Combinatorial approach to the problem of interfacial interactions via gradient polymer brushes

NCMC-9: Combinatorial Methods for Nanostructured Materials, April 24-25, 2006

Clarkson UNIVERSITY

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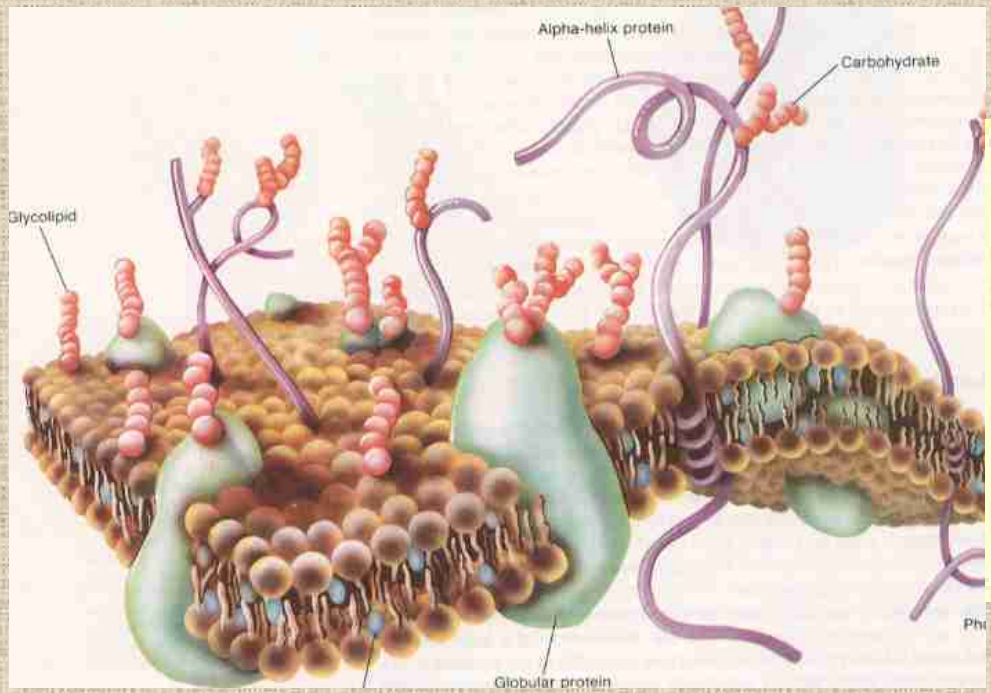
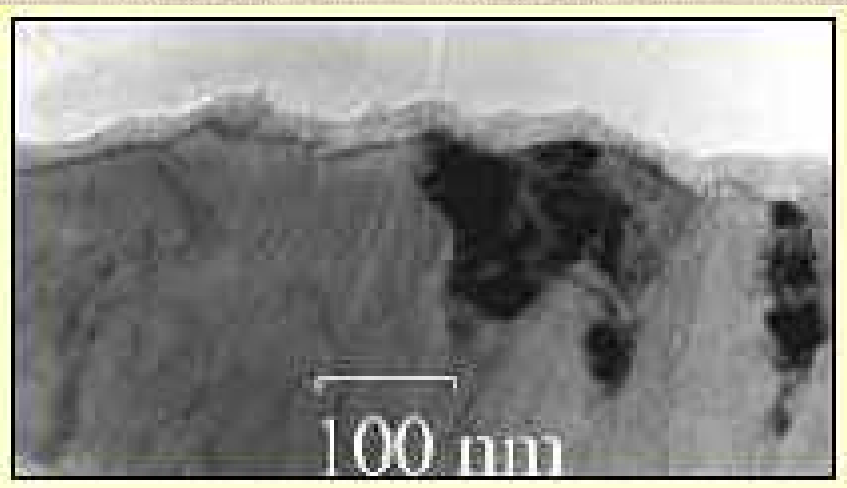
Motivations:

Interactions between phases in complex systems play key role



Cell membrane

http://www.hallym.ac.kr/~de1610/histology/cell-3.jpg

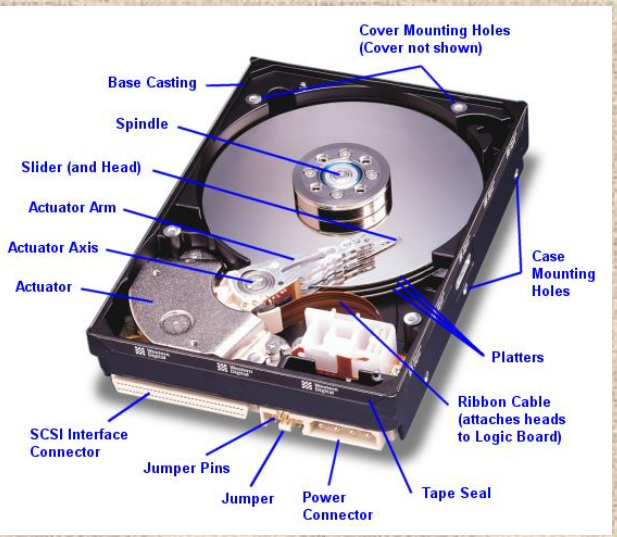


Epoxy adhesive on metal surface

http://www.kratos.com/EApps/Adhapp2.html

Motivations:

Permanently strong interactions



Permanently weak interactions

Salmonella Bacterium

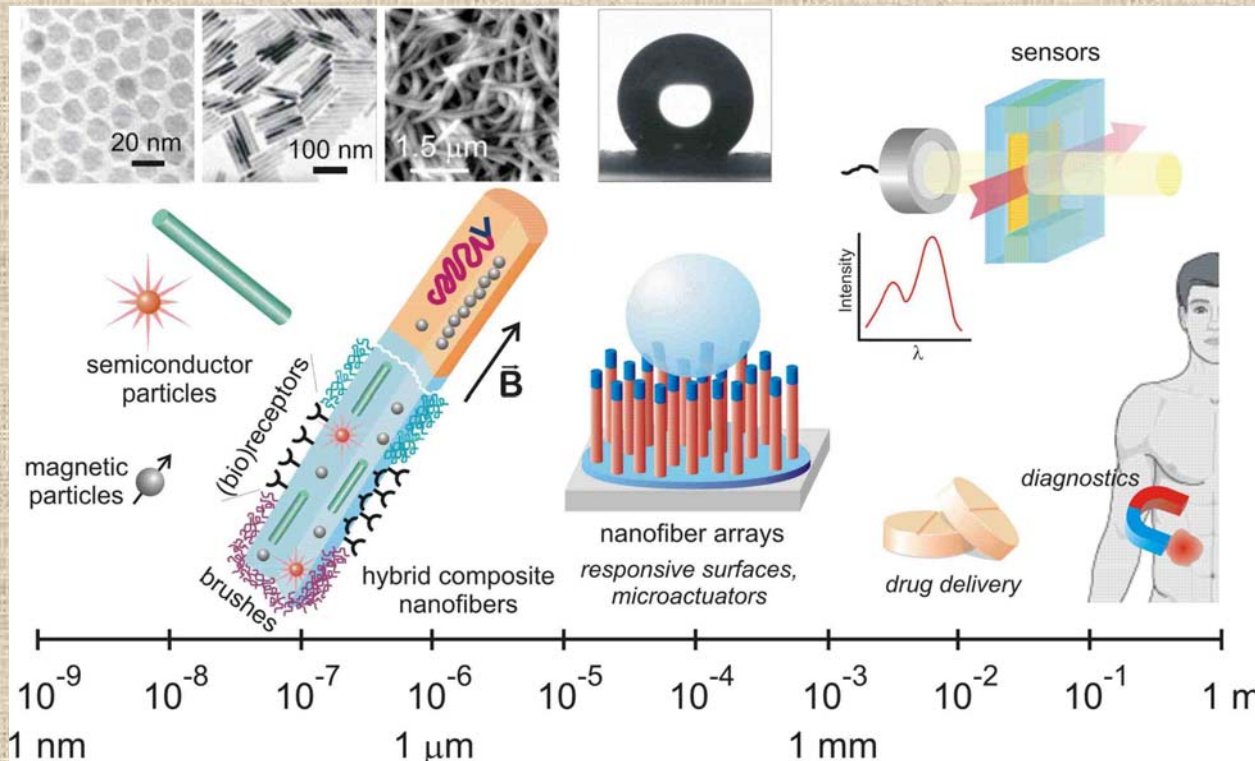
Highly selective, responsive, dynamically changeable interactions

http://library.thinkquest.org/C004535/prokaryotic_cells.html

Motivations:

- **Precise regulation of interactions**
- **Responsive interactions**
- **Selective interactions**

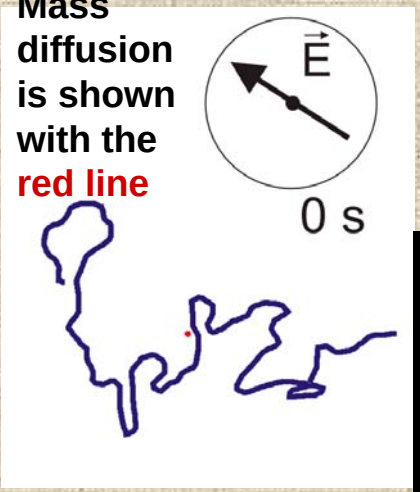
Hierarchically designed materials and devices perform based on precisely adjusted selective and responsive interactions



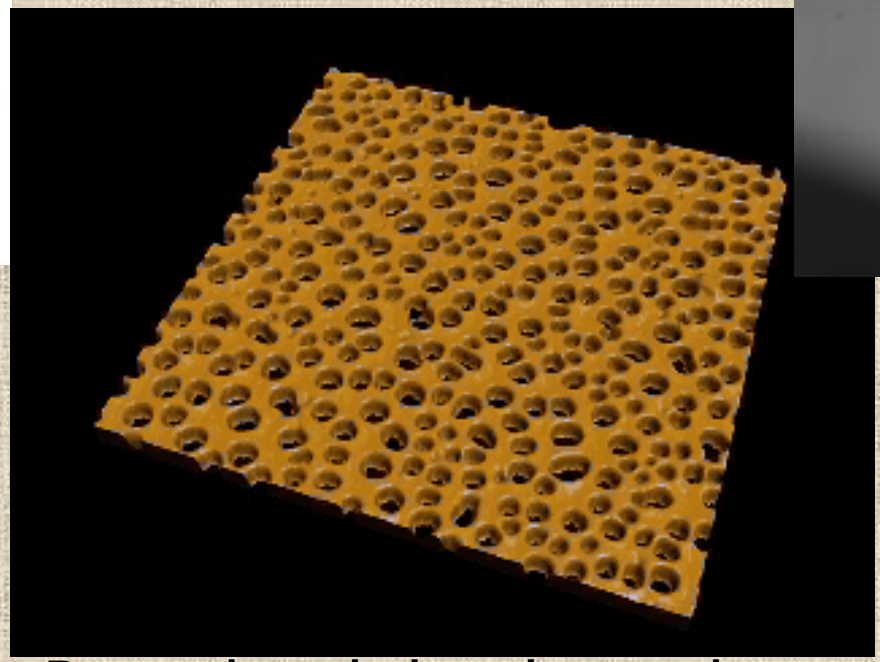
Applications:

Smart responsive materials and devices from drug delivery systems to construction materials

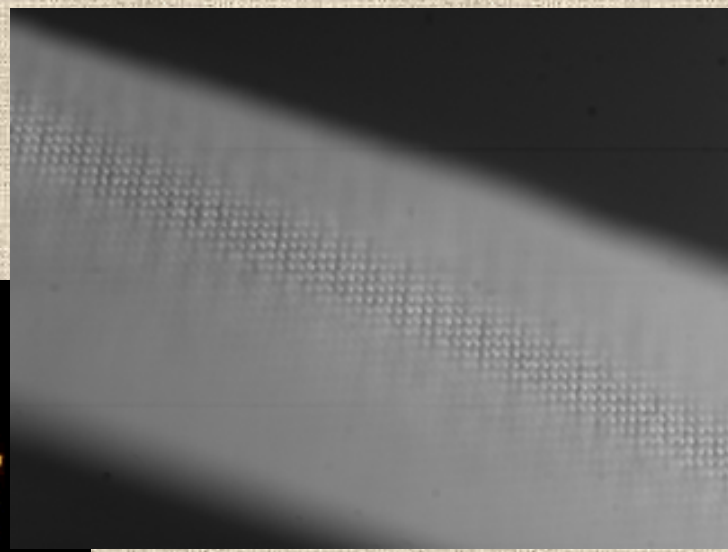
Center of Mass diffusion is shown with the red line



Diffusion of polyelectrolyte molecule in electrical field (NSF project)



Responsive polyelectrolyte membrane (current ARO project)



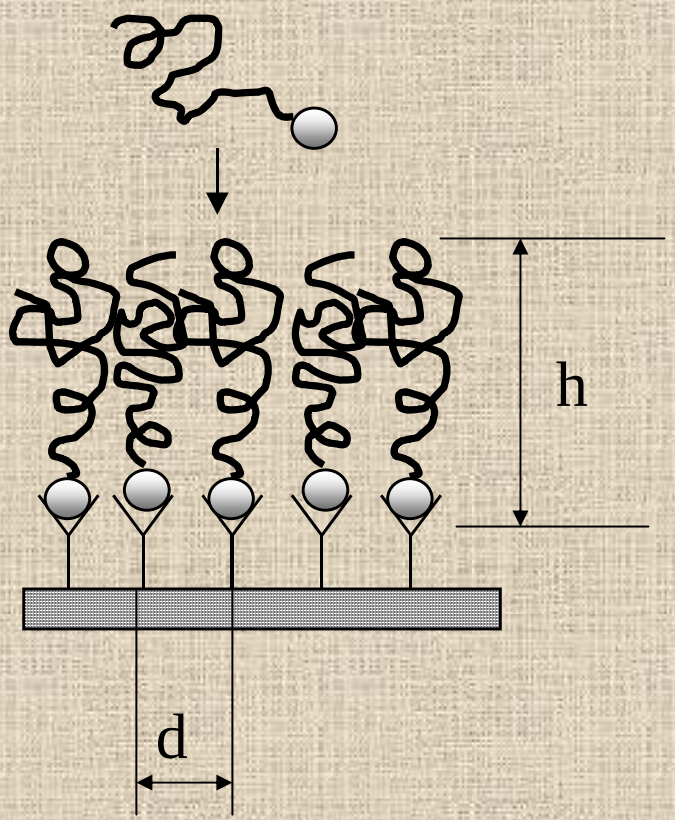
Ultrahydrophobic textile (current NTC project with Igor Luzinov, Clemson University)

Contents:

- What is polymer brush?
- Why polymer brushes?
- Properties
- Complex polymer brushes
- Gradient polymer brushes
- Examples

What is polymer brush?

End-tethered polymer chains



$$\Delta f = f_1 + f_2.$$

$$f_1 \approx kTh^2 R_g^{-2};$$

where $R_g \approx N^{1/2} a$ *(chain dimension),*

a-size of the monomer,

$$f_2 \approx kTvN(N\sigma/h),$$

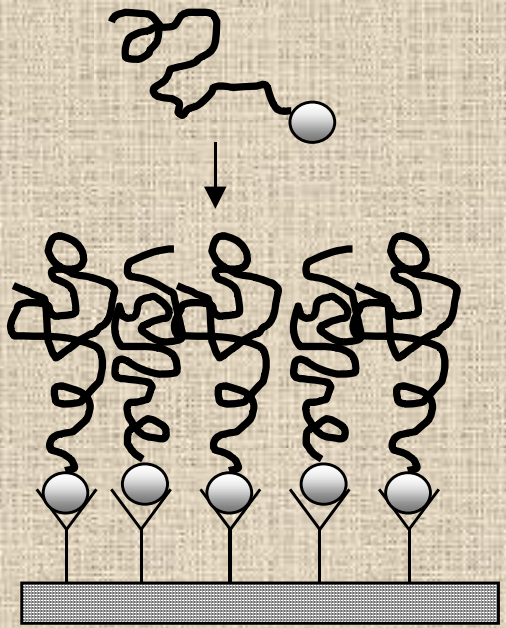
where $\sigma = 1/d^2$ (grafting density)

$$h \approx N(v\sigma a^2)^{1/3};$$
$$f = kTN(v\sigma a^{-1})^{2/3}.$$

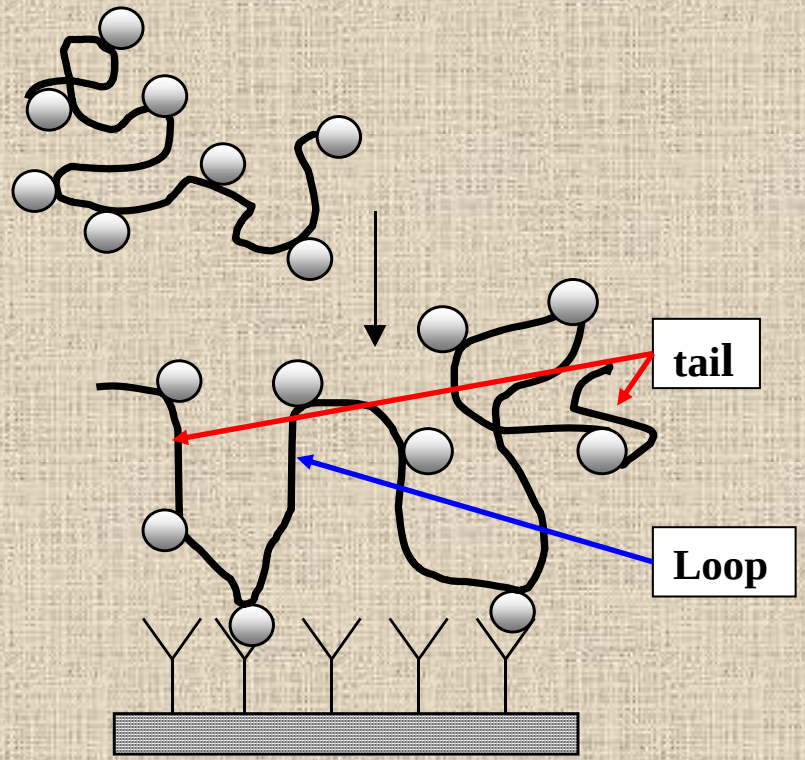
Why polymer brushes?

