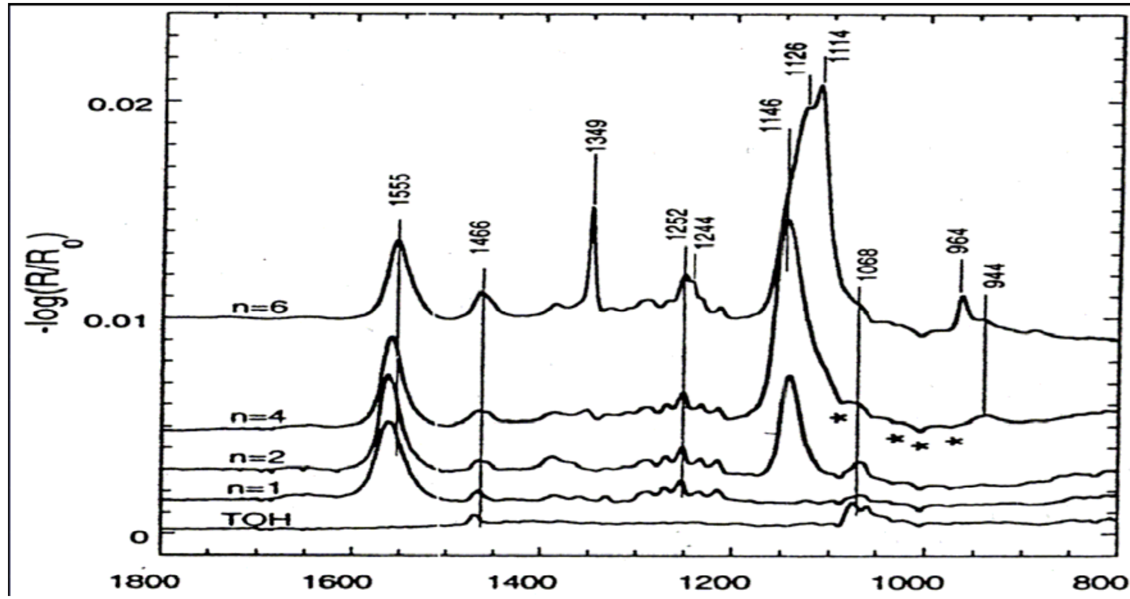


Conformation analysis of ATR-FTIR spectra at beginning and end of surface induced aggregation.

H. Bauer, M. Müller, J. Goette, H.P. Merkle, U.P. Fringeli, *Biochemistry* (1994)

SAM / Au





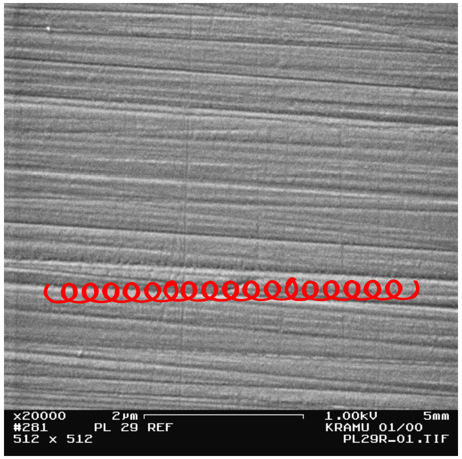
PEG, crystalline[a]	PEG, molten[a]	mode assignment[a]	polarization[b]	EG_1	EG_2	EG_4	EG_6
				2918	2918	2918	2918
				2850	2850	2850	2851
2890 s			∥				2893
2865 s	2865 s		∥		~2870	2868	2869
1470 m/1463 m			⊥/∥	1466	1466	1465	1466
1345 s			∥				1349
1244 m	1249 m		∥	1254[c]	1253[c]	1253[c]	1244/1252[c]
1149 s	1140 sh		⊥		1143	1146	~1146
1119 s			⊥				1126
1102 vs	1107 s		∥			~1108	1114
963 s		CH_2 rock, twist	∥				964
947 m	945 m	CH_2 rock gauche, C–C stretch	⊥			~938	944

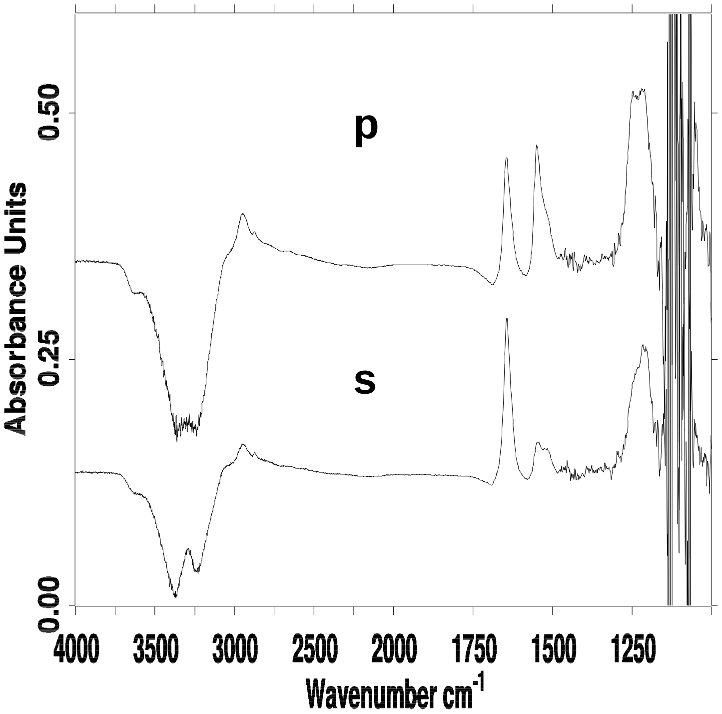
[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; asym, asymmetric; sym, symmetric. [b] Transition dipole moment with respect to the helical axis in crystalline PEG. [c] May overlap with the amide III band.

