B2: Polymer multilayers on solid substrates

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Presentations

- 5 oral IRTG
- 14 poster IRTG
- 2 oral other
- 2 poster other

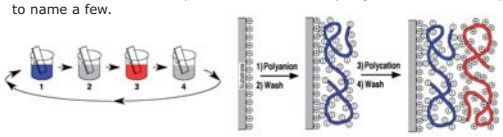
Other activities

- Organization of IRTG Training Camp "Preparation, characterization and properties of thin surface attached films and layer-by-layer assemblies", Freiburg (Apr. 24-25, 2014): joint contribution
- Long term stay at the ILL, Grenoble, France (May 2011 – Dec. 2013): C. Higy
- Participation in Science Days: M. Rothfelder
- Visit to FRM II, Garching, Germany (Jan. 19-21, 2014): C. Higy
- Visit to HFIR, Oak Ridge, USA (March 7-10, 2014): C. Higy
- Visit to the ILL, Grenoble, France (Feb. 25-26, 2013): M. Rothfelder, C. Scheibelein

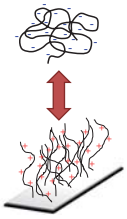
Motivation

Polyelectrolyte multilayers

Polyelectrolyte multilayers are versatile surface architectures that led to advances in biosensors, selective membranes, or photovoltaic devices, to name a few.



Polyelectrolyte brushes are interesting starting materials for layer-by-layer processes and provide ways to control the thickness of each individual layer over a wide range. However, brushes are meta stable systems and chains may degraft upon osmotic drag during complexation.



Crosslinked systems, i.e. **surface-attached polyelectrolyte networks (SAPNs)**, may provide the necessary stability but little is known about their interaction with small and large electrolytes in solution.

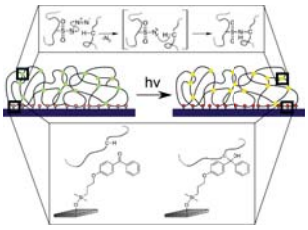
→ **PEL multilayers based on PEL brushes and SAPNs:**
Stability – Multilayer build-up – Conformational features

Surface-attached polyelectrolyte networks

Synthesis

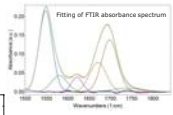
SAPNs were prepared from prepolymers carrying crosslinker units, e.g. styrene sulfon azides (SSAz).

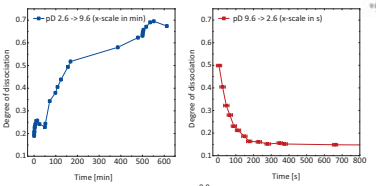
Crosslinking occurs via C,H insertion reactions.



Dissociation of weak SAPNs

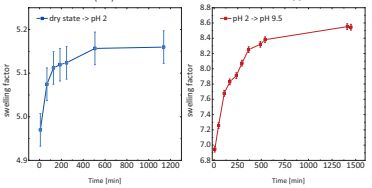
The dissociation of weak poly(methacrylic acid) layers was studied using ATR-FTIR in D_2O.





Sample:
pMAA-6.5-SSAz
d_{dry} =75 nm

Deprotonation is slower than protonation.

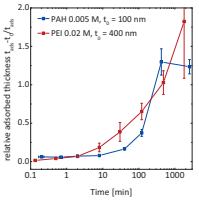


Sample:
pMAA-6.5-SSAz
d_{dry} =670 nm

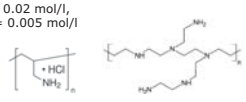
SAPNs swell rather slowly to a multiple of d_{dry}.

Adsorption of PELs

Adsorption of PAH and PEI to PMAA SAPNs



Conditions:
SAPN: pMAA-6.5-SSAz
c(PEI) = 0.02 mol/l,
c(PAH) = 0.005 mol/l
pH: ~10



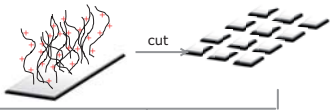
Significant pick-up of material at long adsorption times.