1. **Ability to regulate interaction due to the stretching of the polymer chains** – not possible with low molecular weight surfactants.

2. **Well defined architecture of the interfacial layers –** not the case for adsorbed, randomly grafted, or LBL deposited polymers



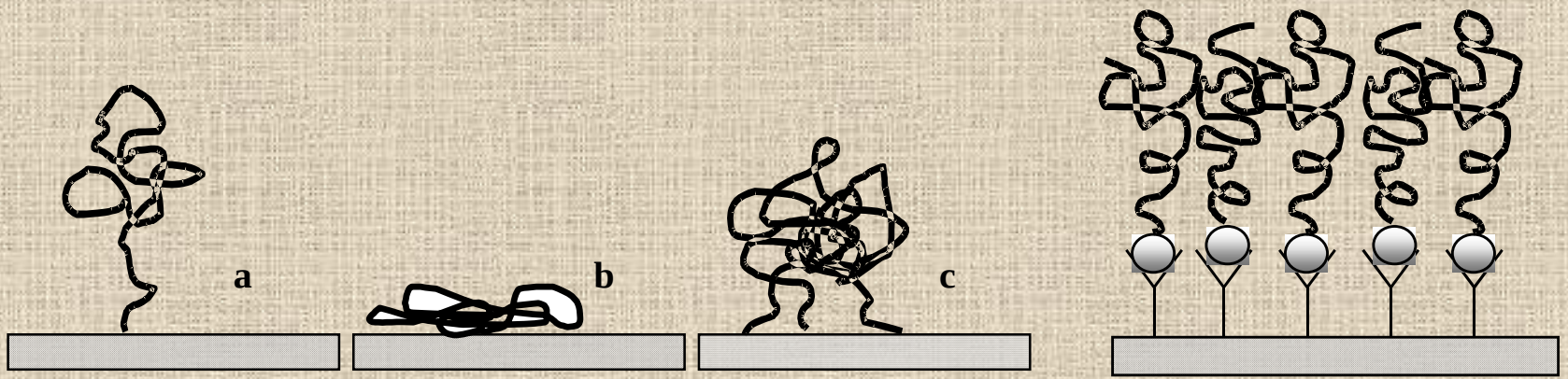
Schematic illustration of end tethered polymer chains forming brush-like layer - well defined architecture



Schematic illustration of the polymer chain grafted via side functional groups. Loops and tails behave similar to polymer brush – less defined architecture

PROPERTIES: interaction with solvent

Different concentration regimes for tethered polymers

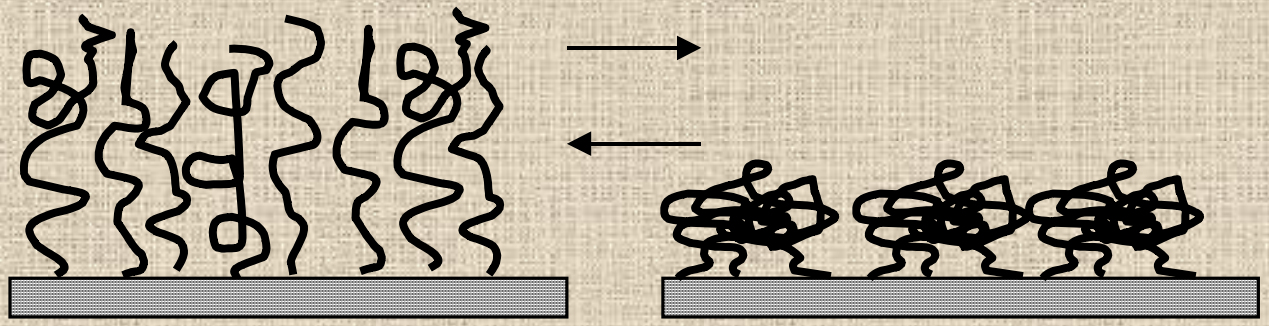


Mushroom	Pancake	Pinned micelle
Good solvent	Poor solvent	Poor solvent

BRUSH

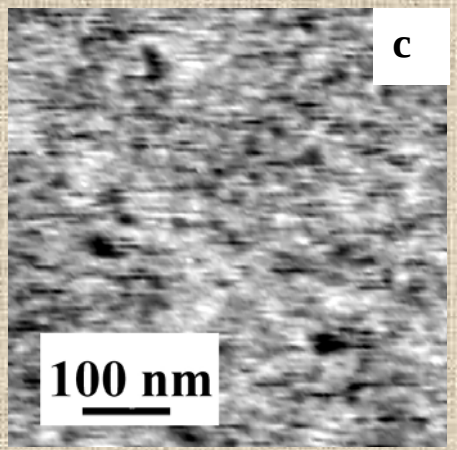
Graftingdensity

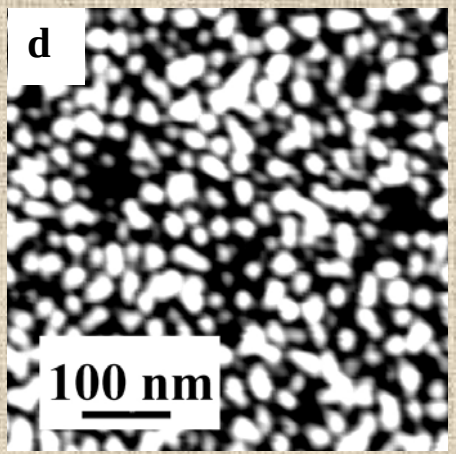
PROPERTIES: interaction with solvent

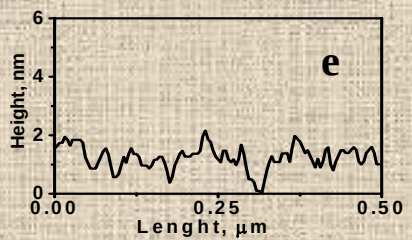


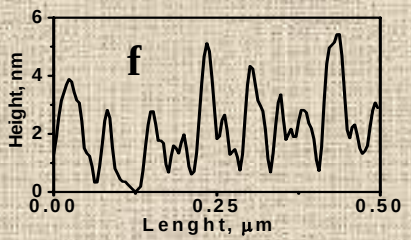
a b

Good solvent Poor solvent

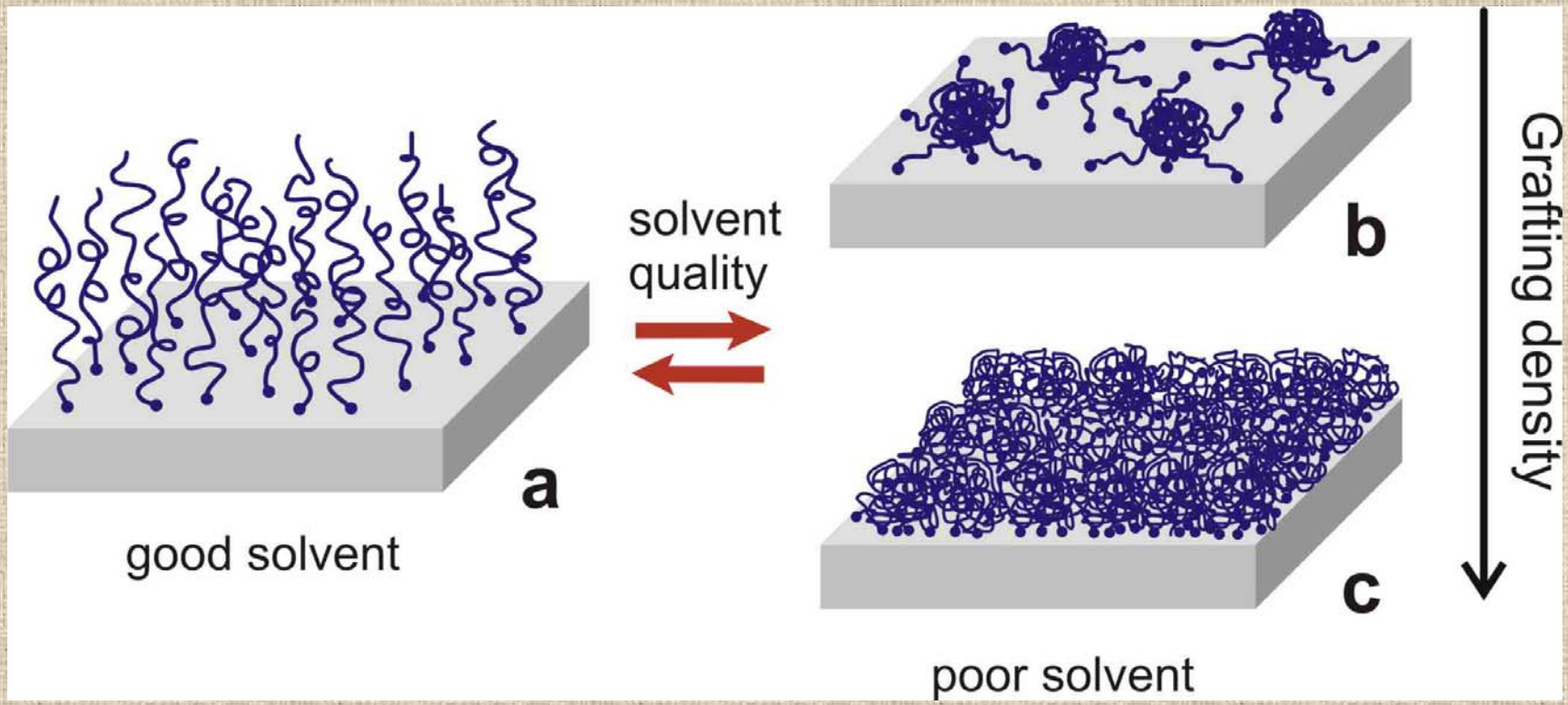








PROPERTIES: interaction with solvent



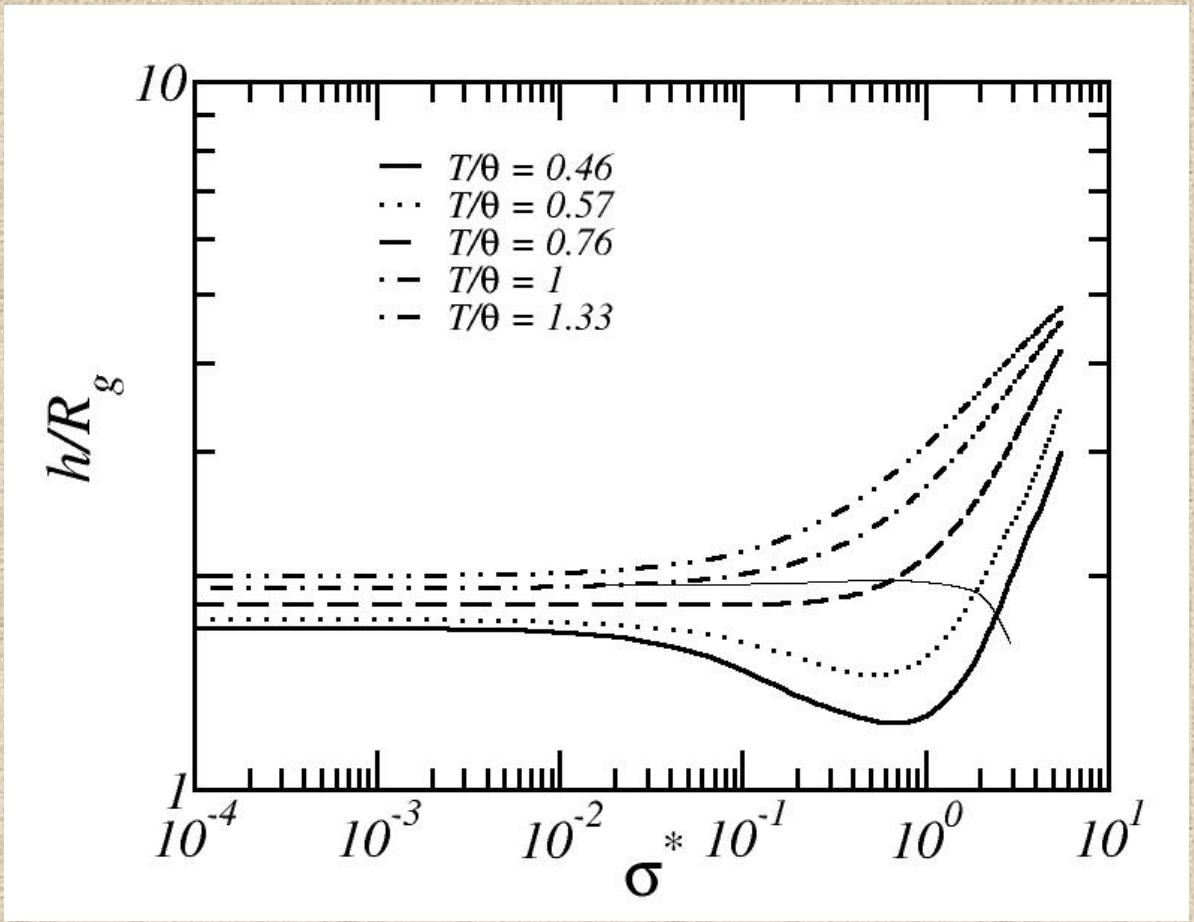
Polymer brush properties as function of solvent quality and grafting density