R. Valiokas, S. Svedhem, S.C.T. Svensson, B. Liedberg, *Langmuir*, 1999, 15, 3390
P. Harder, M. Grunze, R. Dahint, G.M. Whitesides, P.E. Laibinis, *J. Phys. Chem*. 1998, 102, 426-436

System:

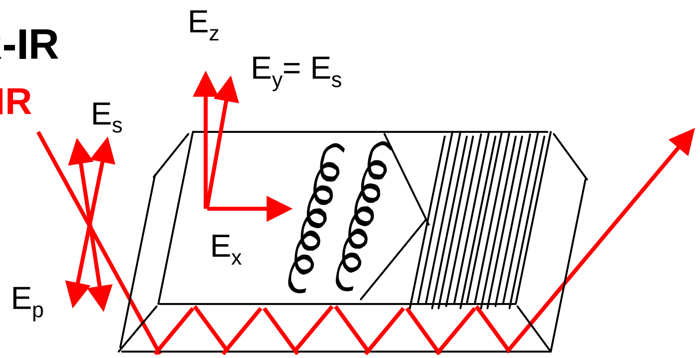
PEM-5 of PLL-246.000/PVS, 0.01 M, 1 M $NaClO_4$



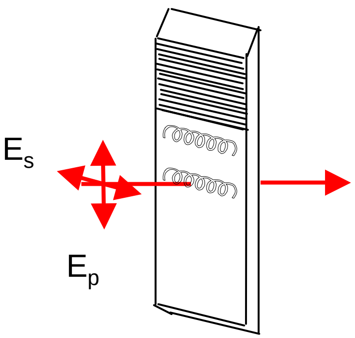


M. Müller, B. Keßler, K. Lunkwitz, *J. Phys. Chem. B*, 107, (2003)

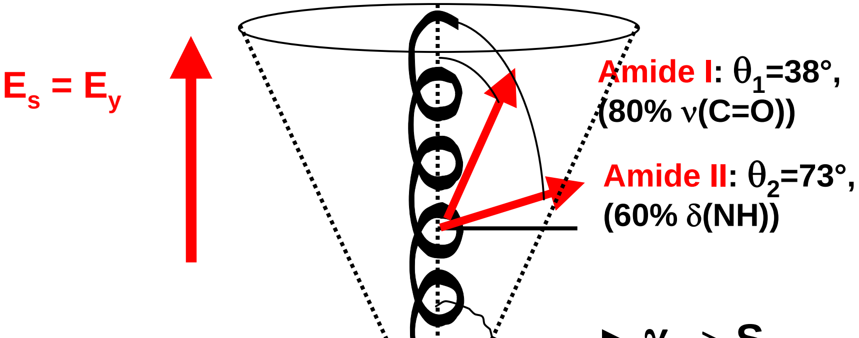
ATR-IR



Trans-IR



IR transition dipole moments $M_{\text{Amide I, Amide II}}$



$$A \propto \vec{E}^2 \bullet \vec{M}^2 \cos^2(\vec{E},\vec{M})$$

Dichroic ratio / ATR-IR

$$R_y^{ATR} = \frac{A_p}{A_s}$$

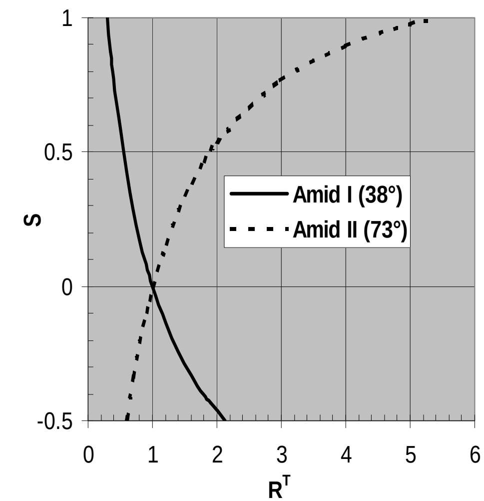
Dichroic ratio / Transmission-IR

$$R^T = R_y^{ATR} \cdot \frac{E_y^2}{(E_x^2 + E_z^2)}$$

Order parameter S

$$S = \frac{(1 - R^T)}{(2R^T + 1)} \cdot \frac{2}{(3\cos^2\theta - 1)}$$

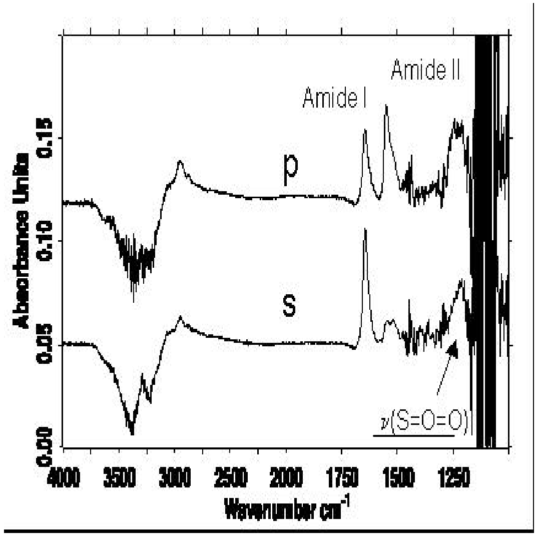
S= 0: no order
S= 1: high order (θ)
S= -1/2: high order (θ–90°)