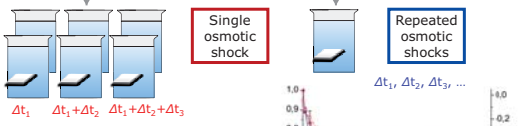
SAPNs swell less than the corresponding free gels → high segment density / strong self screening.

Stability of PEL brushes

PEL brushes respond remarkably strong to their environment, e.g. by swelling to a multiple of their dry layer thickness. This strong osmotic pull on the surface anchors often leads to degrafting → entropic death.

Entropic death monitored by subsequent decrease in thickness:

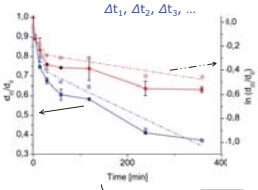




Strong entropy loss is sufficient to break covalent bonds

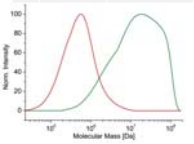
Strong kinetic component

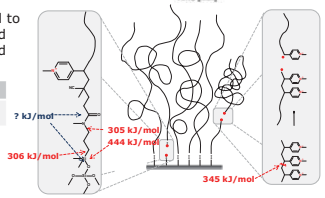
Stability of brush depends on swelling history



Where does the chain break?
PEL brushes were subjected to an osmotic shock. Degrafted polymers were collected and analyzed by GPC.

	Free Polymer	Cleaved Polymer
M_w	5.57 x 10^5	3.22 x 10^5
PDI	4.71	2.34



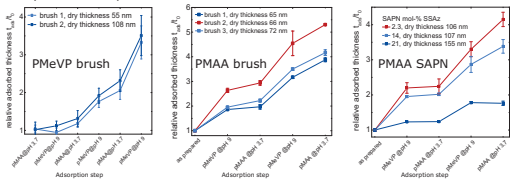


Homolytic C-C bond cleavage (analogy: mastication)?

Multilayer investigations

PEL brush & SAPN templates

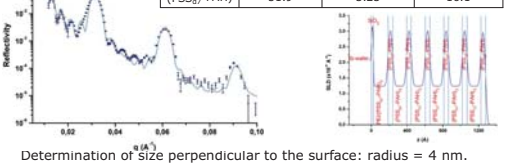
PMAA and PMeVP brushes and PMAA-SAPNs were used as starting layers for LbL processes.



Neutron reflectometry

Reflectometry scan and SLD profile of a dipped (PSS-PAH) film measured on N-REX in FRM II.

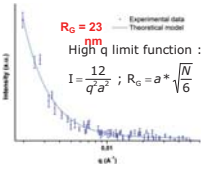
Layer pair	Thickness (Å)	SLD (x10^{-6} Å^{-2})	Roughness (Å)
(PSS_{h7}-PAH)	51.9	1.24	16.1
(PSS_{d7}-PAH)	51.9	3.23	16.1

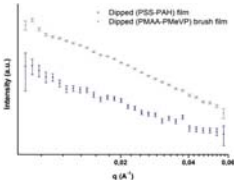


Determination of size perpendicular to the surface: radius = 4 nm.

GISANS/SANS

On left, a dipped (PSS-PAH) film measured by GISANS (FIGARO / ILL). On right, preliminary data of a dipped (PMAA-PMeVP) film on a PMAA brush layer and a dipped (PSS-PAH) film measured by SANS on GP-SANS in HFIR.





Determination of size parallel to the surface: radius = 23 nm.

Flattened coil conformation for (PSS-PAH) film.

Different SANS curves for brush and non-brush films → Different structure expected

Conclusions

Interaction between PEL brushes and SAPN and free PELS is the result of a complex interplay of thermodynamic and kinetic parameters.

Charge compensation leads to strong changes in solubility / swelling which leads to an arrest of non-equilibrium conformations.

Surface attached PEL brushes and SAPNs are meta-stable architectures: Entropic death.