A – stretched brush regime

B- pined micelles regime

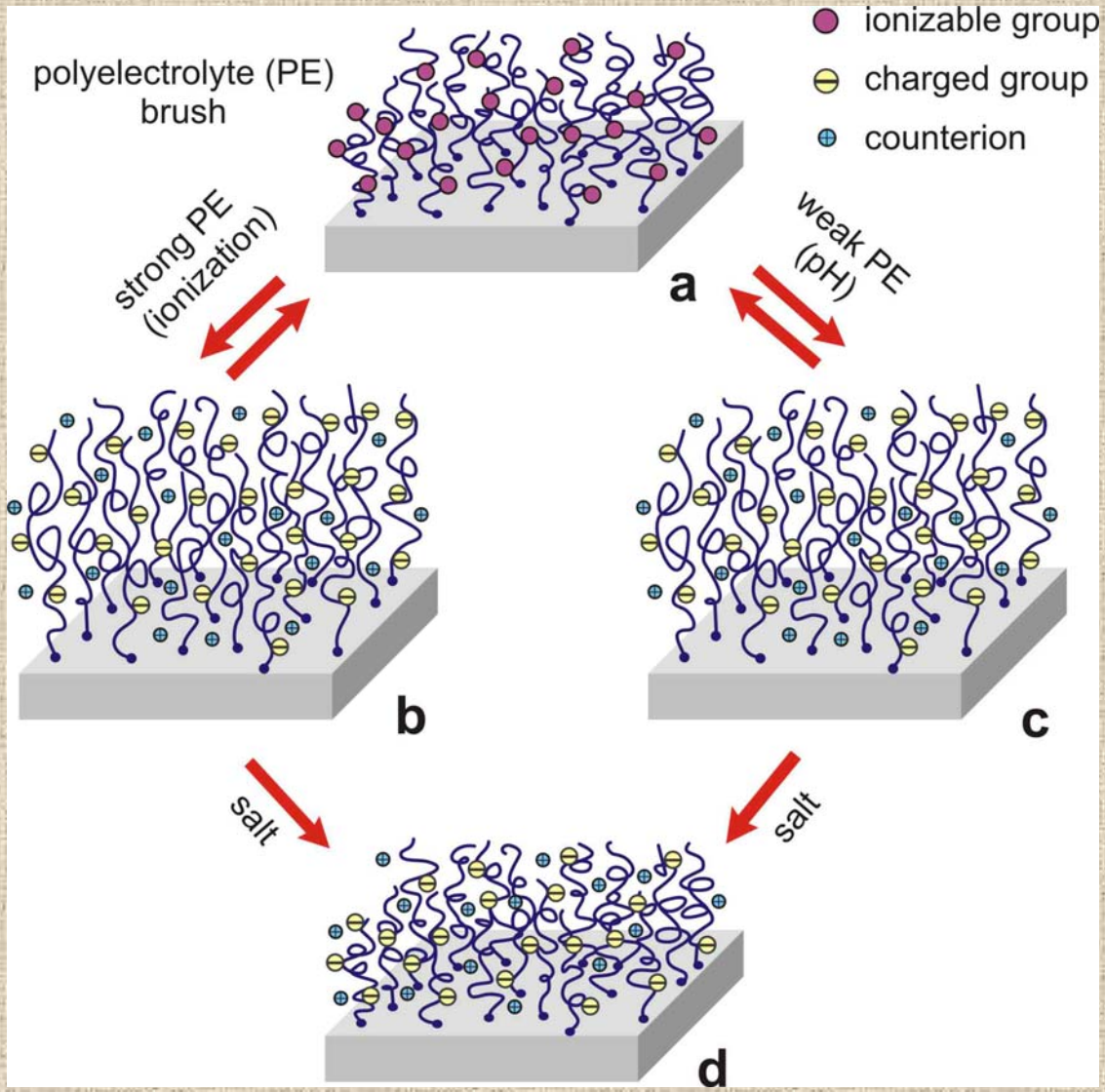
C- collapsed brush regime

PROPERTIES: interaction with solvent

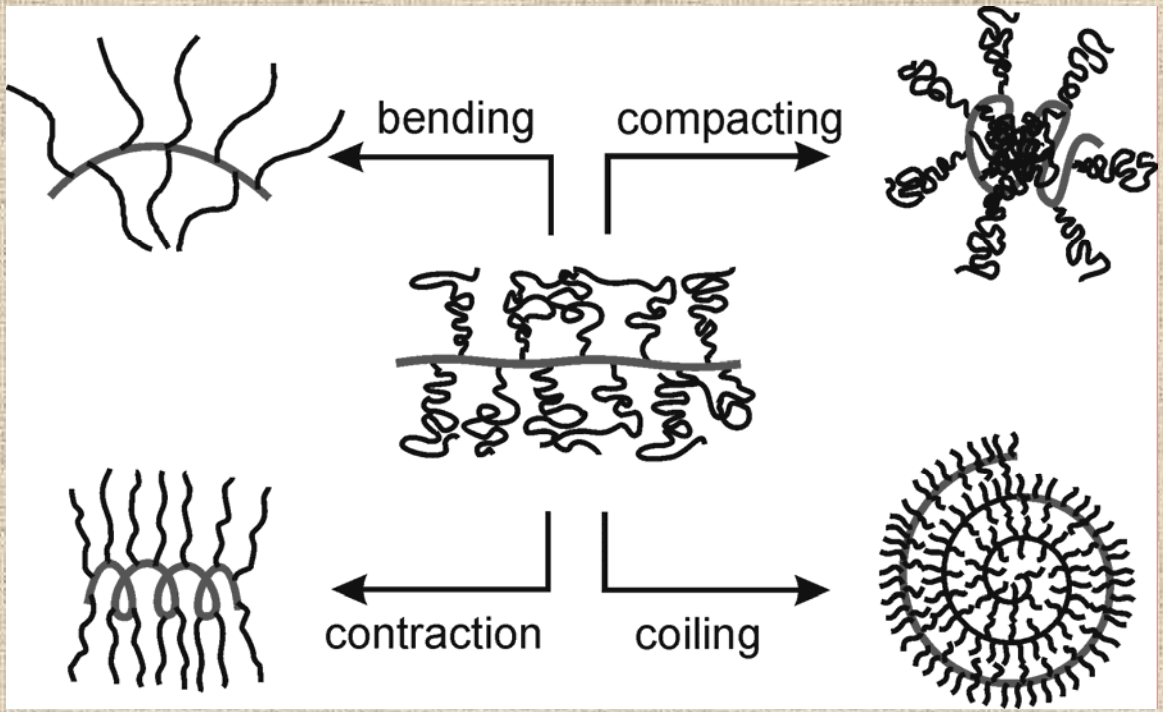


Height of the brush layer, scaled by the bulk radius of gyration of the chain in good solvent, as a function of the scaled surface coverage for a variety of qualities of solvents. Szleifer, I.; Carignano, M. A. "Tethered polymer layers", *Adv. Chem. Phys.* 1996, *94*, 165-260.

Diversity of polymer brushes:
polyelectrolyte brushes



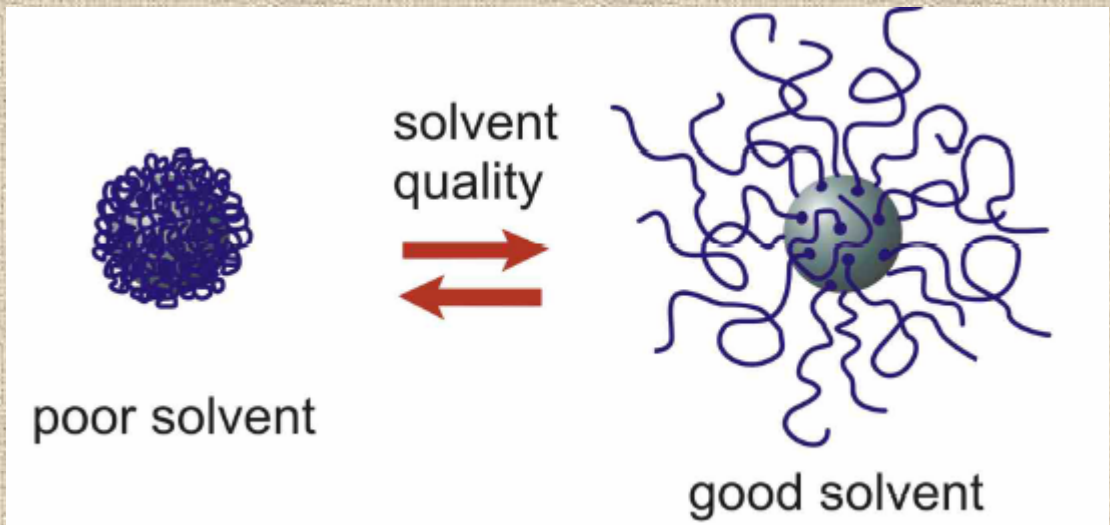
Diversity of polymer brushes:



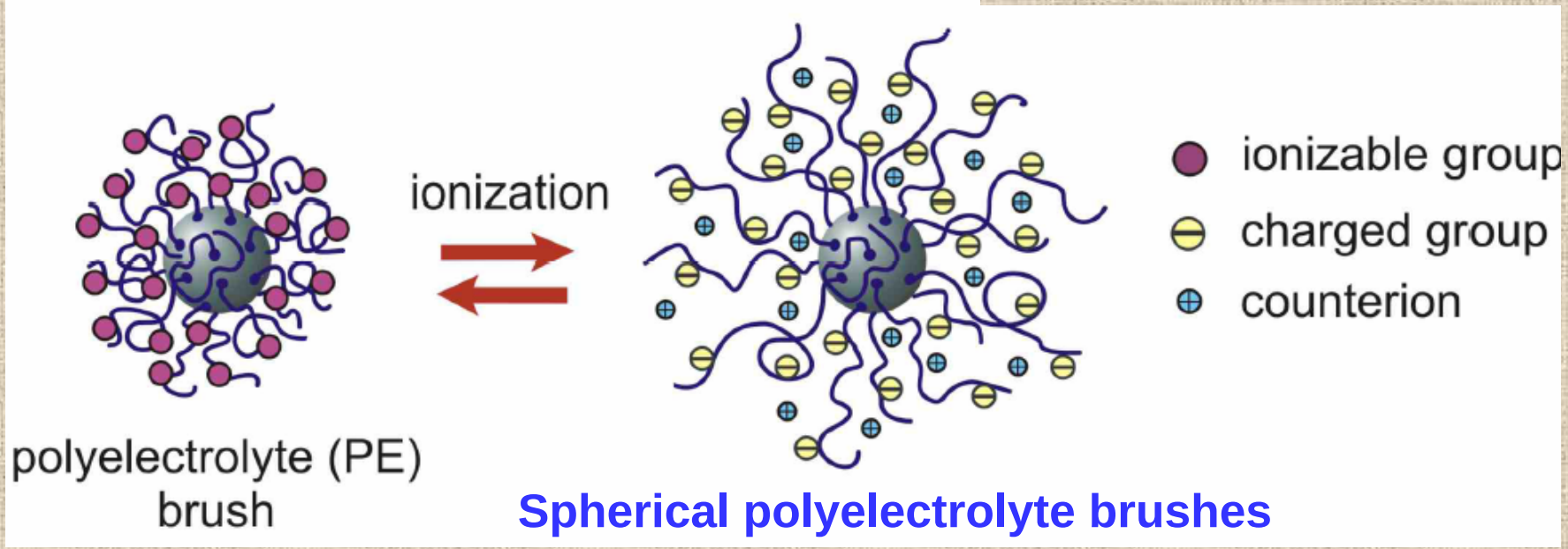
Molecular brushes

Boyce, J. R.; Sun, F. C.; Sheiko, S. "Stimuli-responsive brush-like macromolecules", In *Responsive polymer materials: design and applications*; Minko, S., Ed.; Blackwell Publishing Professional: Ames, 2006; pp 1-21

Diversity of polymer brushes:



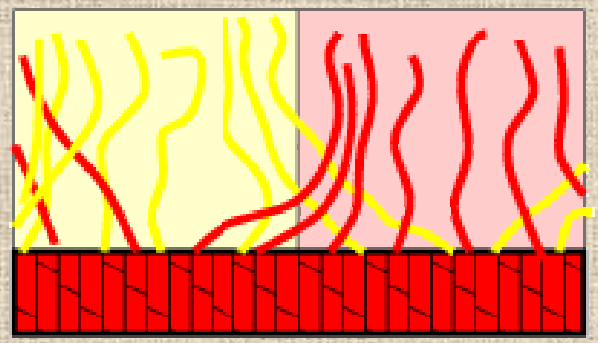
Spherical brushes

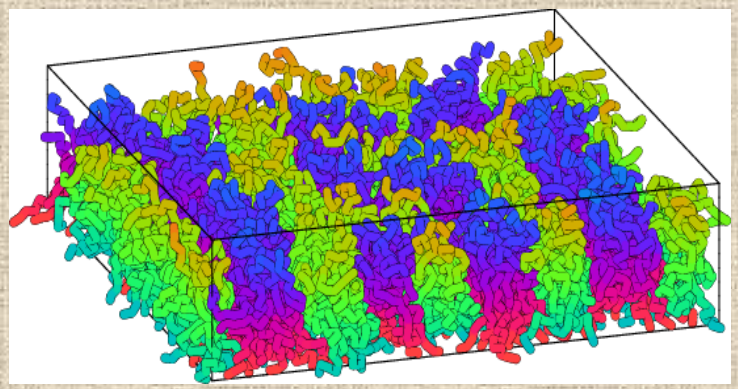


Spherical polyelectrolyte brushes

Complex polymer brushes:
Mixed polymer brushes

brush of two incompatible
polymers in a common solvent





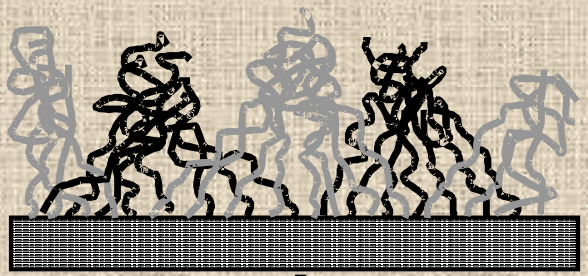
chains avoid energetically unfavorable contacts and pay entropic penalty

Phys. Rev. Lett. **2002, 88, 3, 035502**

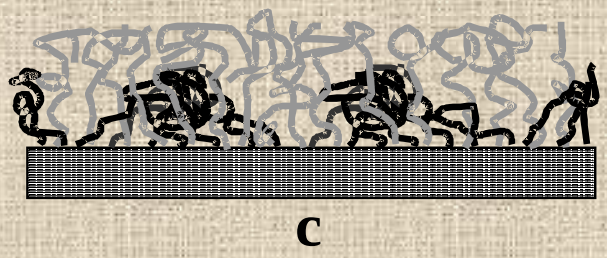
Complex polymer brushes:

Mixed polymer brushes

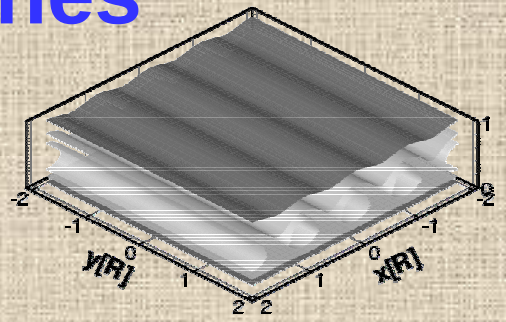
a



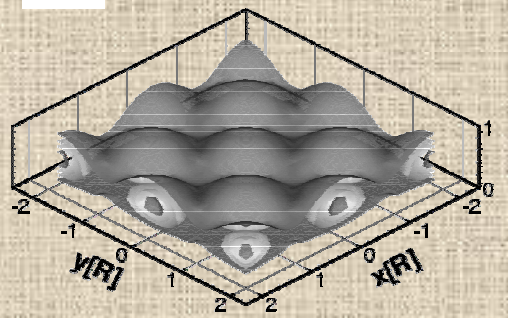
b



c



a



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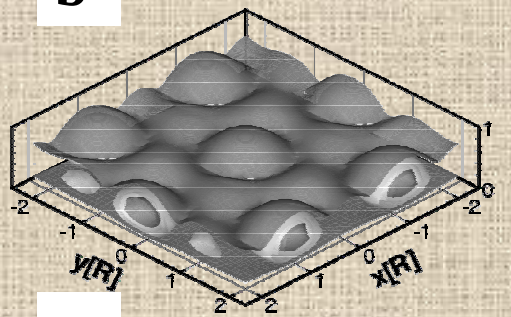
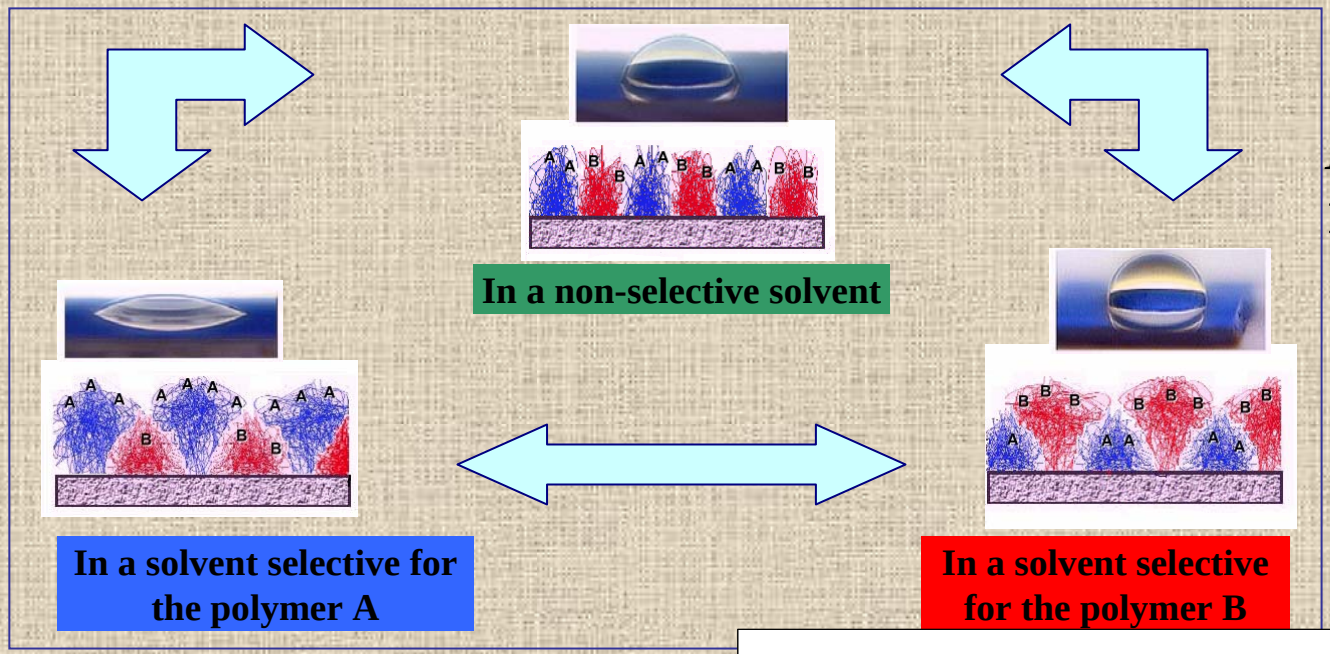


c

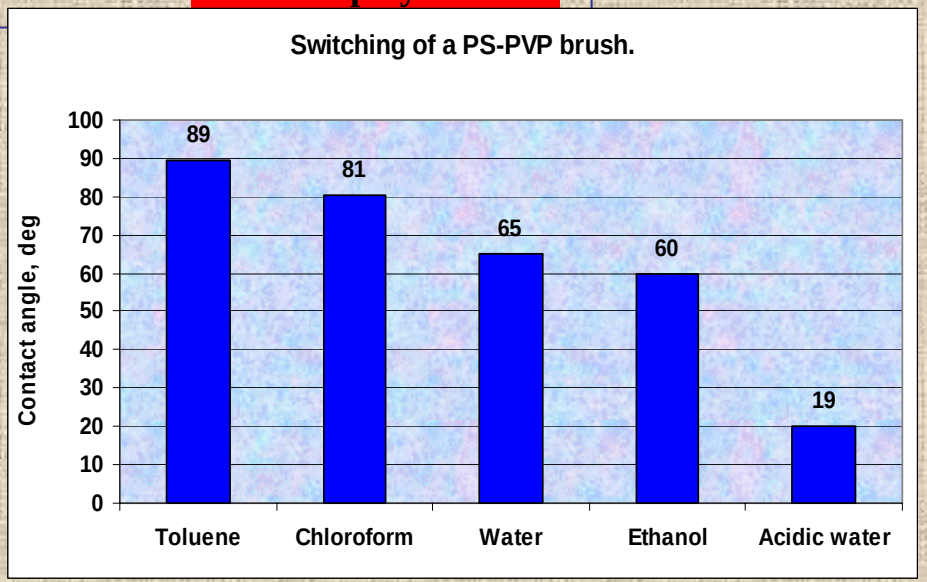
Macromolecules; **2003; *36*(19); 7268-7279.**