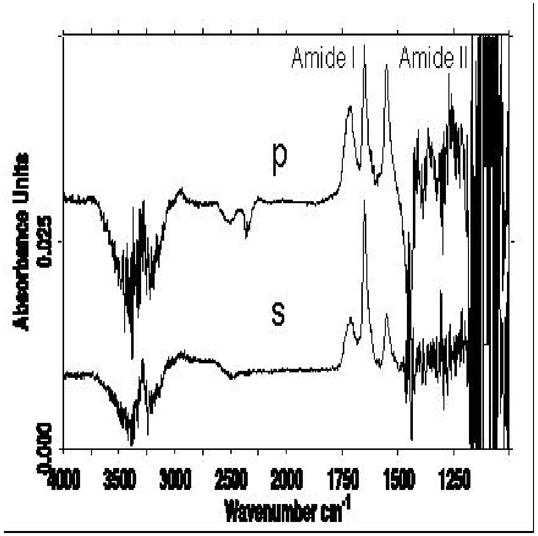
Cone opening angle γ

$$\gamma = \arccos\left(\sqrt{\frac{2}{3}S + \frac{1}{3}}\right)$$

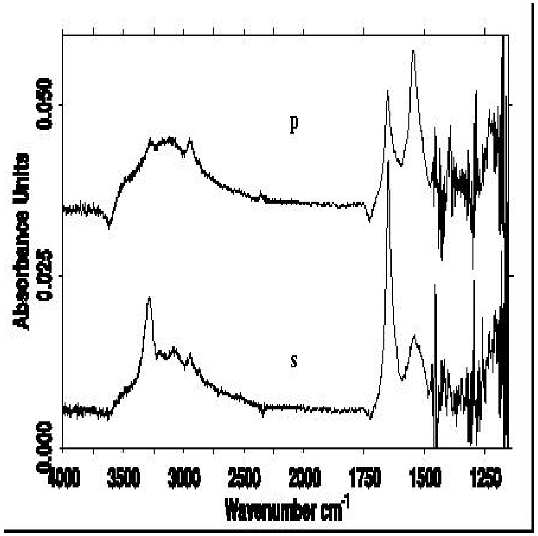
M. Müller, B. Keßler, K. Lunkwitz, *J. Phys. Chem. B*, 107 (32), 8189 (2003) α-PLL/PVS-5



PDADMAC/α-PLG-4



α-PLL/α-PLG-6

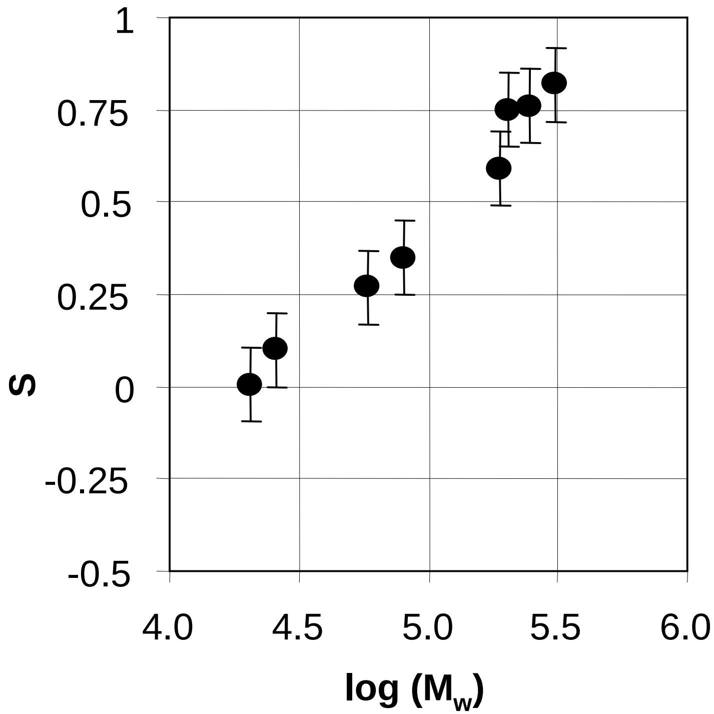


Dichroic ratio **$R_{Amide\ II}$**	**4.47**	**2.48**	**3.33**
Order Parameter **S**	**0.75**	**0.38**	**0.58**
Orientation angle γ	**24°**	**40°**	**32°**

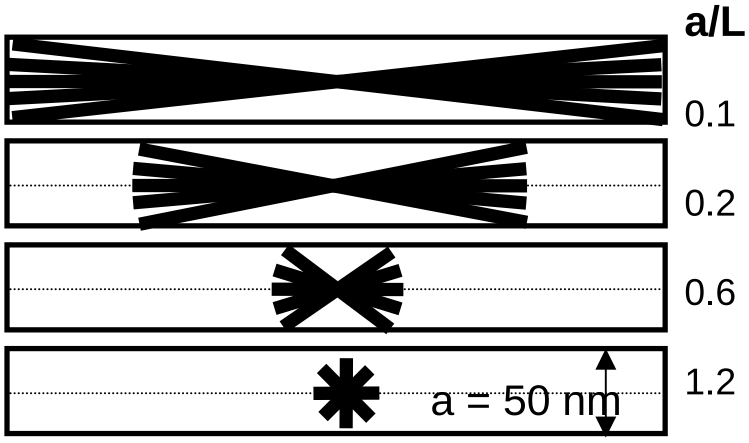
M. Müller, B. Keßler, K. Lunkwitz, *J. Phys. Chem.*B, 107 (32), 8189 (2003)

System: PEM-5 of α-PLL/PVS, 1M $NaClO_4$

M_w [g/mol]	L [nm]	S	γ [°]
3.400	3	---	---
20.700	15	-0.09	58
25.700	18	0.10	51
57.900	42	0.27	44
80.000	57	0.35	41
189.400	136	0.59	32
205.000	147	0.75	24
246.800	177	0.79	22
309.500	222	0.82	20