Switching/adaptive properties of mixed polymer brushes

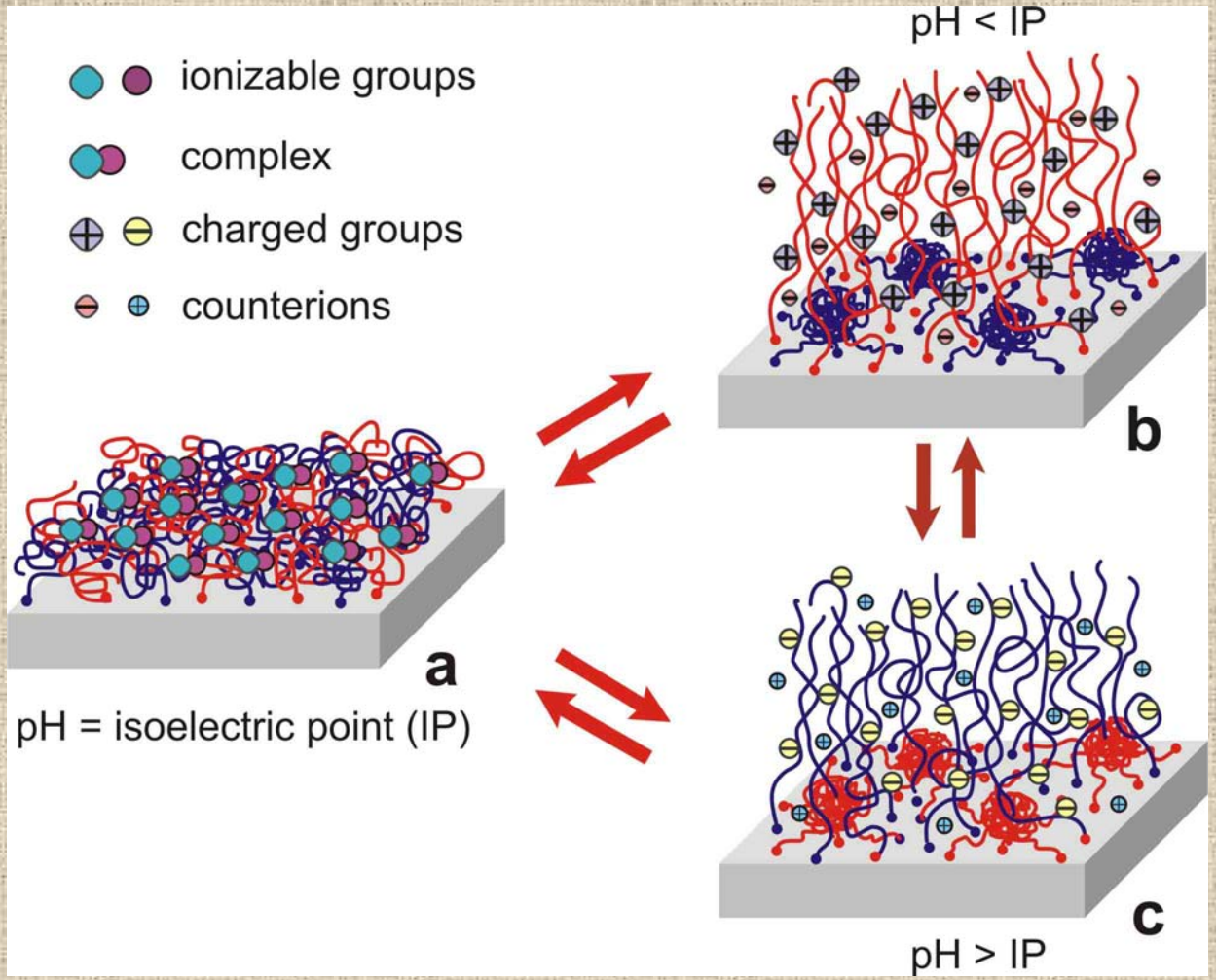


***Langmuir*, 2002, 18, 289-296**

***Macromol. Rapid. Commun.*, 2001, 22, 206-211**

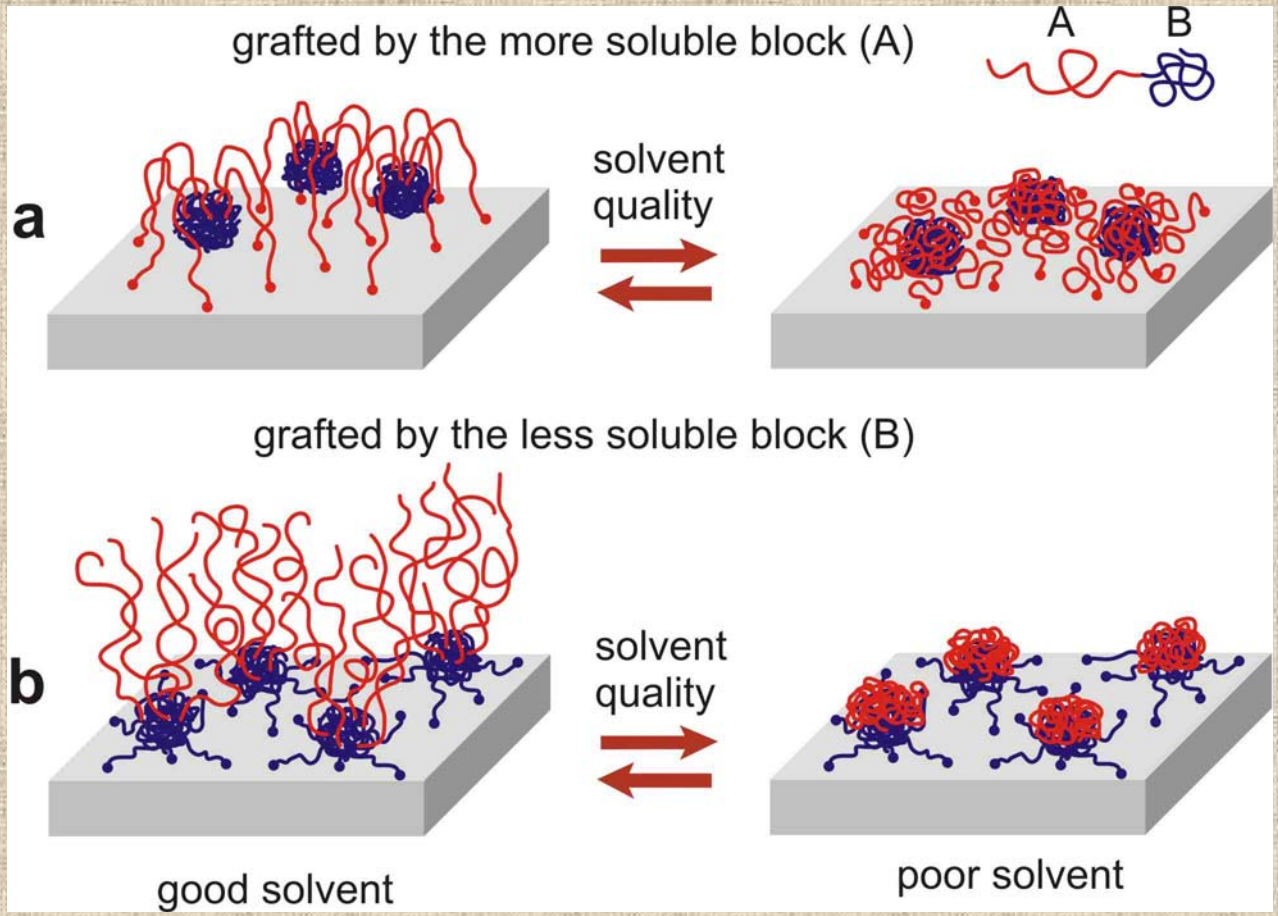


Complex polymer brushes:
Mixed polyelectrolyte brushes

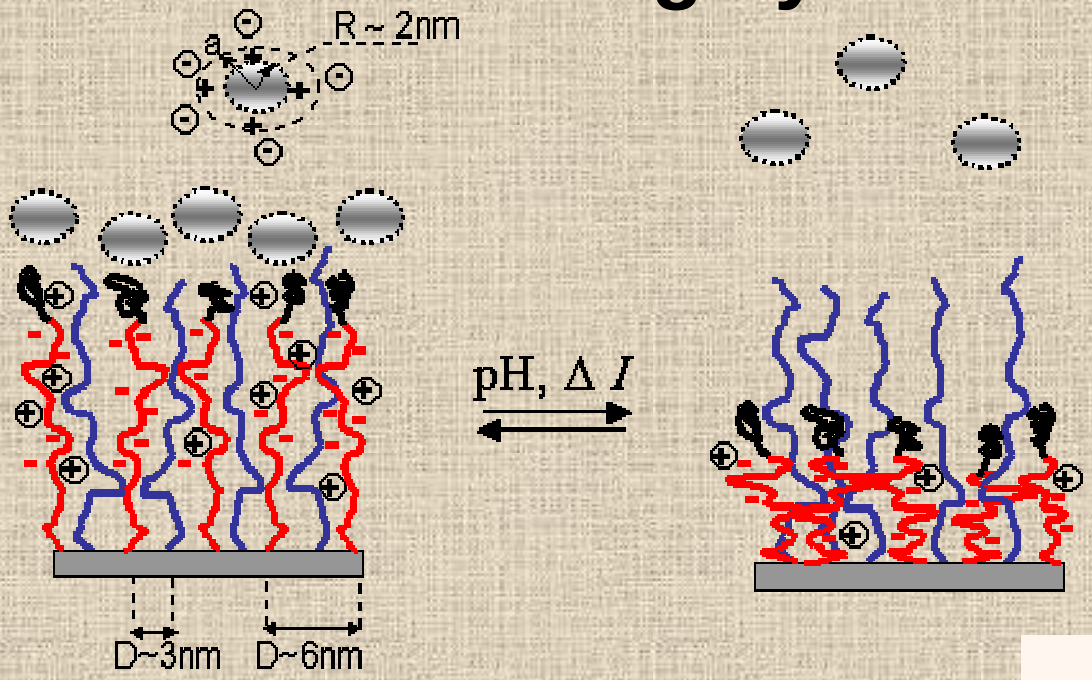


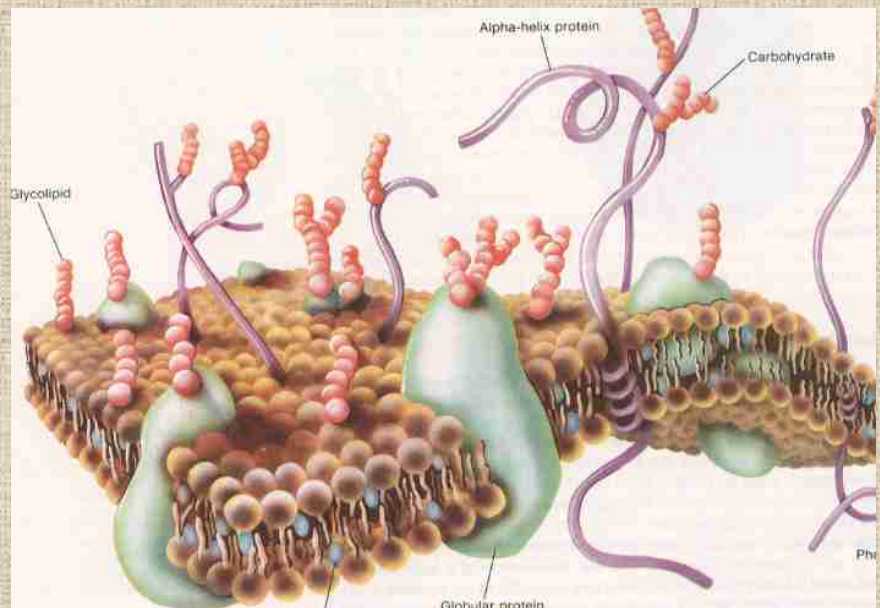
Macromolecules **2003**, *36(16)*, 5897-5901

Complex polymer brushes:
Block-copolymer brushes

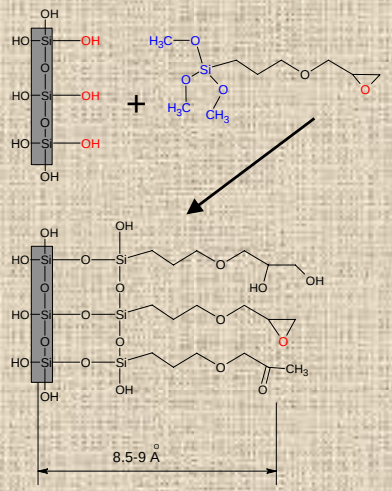


Complex interactions – mimicking living systems

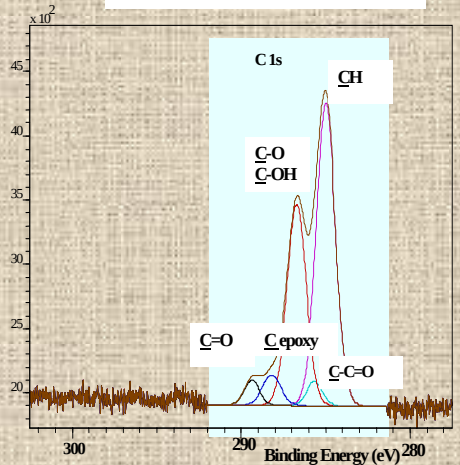




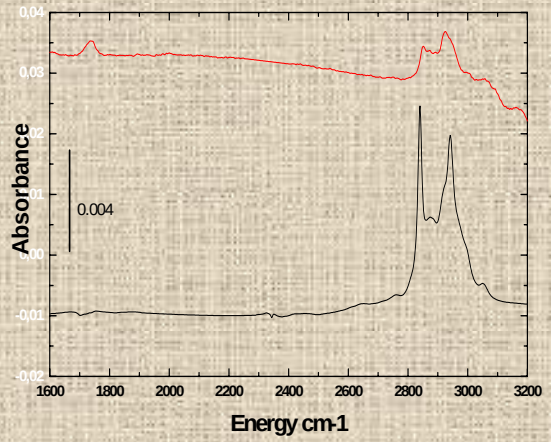
SYNTHESIS



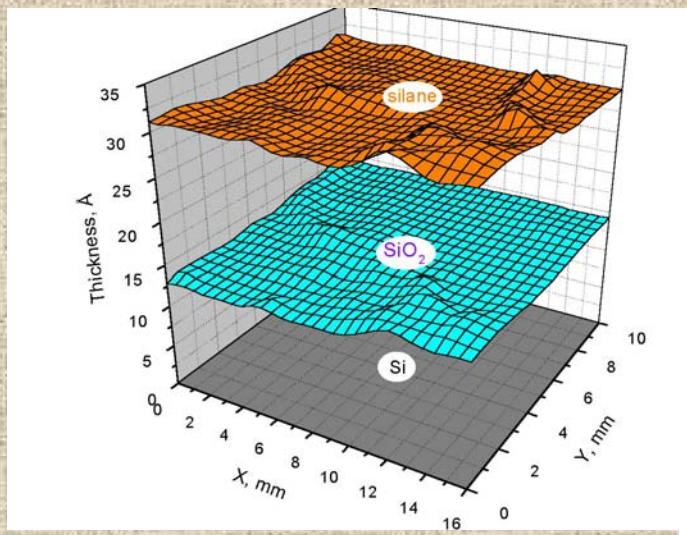
XPS of epoxy-silane on Si-wafer



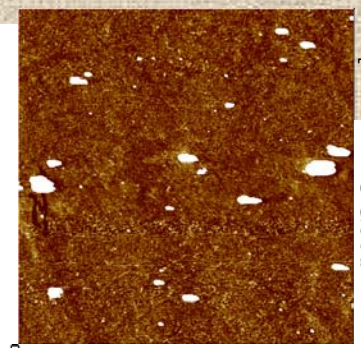
FTIR-ATR of epoxy-silane on Si-wafer



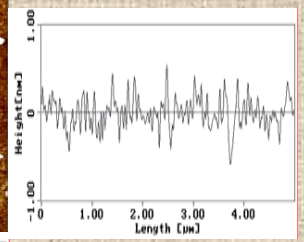
Ellipsometric topography of the epoxy-silane layer