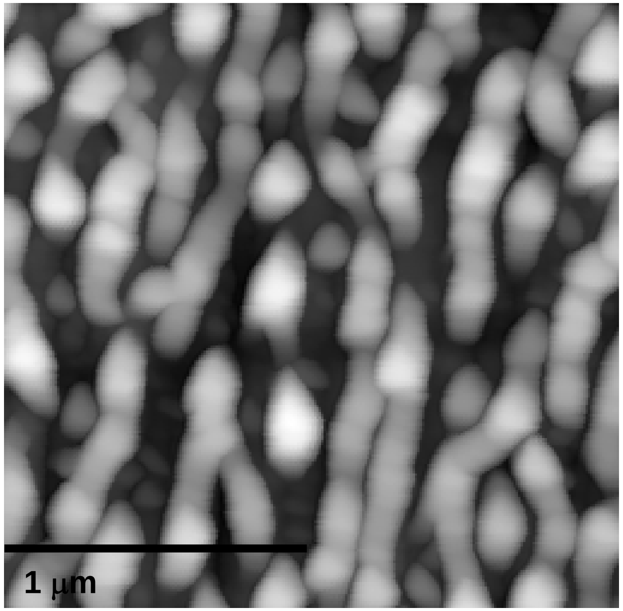


• Confinement of polymer rods with contour length L in surface grooves

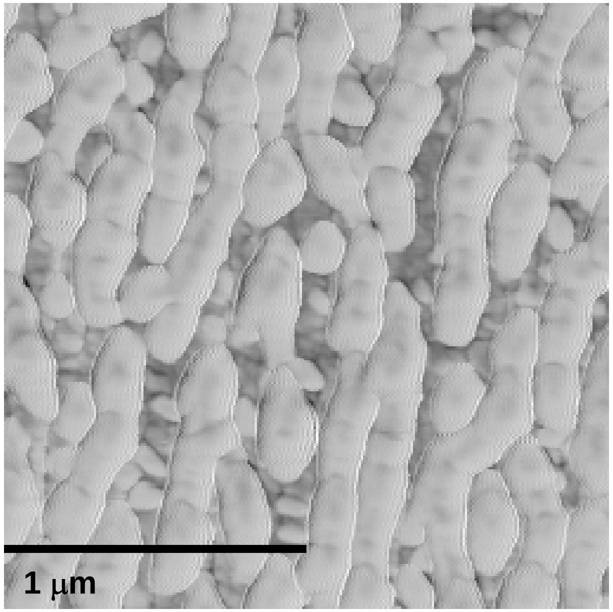


M. Müller, T. Reihs, B. Keßler, H.J. Adler, K. Lunkwitz, *Macromol. Symp.*, 211, 217 (2004)

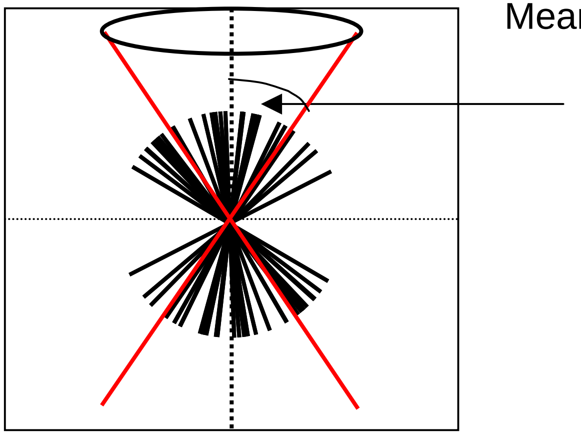
PEM-5 of PLL-246.000/PVS, 1M $NaClO_4$



AFM, Topography



AFM, Phase

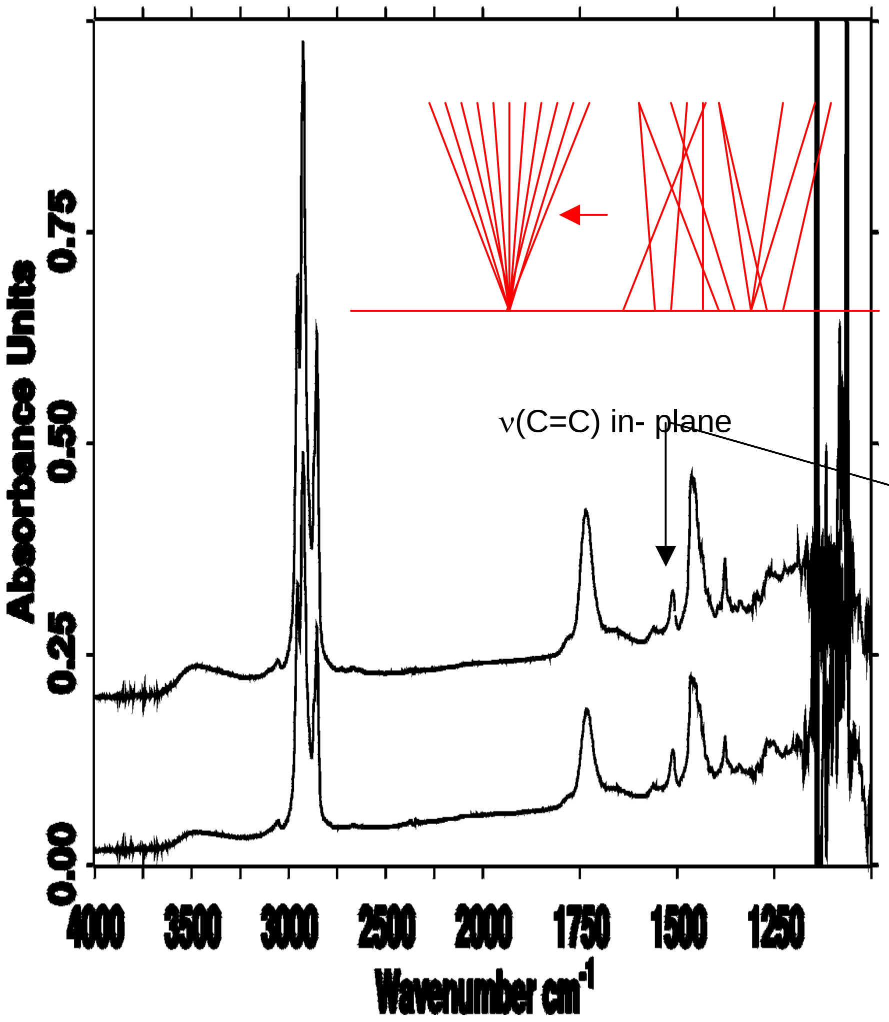


Mean angle of stretched vectors

$\langle\gamma\rangle \approx$ **20°** (ATR-IR: 22°)

M. M., T. Reihs, H.J. Adler, K. Lunkwitz, *MRC*, 25, F56 (2004)
M. M., *J. Adhesion*, 80(6), 521 (2004)

Brushes of modified poly(thiophene)