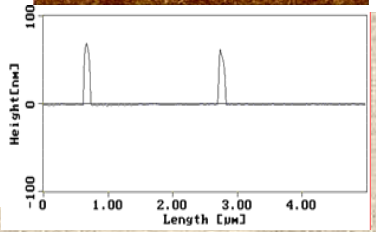


AFM-imaging of the epoxy-silane layer

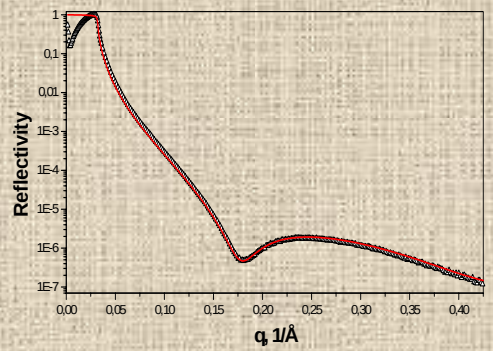


Topography 5x5μm





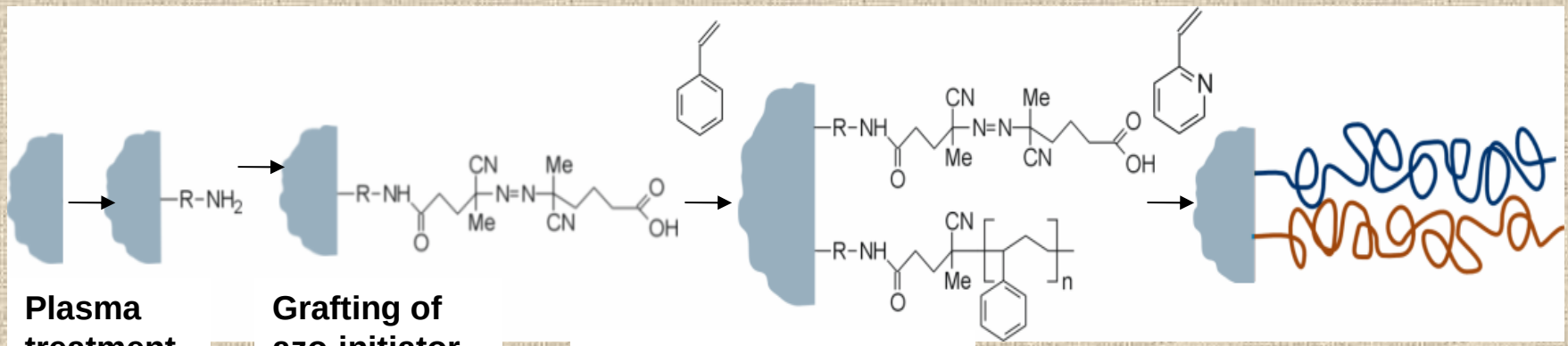
X-ray reflectivity



Epoxy-silane
h =1.7 nm, RMS=0.42 nm

Langmuir **2002**, *18(1)*, 289-296.

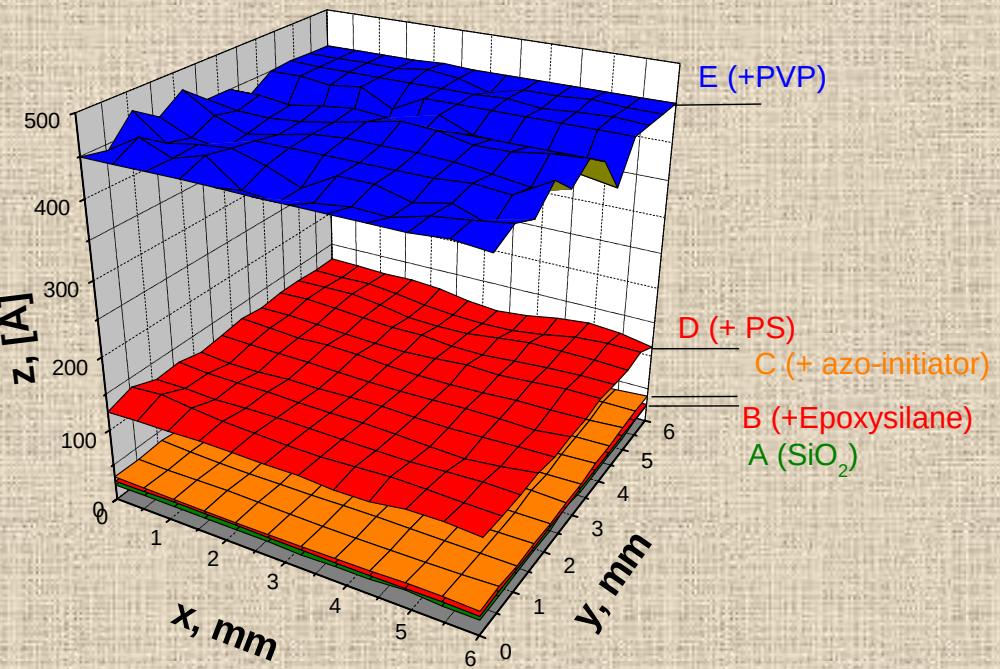
SYNTHESIS: grafting from

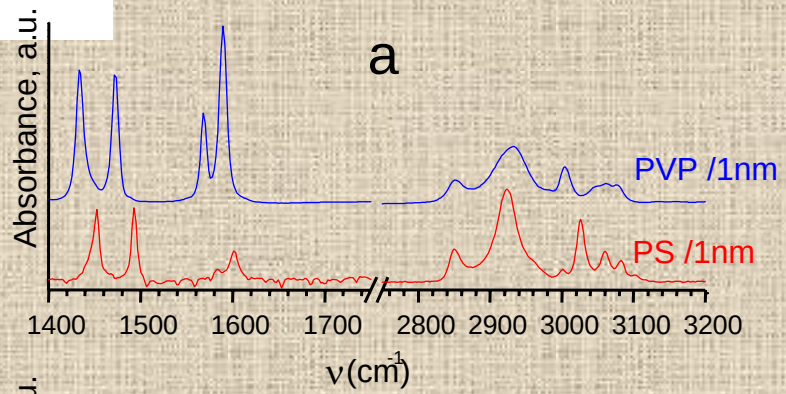


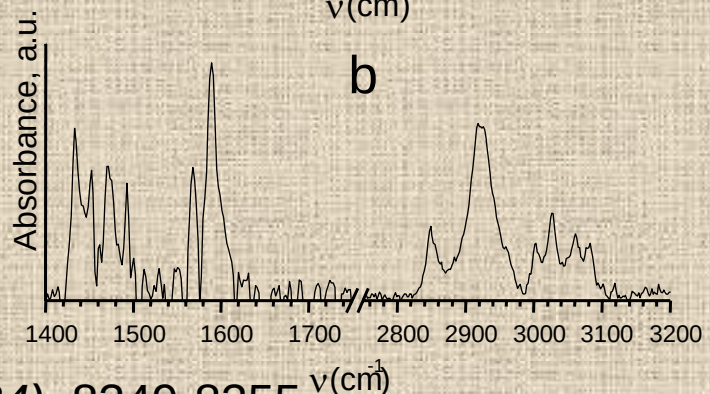
Plasma treatment

Grafting of azo-initiator

Free radical polymerization

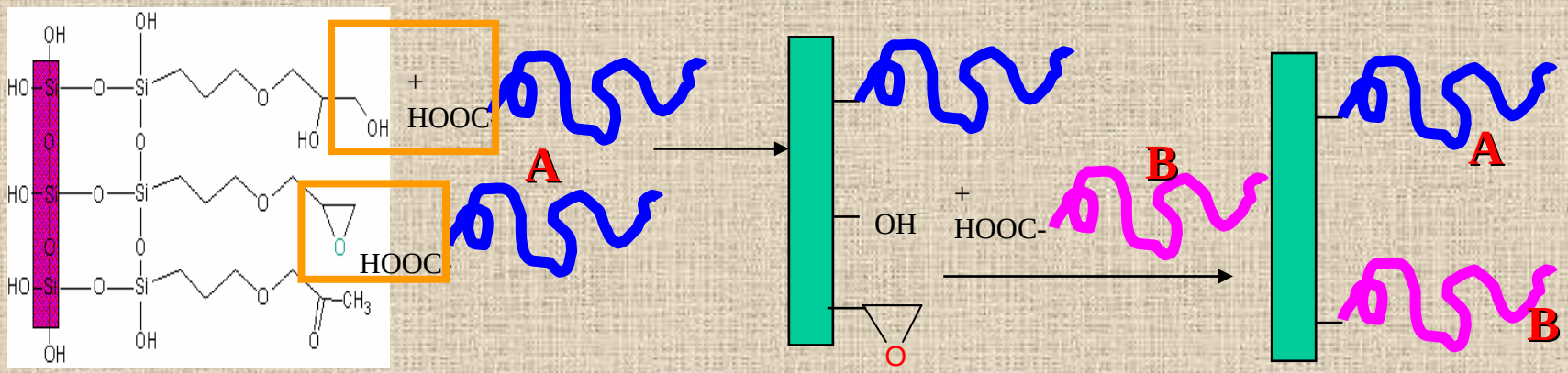


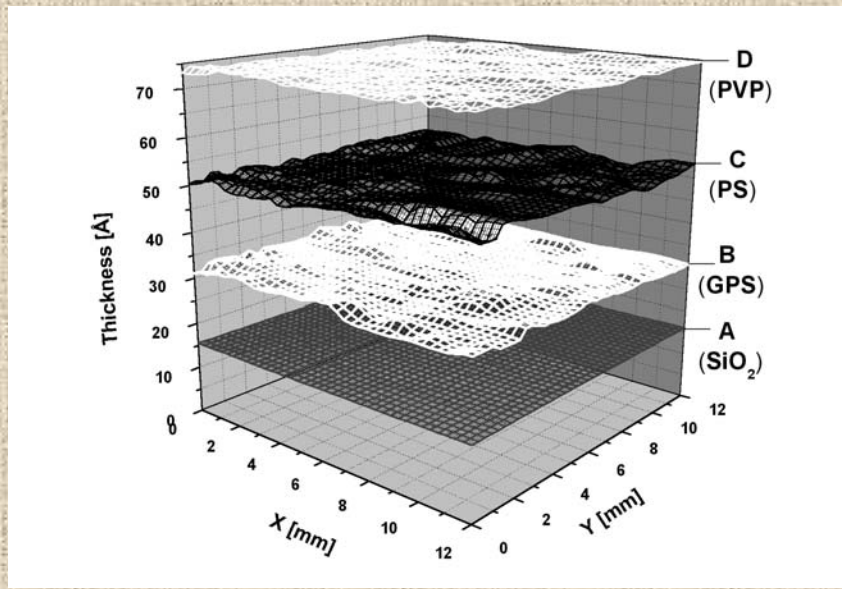




Langmuir **1999**, *15(24)*, 8349-8355

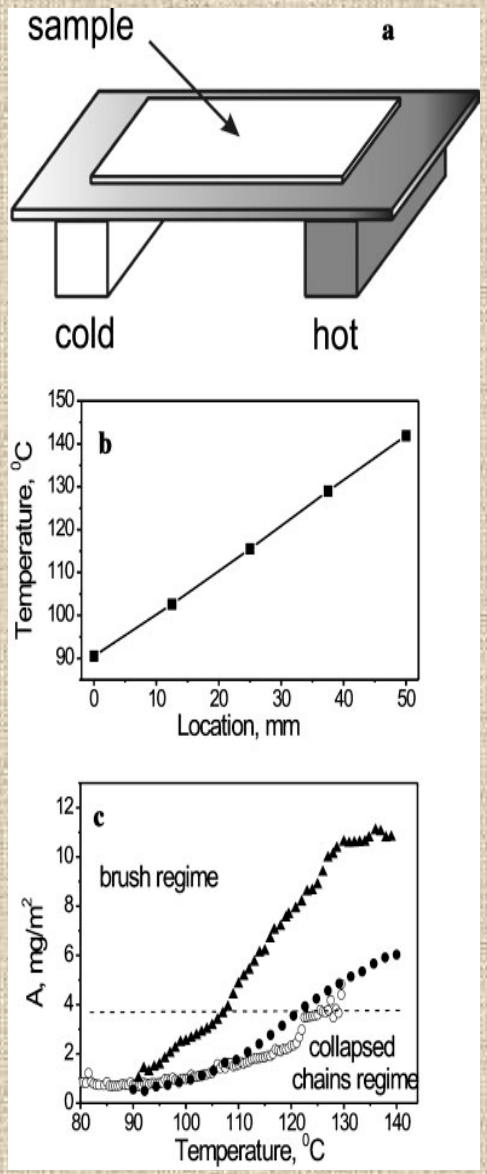
SYNTHESIS: grafting to

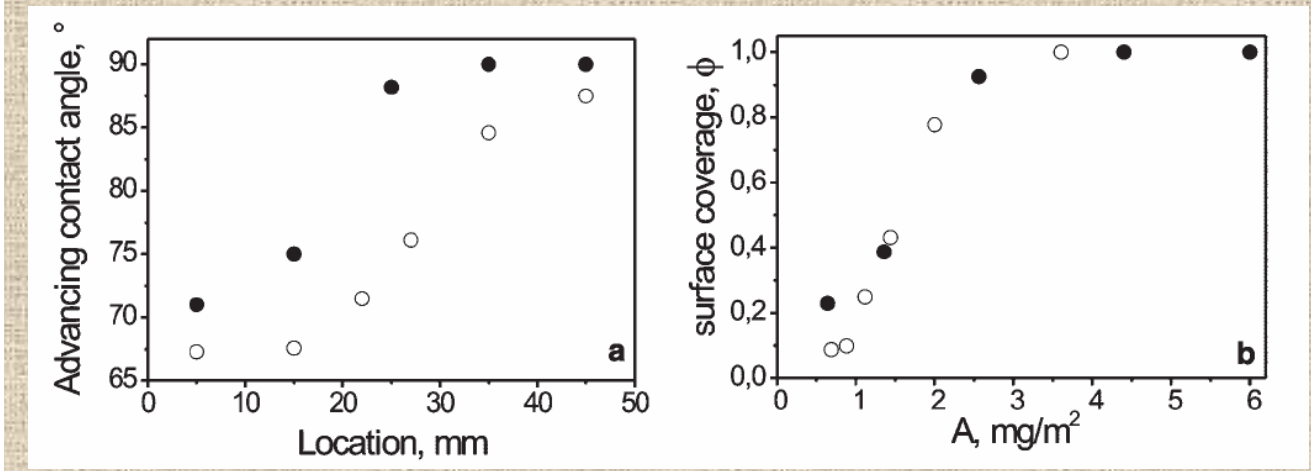




Langmuir **2002**, *18(1)*, 289-296.