$R_z^{ATR} = A_p/A_s$

$R_z^{ATR} = E_x^2/E_y^2 + E_z^2/(E_y^2 * R^T)$

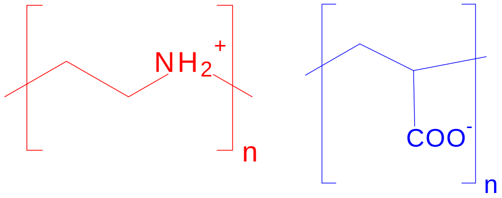
R_z^{ATR} (isotropic) = 1.13

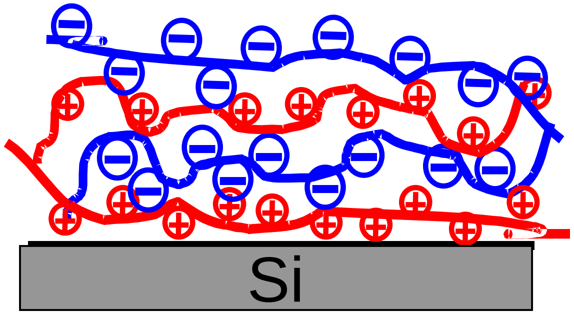
$R_z^{ATR} \neq 1.13$

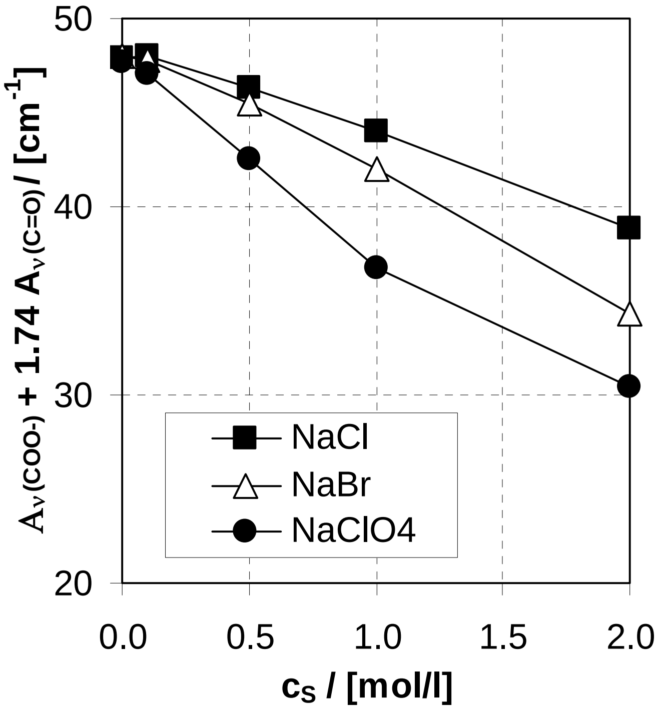
p- and s-polarized ATR-FTIR spectra on grafted modified poly(thiophene) film **(200 nm).**
Bottom: s-polarized spectrum,
Top: p-polarized spectrum. Note that only the band at 1510 cm-1 has a dichroic ratio R = Ap/As which is deviating from that of isotropy.

N. Khanduyeva, V. Bocharova, A. Kiriy, U. Oertel, M. Mueller and M. Stamm, *PMSE Preprint* (2006, submitted)

System: (PEI/PAC)$_{20}$



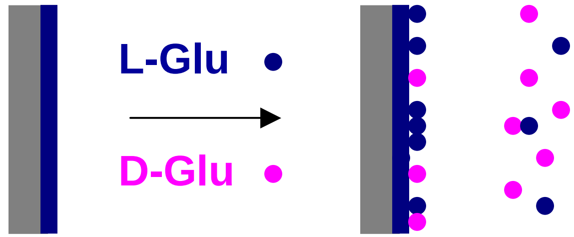




✓ ATR-IR: ΔA ~ Δc

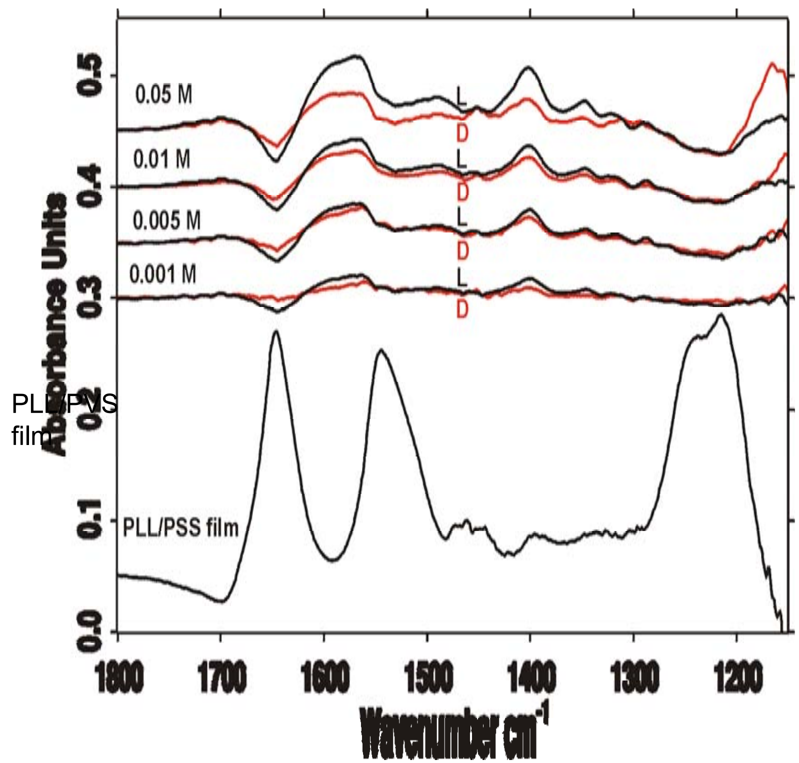
✓ Reversible Swelling of PEM-PEI/PAC depends on ion radius (ClO_4 > Br > Cl).