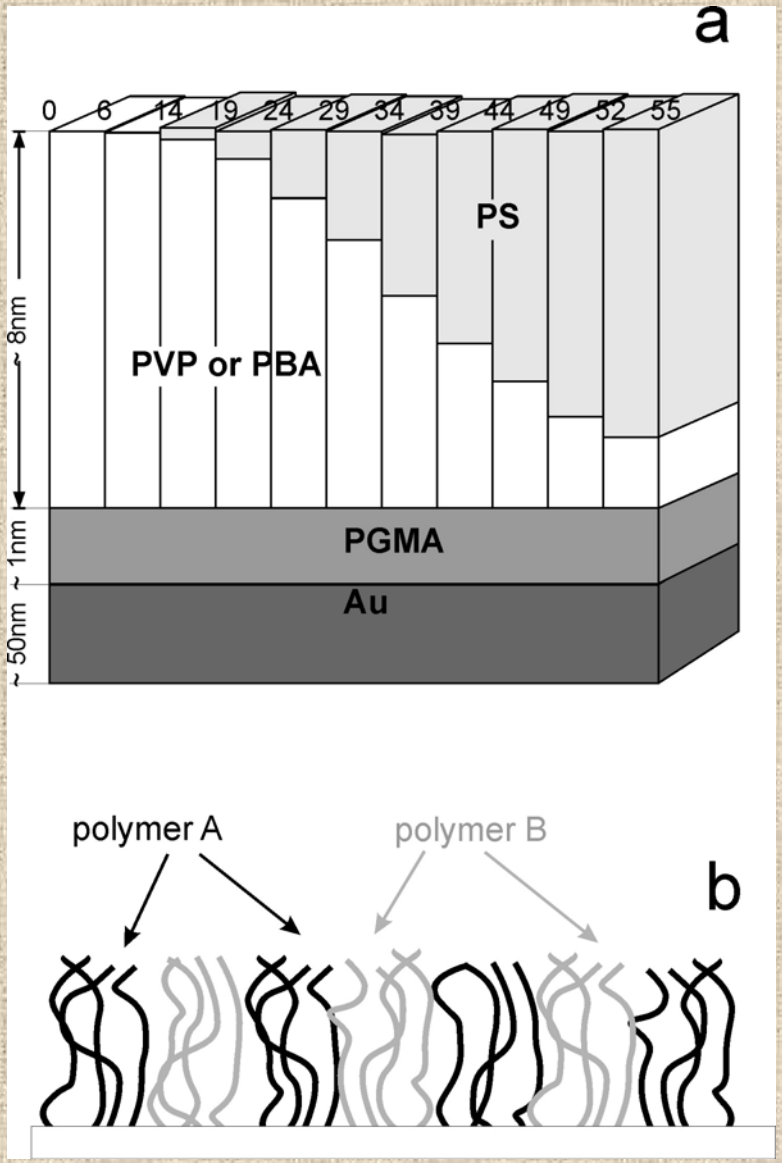
Gradient Polymer Brushes by ‘‘Grafting To’’ Approach

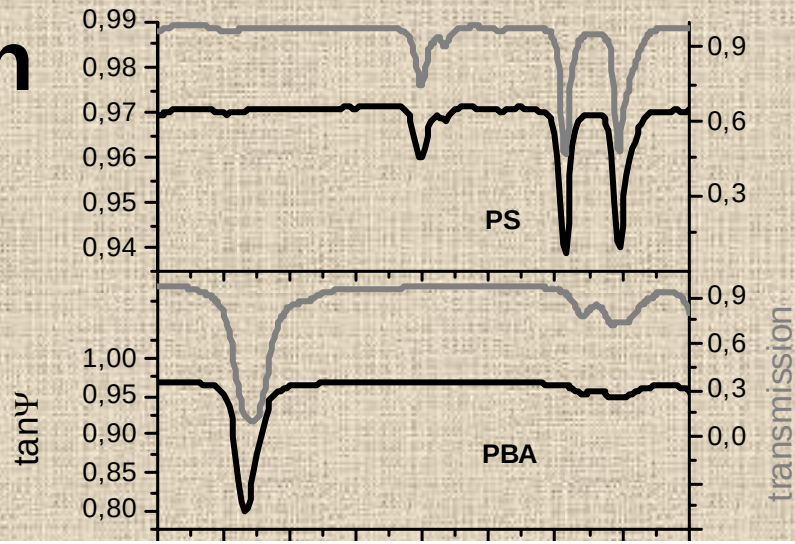


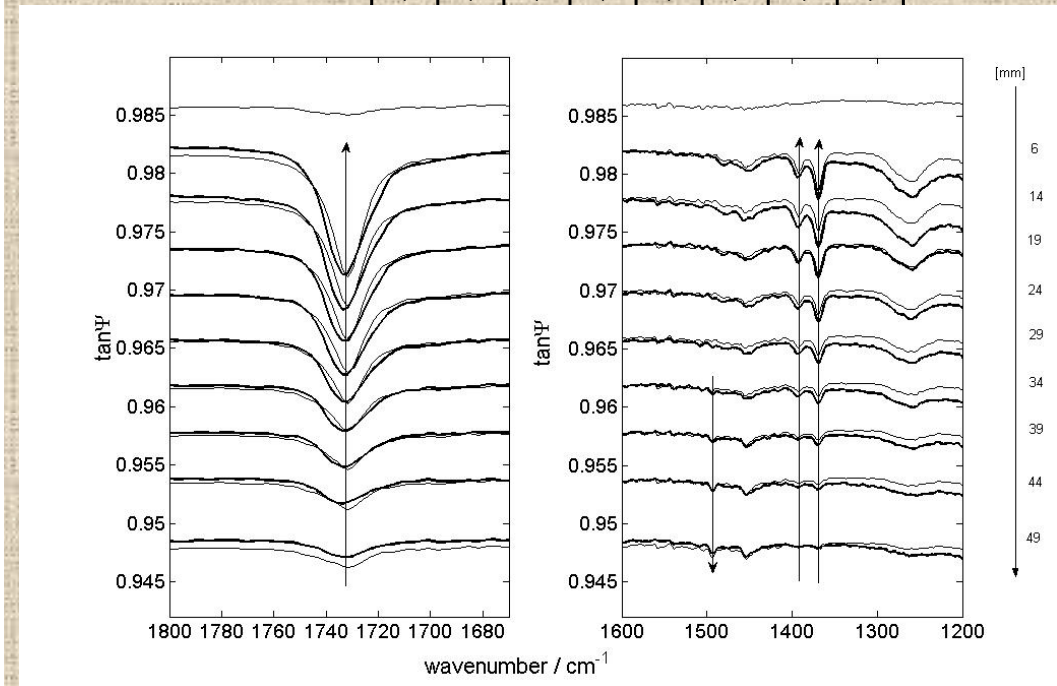


Macromol. Rapid Commun. 2004, 25, 360–365

Gradient mixed brush

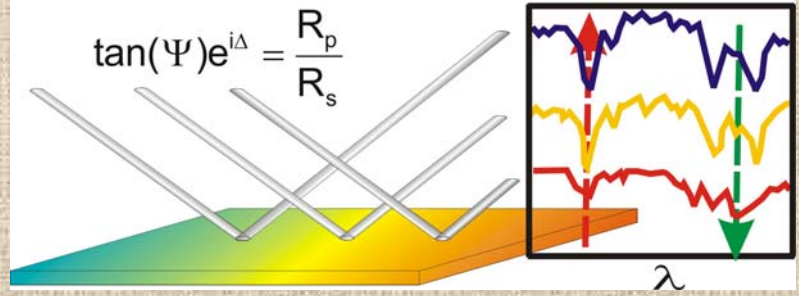


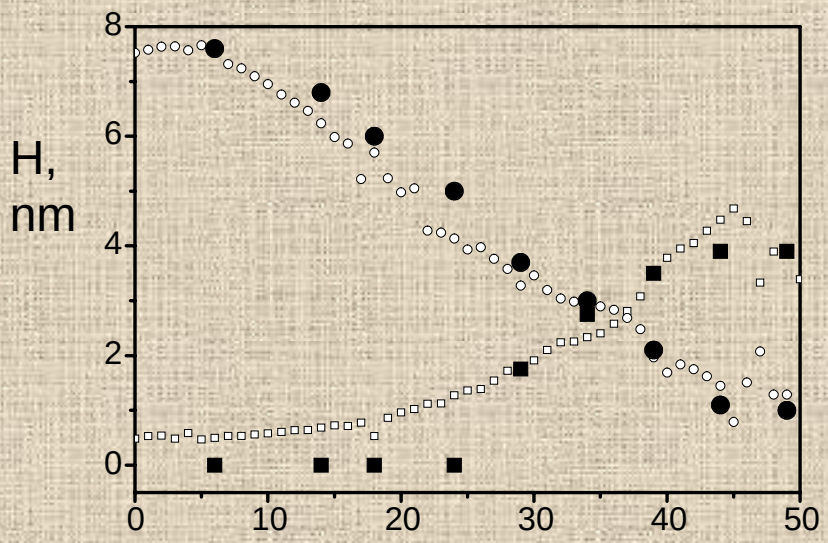


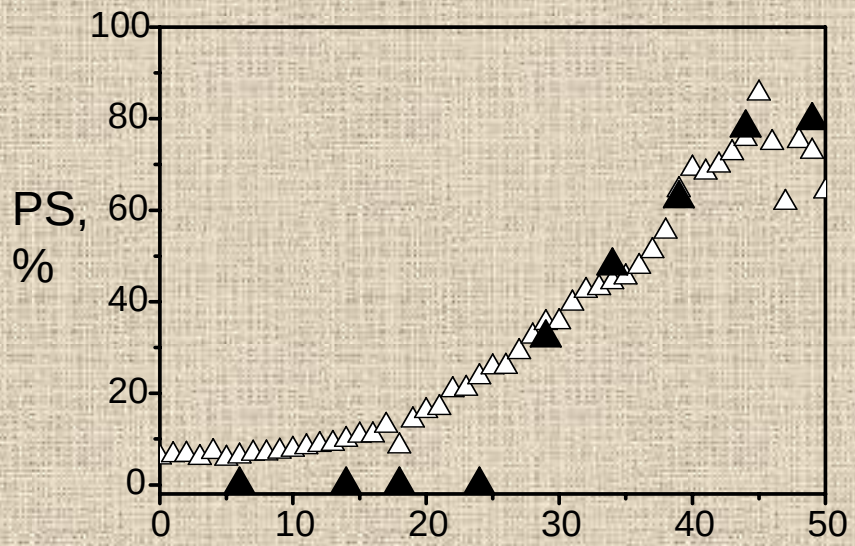


Langmuir **2005**, *21(19)*, 8711-8716

Gradient mixed brush





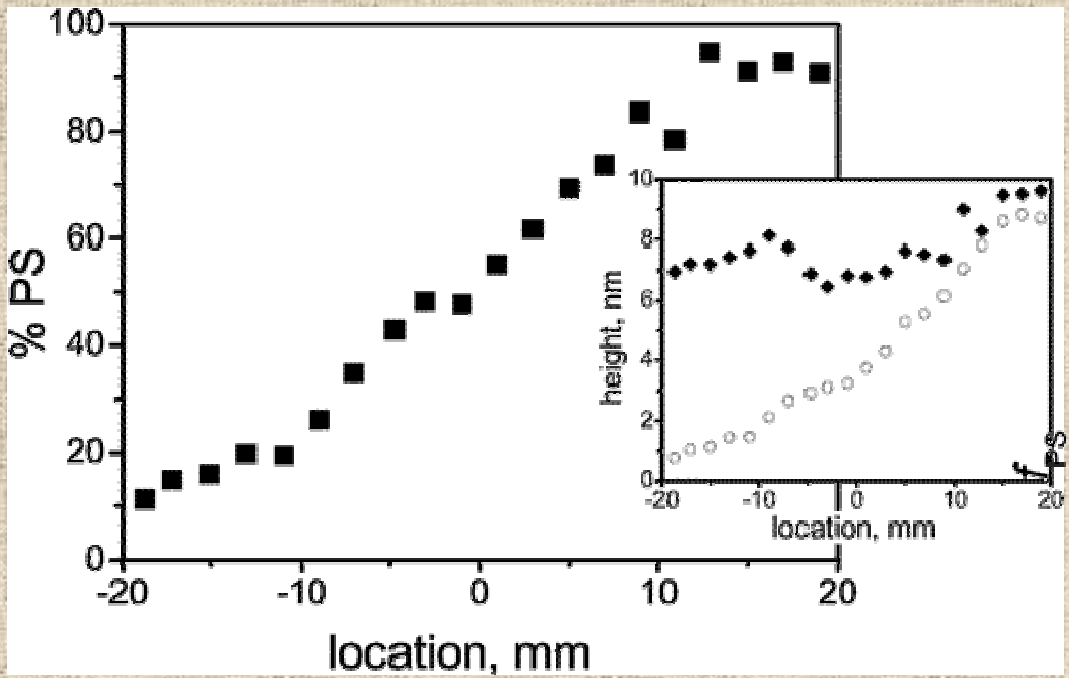


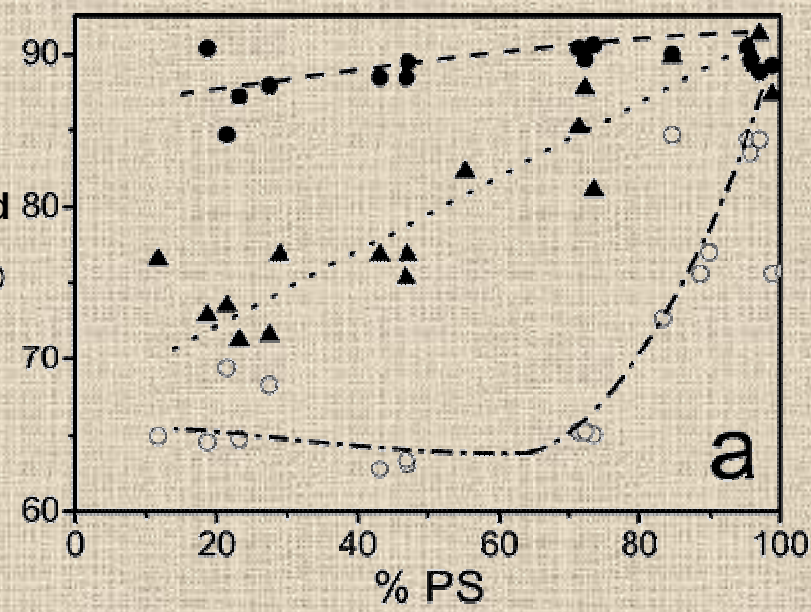
Ellipsometric mapping of thickness (a) and composition (b) of gradient PS-*mix*-PBA brush from single wavelength ellipsometry and IR-ellipsometry (solid)

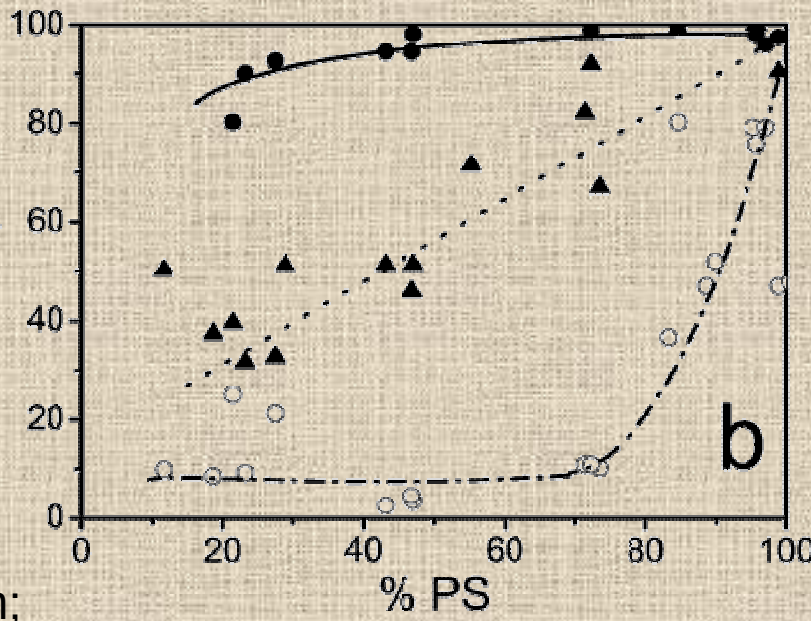
Langmuir **2005**, *21(19)*, 8711-8716

Switching gradient

Fraction of grafted polystyrene vs location of the measured spot (on *X* axis) for the gradient PS-*mix*-P2VP brush. The inset demonstrates the ellipsometric thickness of the homopolymer PS and PS-*mix*-P2VP brushes (empty circles, PS; black circles, PS-*mix*-P2VP).



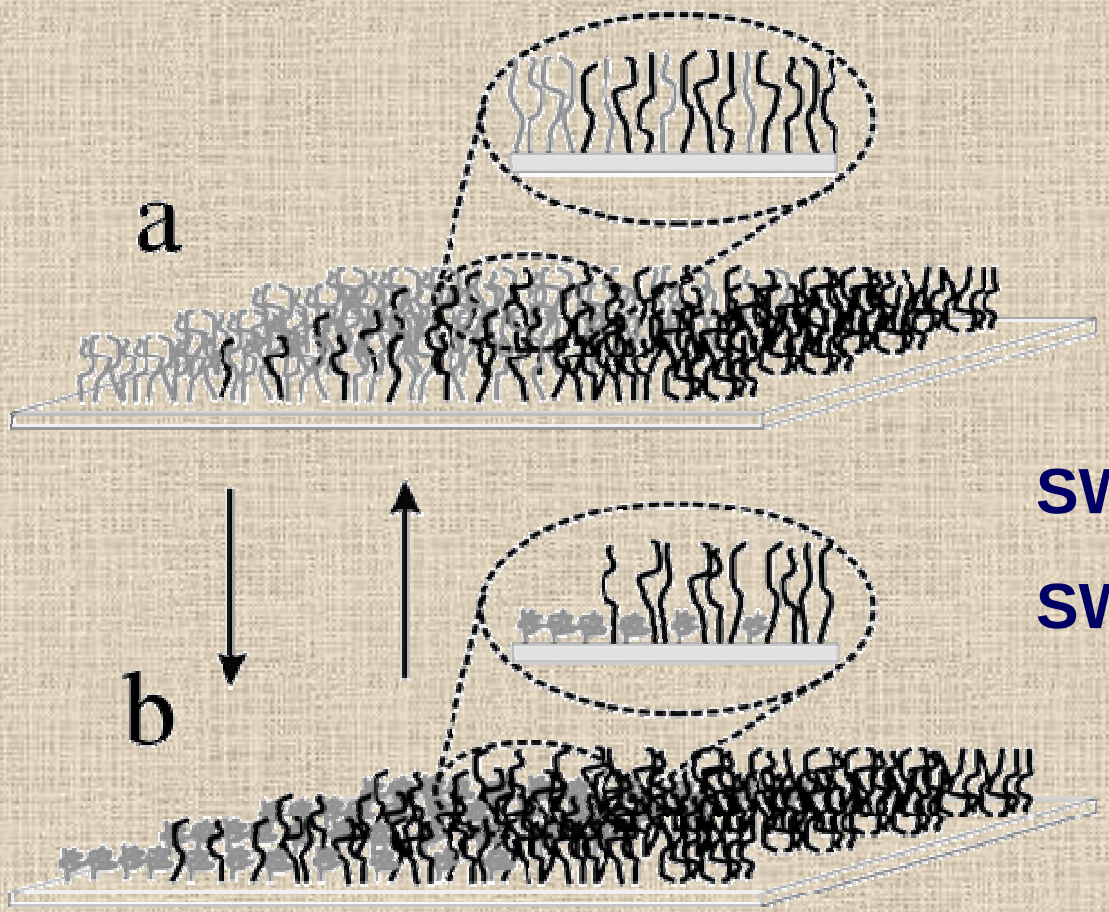




black circles, toluene; black triangles, chloroform; empty circles, ethanol

Macromolecules **2004**, *37(19)*, 7421-7423.

GRADIENT:

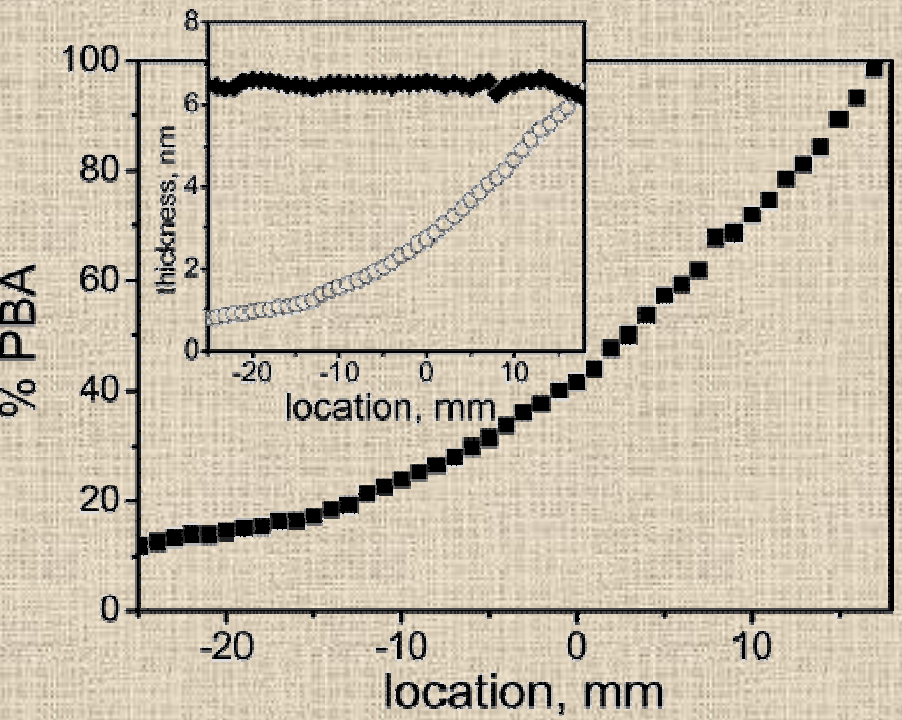


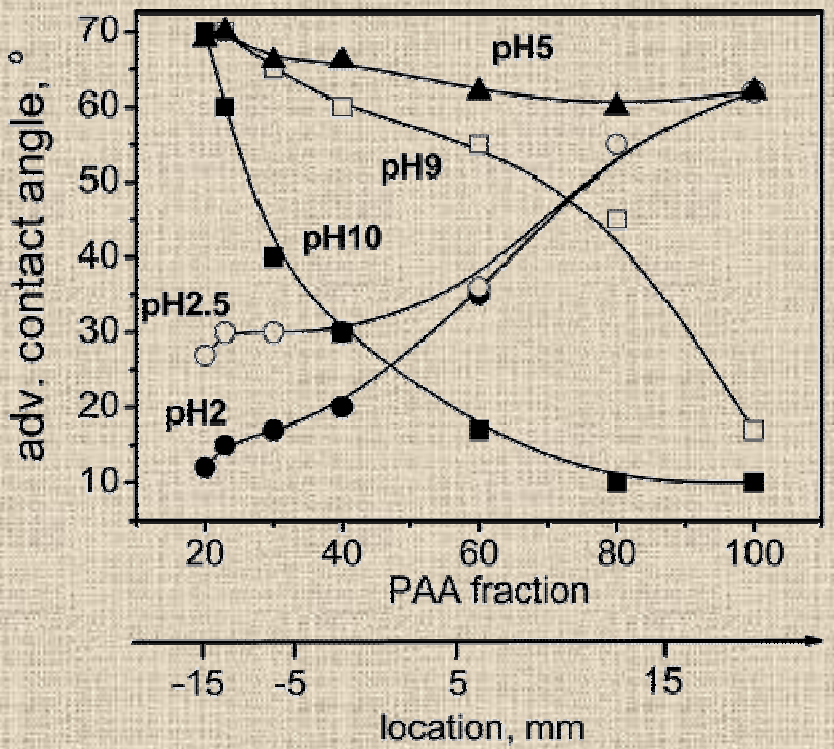
SWITCHING ON

SWITCHING OFF

Macromolecules **2004**, *37(19)*, 7421-7423.

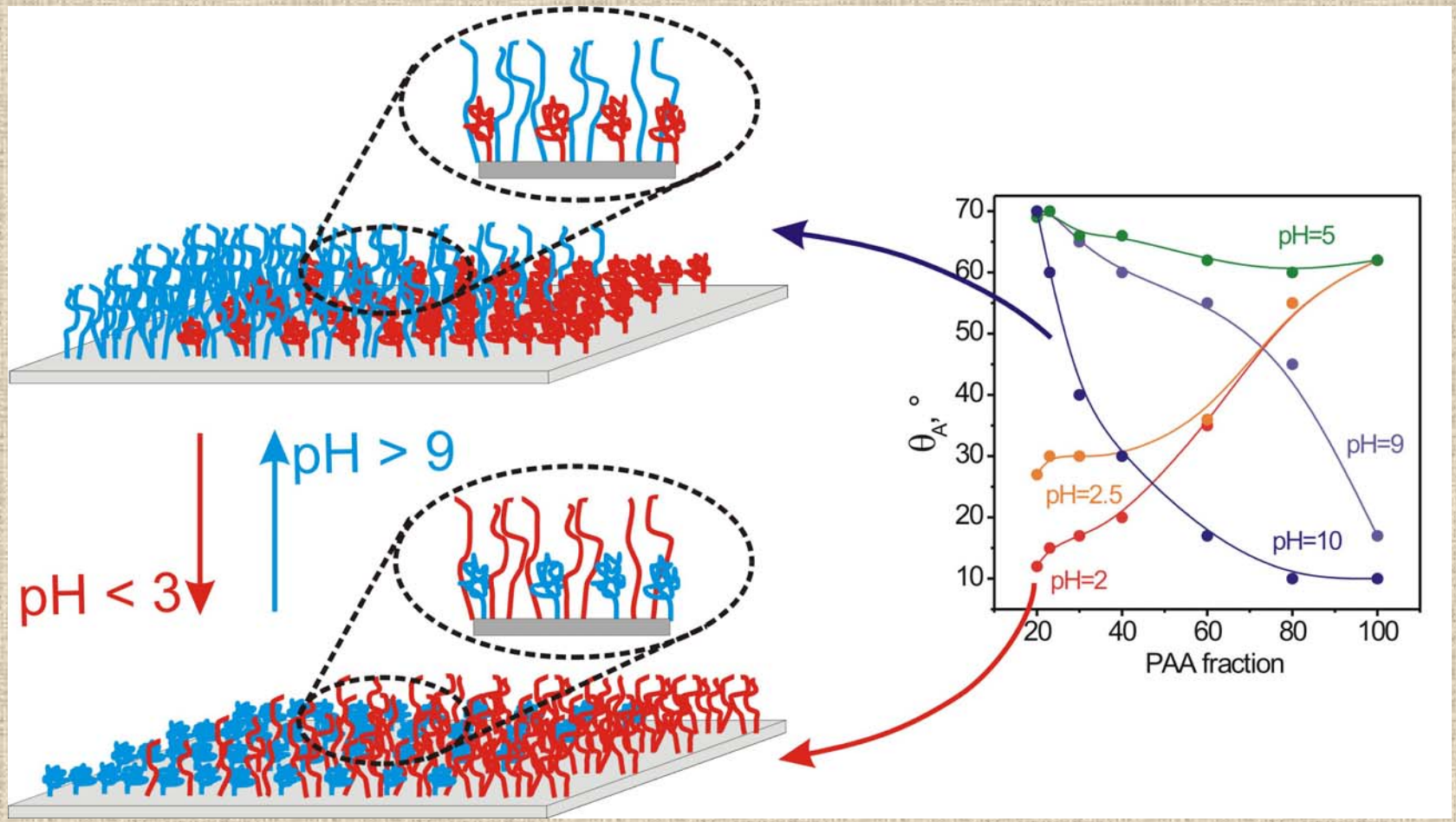
Inverse and Reversible Switching Gradient Surfaces from Mixed Polyelectrolyte Brushes





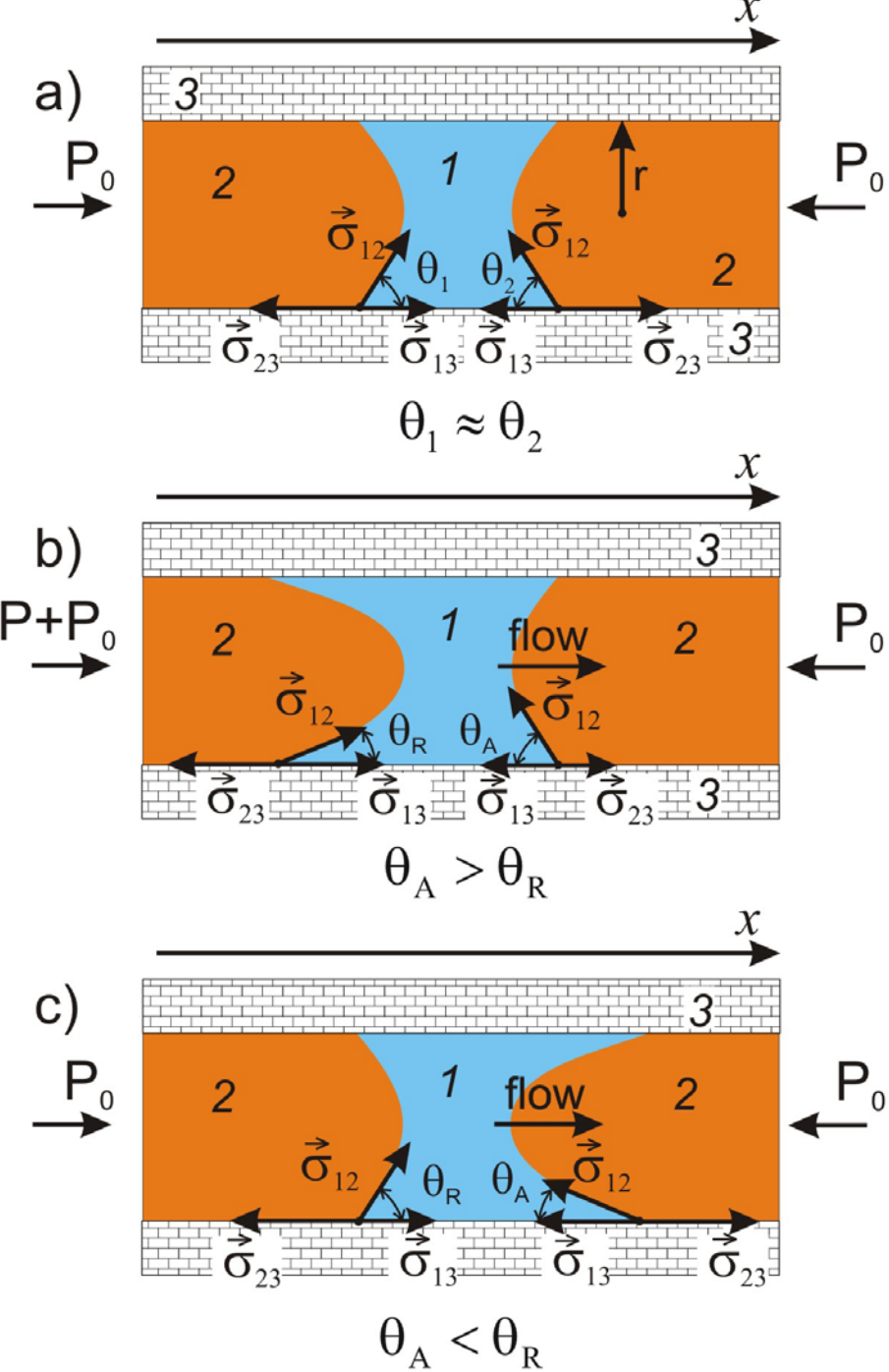
Fraction of grafted poly(*tert*-butyl acrylate) vs location for the gradient PBA/P2VP brush.

Langmuir, **20** (23), 9916 -9919, 2004



Langmuir, **20** (23), 9916 -9919, 2004

EXAMPLES:



steady state
no flow

$$\frac{\partial \sigma_{23}}{\partial x} = 0$$

J. C. Jamin, *Phil. Mag.* **1860,** *4*, 204.

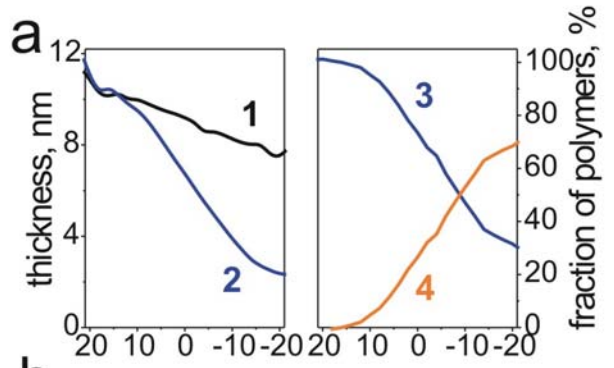
$P-P_0 = 2\ \sigma_{12}(\cos\ \theta_R - \cos\ \theta_A)/r,$

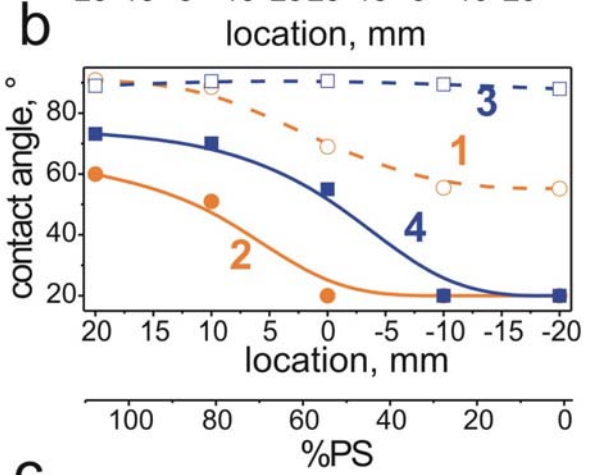
enforced flow

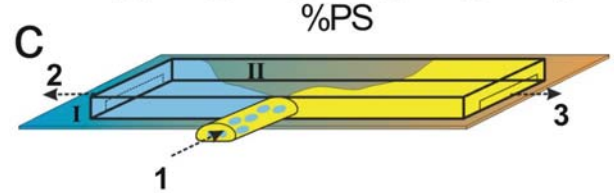
$$\frac{\partial \sigma_{23}}{\partial x} = 0$$

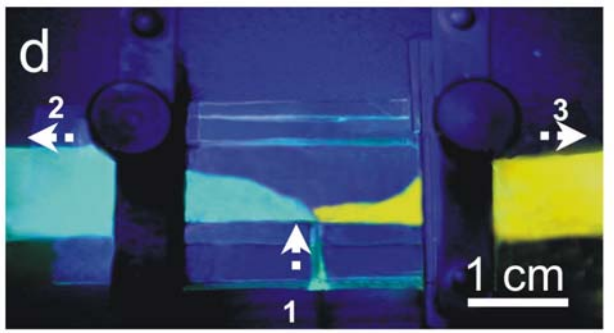
spontaneous
flow

$$\frac{\partial \sigma_{23}}{\partial x} > 0 \qquad \frac{\partial \sigma_{13}}{\partial x} < 0$$