System: PLL / PVS
PEM-11 + **L/D**-Glu
crosslinked



<u>Enantiomeric excess (EE):</u>

EE = $(\Gamma_L - \Gamma_D)/(\Gamma_L + \Gamma_D)$



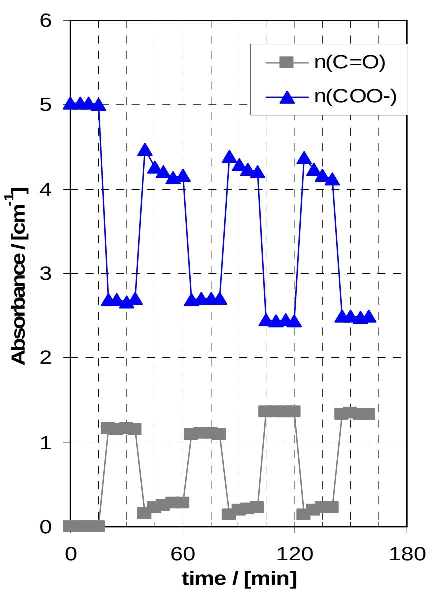
<u>Selective Uptake:</u>

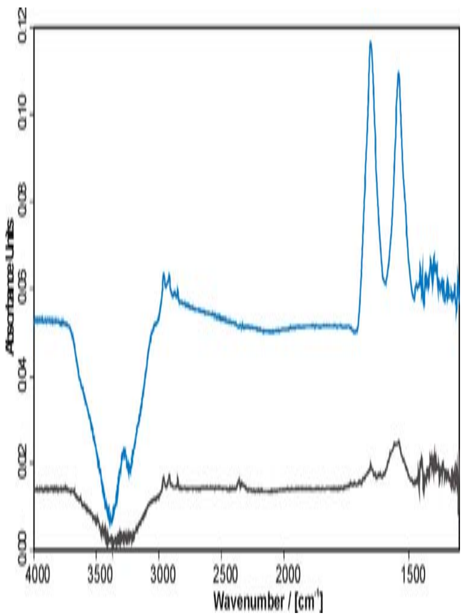
- L-Glu > D-Glu
- EE: 30%

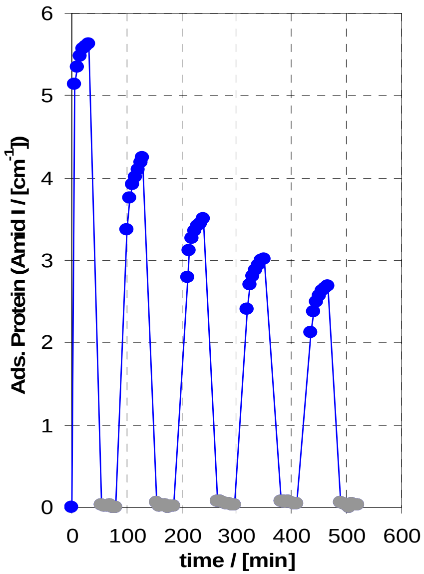
3.3. Interaction: Reversible protein adsorption at PEL multilayers

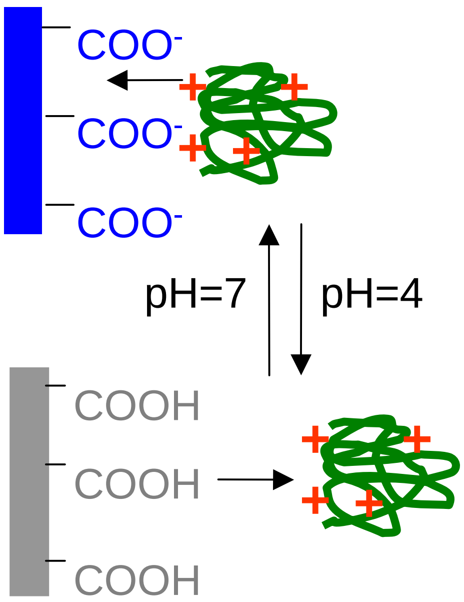
System: PEM-6 of **PEI/PAC**

Protein: Lysozyme (LYZ, IEP = 11.1), pH = 7.3 –> 4.0









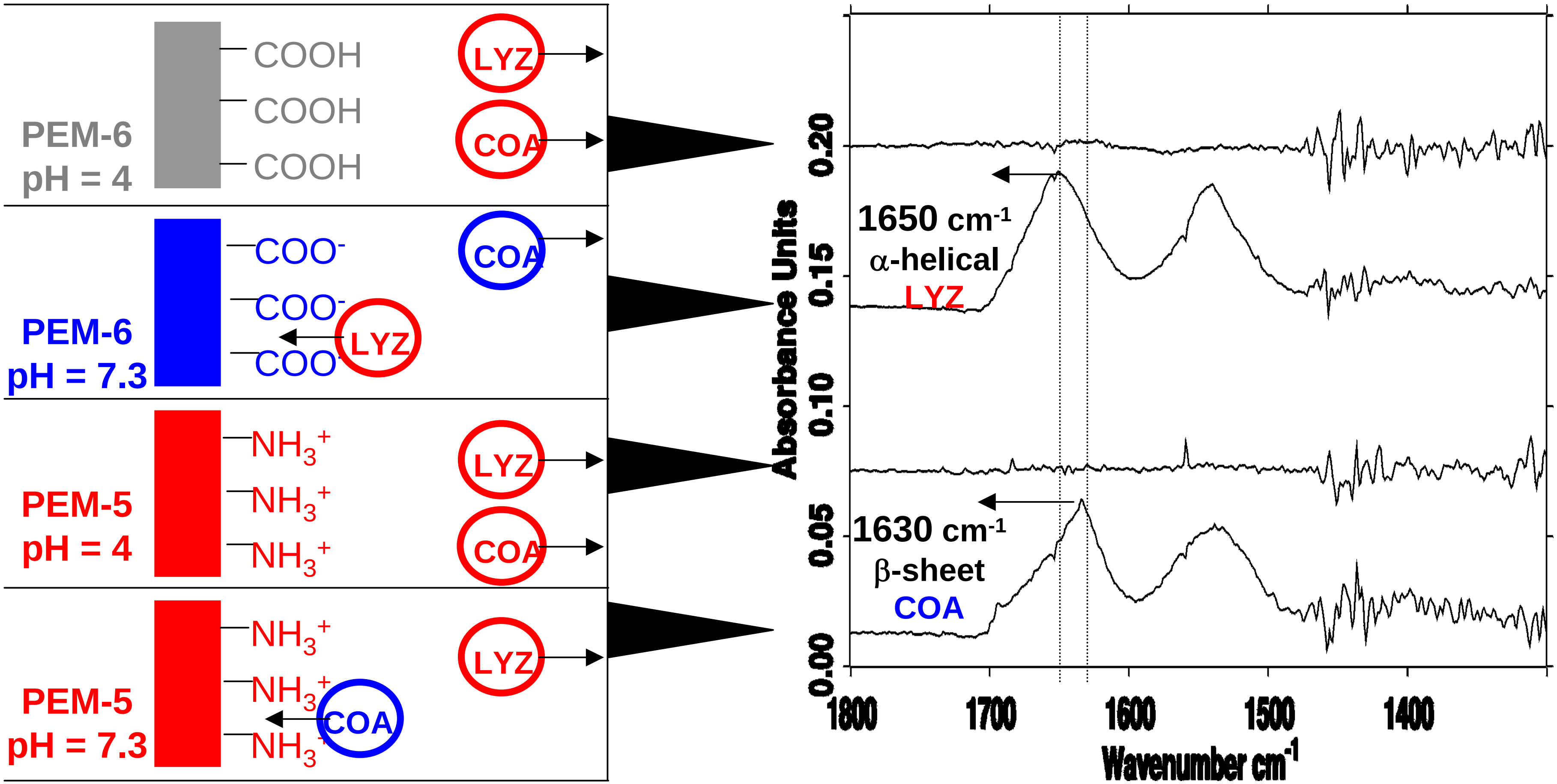
- *Uptake at pH = 7.3 (PBS buffer)* *anionic surface*
- *Release at pH = 4.0 (citrate buffer)* *neutral surface*
- *LYZ for both pH* *cationic charge*

M.M., B. Keßler, H.-J. Adler, K. Lunkwitz, *Macromol. Symp.*, 210, 157-164 (2004)

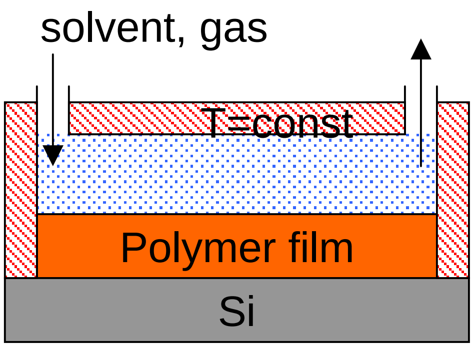
System: **PEM of PEI/PAC**

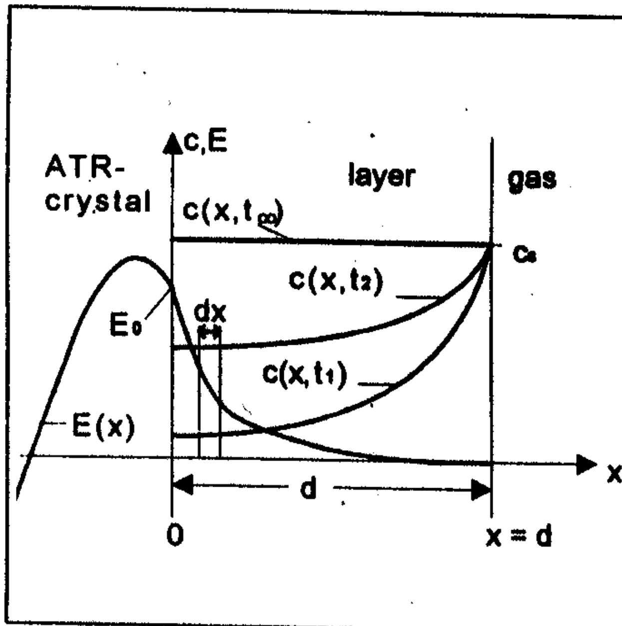
Protein mixture: **Lysozyme** (LYZ, 1 mg/ml) 14.600 g/mol, IEP = 11.1, 46% α-helix

(PBS, citrate buffer) **Concanavalin A** (COA, 1mg/ml)) 71.000 g/mol, IEP = 5.4, 64% β-sheet



M.M., K. Bohata et al. *Biomacromolecules*, 7(4), 1285 (2006)





ATR-detection of diffusion into polymer film:

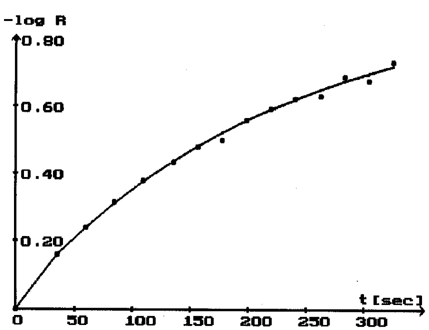
$$c(x,t) = c_S\left[1 - \mathrm{erf}\left(\frac{1}{2}\frac{x}{\sqrt{D\cdot t}}\right)\right] \quad (2.a)$$

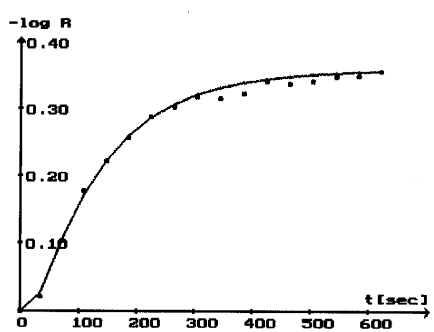
$$\mathrm{erf}(\xi) = \frac{2}{\sqrt{\pi}}\int_0^{\xi}\exp(-y^2)\,dy \quad (2.b)$$

$$A(ATR) = \varepsilon\cdot N\cdot\int_0^d c(x,t)\cdot\exp\left(\frac{-2x}{dp}\right)\cdot dx \quad (2.c)$$

- $c(x,t)$: conc. at the time t as a function of x
- c_s: conc. at the surface of the polymer layer
- $E(x)$: evanescent electric field
- E_0: electric field in the rarer medium
- d: the thickness of the polymer layer
- x: distance to ATR-crystal surface

Fig. 4. Combined ATR-diffusion model [4, 5] for the evaluation of diffusion coefficients in polymer films (Fig. from [5]).