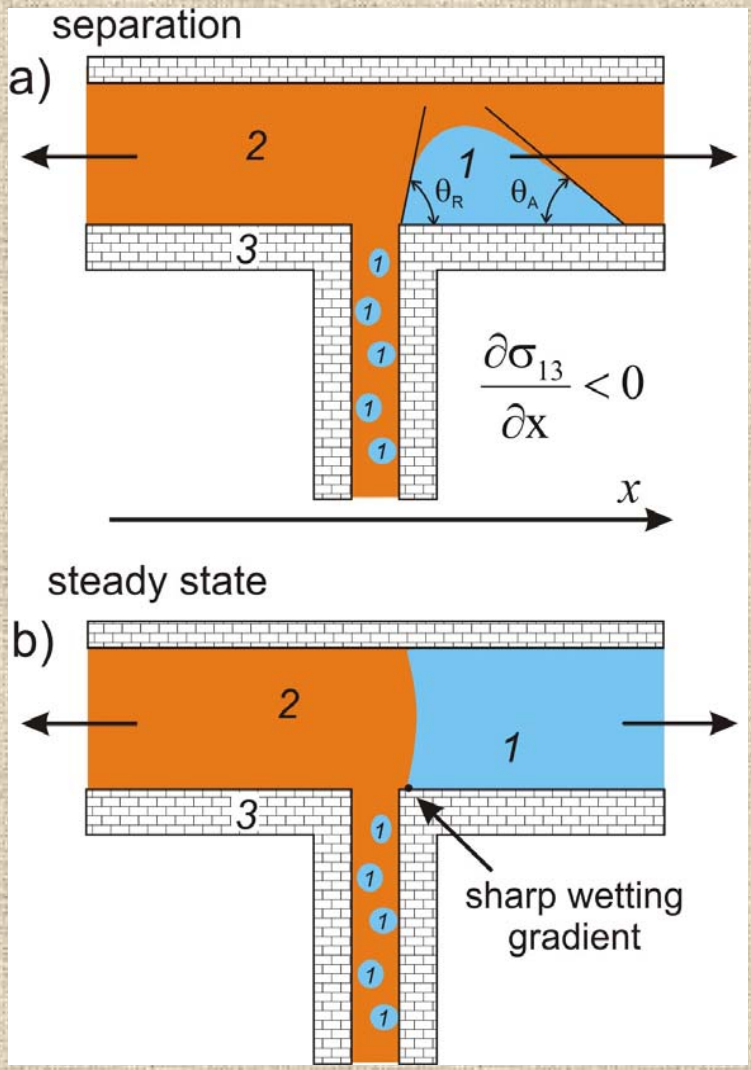






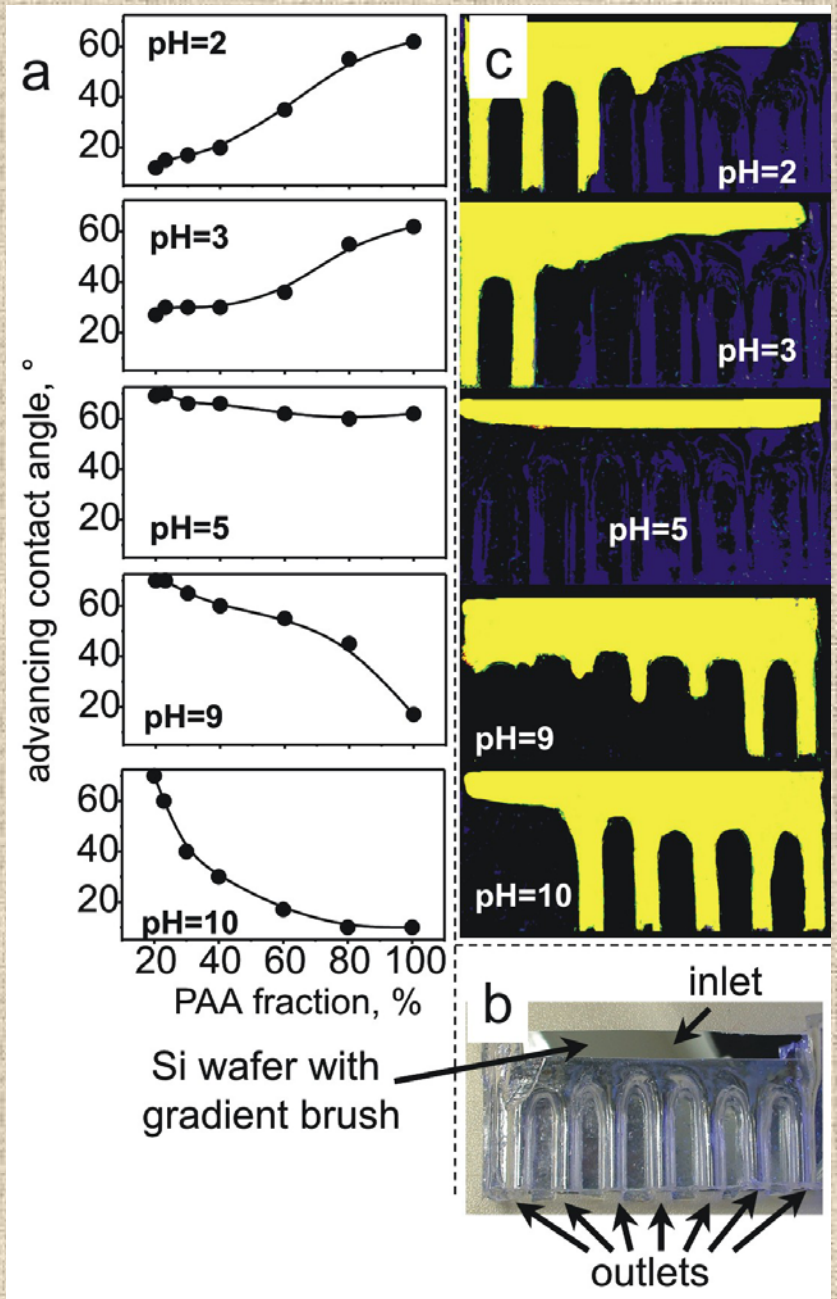


Separation of emulsions:



Advanced Functional Materials in press

EXAMPLES: Chemical gates

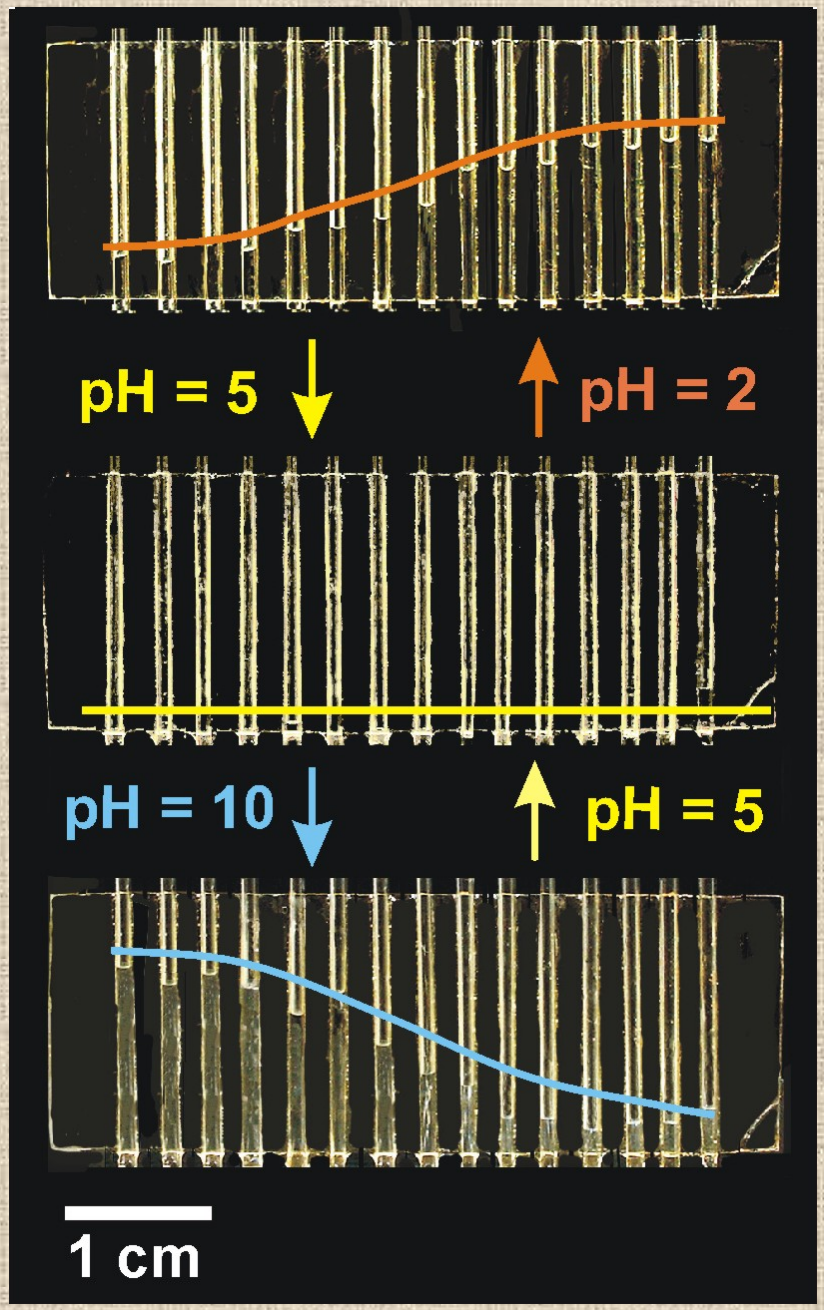


Advanced Functional Materials in press

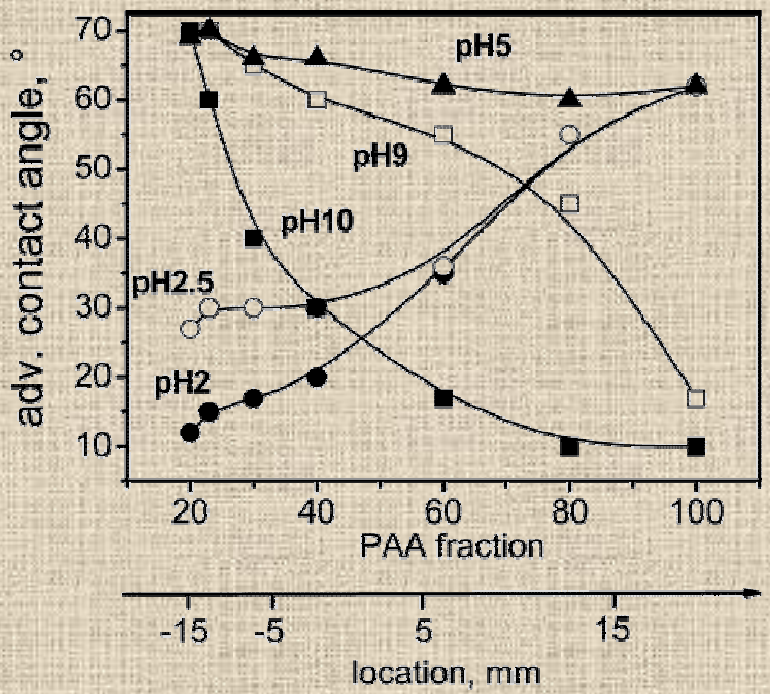
Capillary Rise

Laplace equation for capillary rise

$$\frac{2\sigma_{12}\cos\theta_A}{r} = p$$

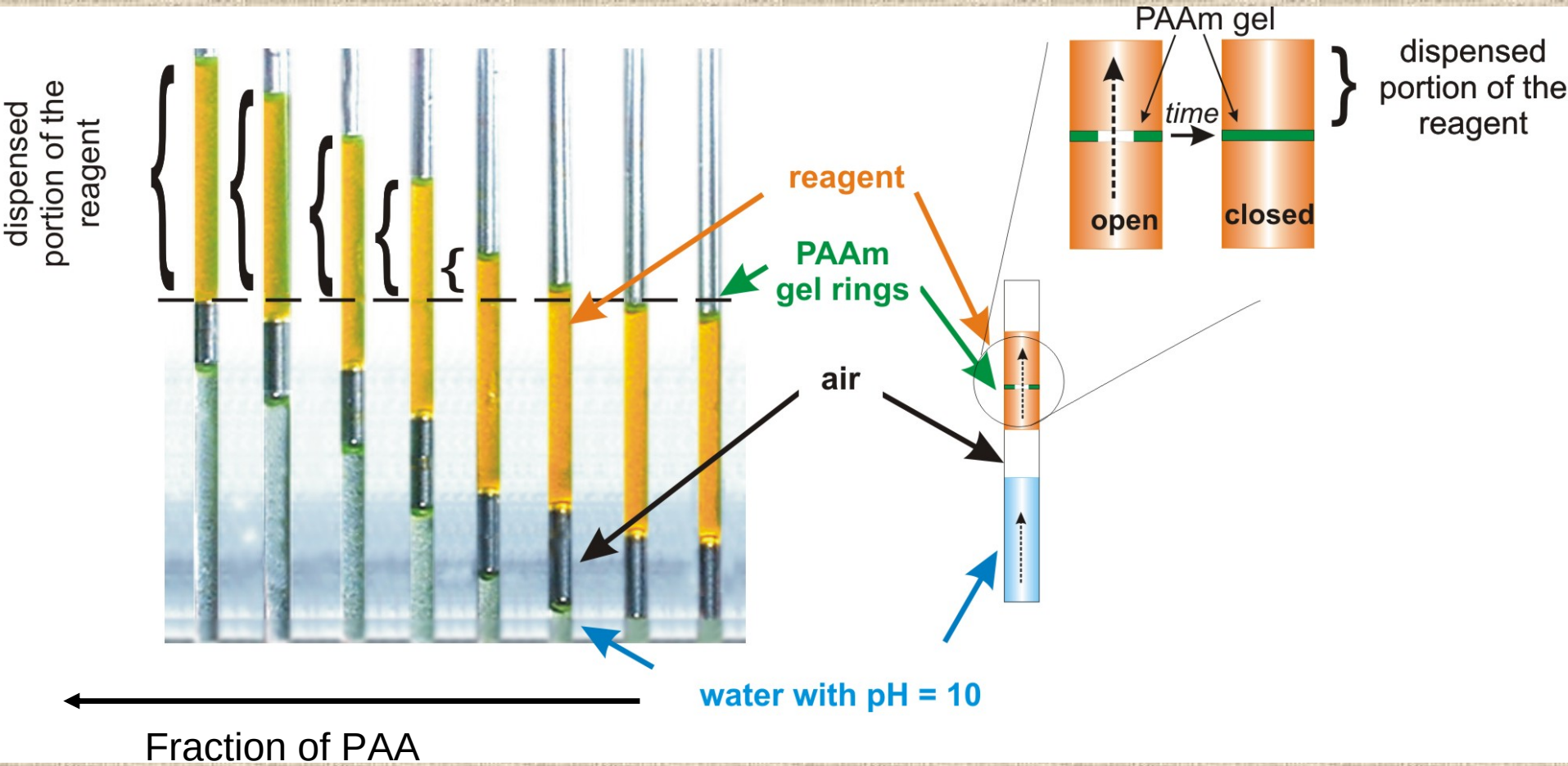


Fraction of PAA



Advanced Functional Materials in press

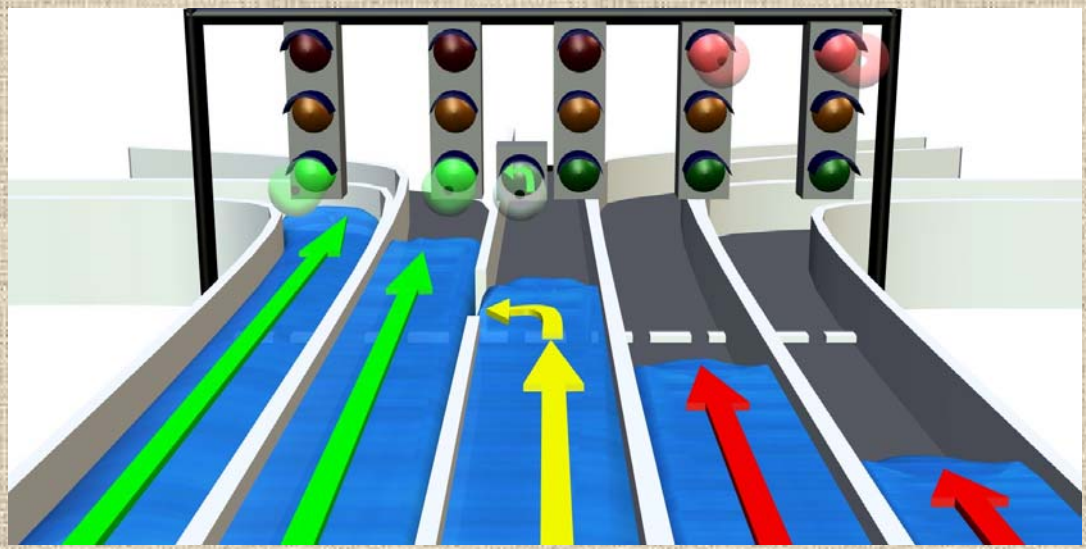
Microfluidic dispenser



Advanced Functional Materials in press

CONCLUSIONS

- **Gradient brushes of complex compositions allow for a precise regulation of interfacial interactions.**
- **Combinatorial approach is very important for the optimization of the brush composition. Theoretical predictions are limited by simple systems.**
- **Wetting experiments, adsorption, separation, selection, sensing, and dispensing small volumes of liquids could be used to collect the data about interfacial interactions.**



Acknowledgement:

Igor Tokarev Clarkson

Michael Motornov Clarkson

Leonid Ionov, IPF, Germany

Nikolai Huobenov, Germany

Manfred Stamm, IPF, Dresden, Germany

Alex Sidorenko, Bell Labs, NJ

Constantinos Tsitsilianis, Univ. Patras, Greece

Igor Luzinov, Clemson University, SC

Marcus Mueller, Germany

PhD students:

Robert Lupytskyy, Clarkson

Maxim Orlov, Clarkson

Roman Sheparovych, Clarkson

Financial support:

Clarkson University, NSF, NATO, ARO,

NYSTAR- CAMP, P&G, Xerox Co.

DFG, BMBF, Volkswagen Foundation, AiF