D = 1.71 10^{-12} cm²/s

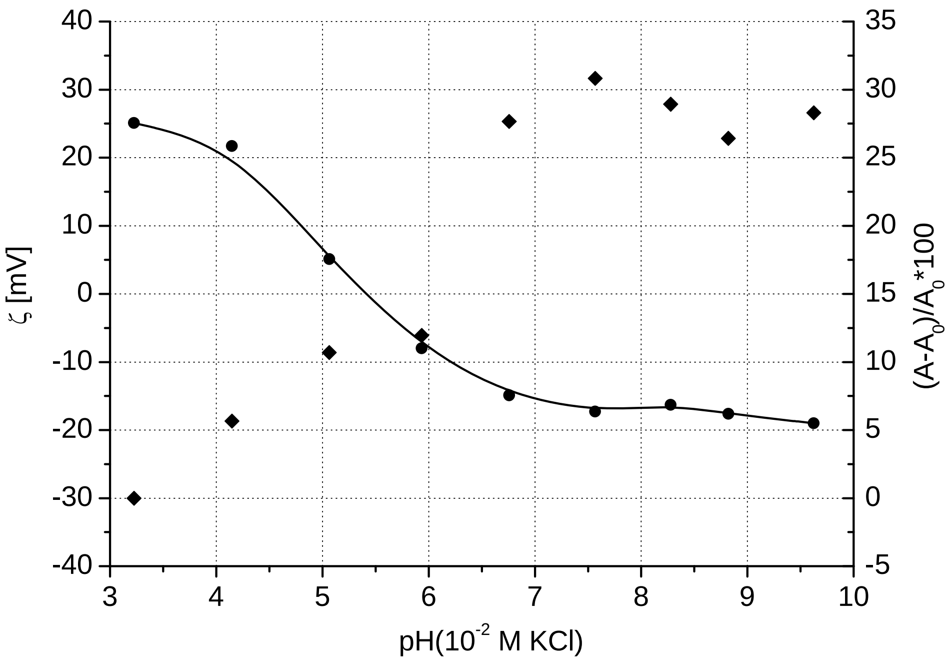
D = 1.75 10^{-7} cm²/s

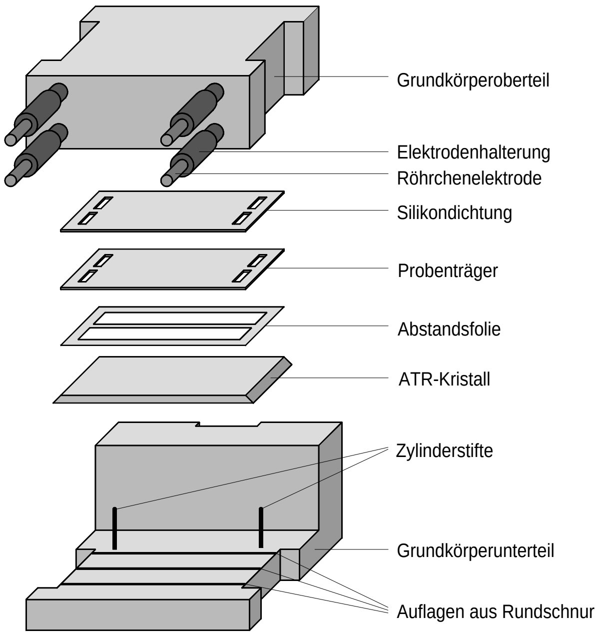
U. Hellstern, V. Hoffmann, J. Mol. Struct., 349, 329 (1995)
M. Müller, F.J. Schmitt, Macromol. Symp., 119, 269 (1997)

- **Synchronous measurement of surface charge and amount of responsible functional groups (charge carriers).**

- **Example**

pH dependence of the zeta potential of a Si ATR crystal after adsorption of fibrinogen (●) and simultaneously measured change of the $\nu(COO^-)$ band in the ATR-FTIR spectrum (♦).





DE 102 15 731.6-52
R. Zimmermann, M. Müller, C. Werner

Comparison of different methods

Method	Abbreviation	Information	Detection limit
Transmision Infrared Spectroscopy	TRANS-IR	Molecular information on films, adsorbates (dry state). Direct access to surface concen-trations [µg/cm2] via the Lamber-Beer law, knowing the thickness d. Lacking sensitivity. Access to x-ans y-axial polymer orientation.	$\Gamma_{MIN} \approx 0.375$ $\mu g/cm^2$ (PMI-P sample)
Attenuated Total Reflexion IR	ATR-IR	Molecular in-situ detection of films and adsorbates on various surfaces (e.g. Si, Ge, diamond, polymer films) in contact to solu-tion and in dry state. Quantification [$\mu g/cm^2$] via modified Lamber-Beer-Law knowing d. Access to x-, y- z-axial polymer orientation.	$\Gamma_{MIN} \approx 0.025$ $\mu g/cm^2$ (PMI-P sample)
Grazing incidence, Reflexion-absorption IR	GIR, RAIR	Most sensitive IR method for detection of ultrathin films. Limited to gold substrates. No direct correlation between the measured absorbance A and the surface concentration. Access to z-axial polymer orientation	$\Gamma_{MIN} \approx 2$ $\mu g/cm^2$ (PMI-P sample)
Diffuse reflexion IR (Fourier Transform)	DRIR, DRIFT	Molecular information on modifying layers on powdered samples (e.g. silica, granulate a.o.). Quantification not straightforward.	$\Gamma_{MIN} \approx 1/1600$ (w/w: PMI-P/ silica)
(Surface Enhanced) Raman Spectroscopy	(SERS) RAMAN	Well apted for polymer fibres, not for polymer films. Improvement by SERS.	$\Gamma_{MIN} \approx 20$ $\mu g/cm^2$ (SERS, Kieselgel)
Ellipsometry	ELL	in-situ detection of d of films and adsorbates on various surfaces (e.g. glass, Si, polymer films) in contact to solution/dry state. Quanti-fication of Γ [$\mu g/cm^2$] via de Fejter approach.	$d_{MIN} < 1$ nm
Surface Plasmon Resonance	SPR	in-situ detection of films and adsorbates on various surfaces (e.g. gold, polymer films) in contact to solution/dry state. Quantification [$\mu g/cm^2$] possible.	$\Gamma_{MIN} < 1$ ng/cm^2 (proteins)