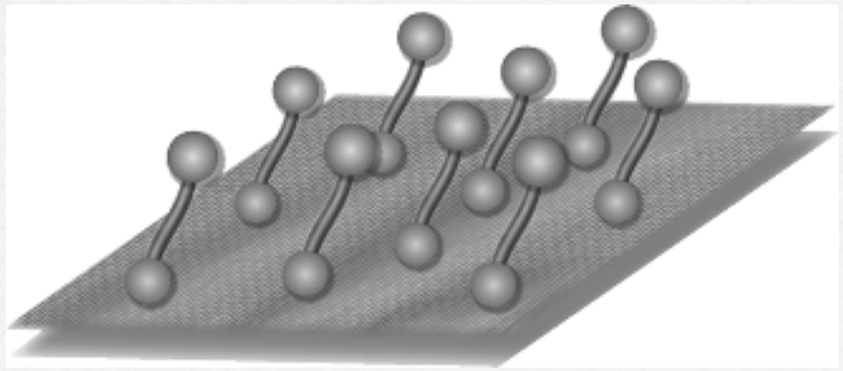
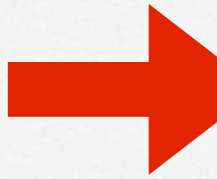
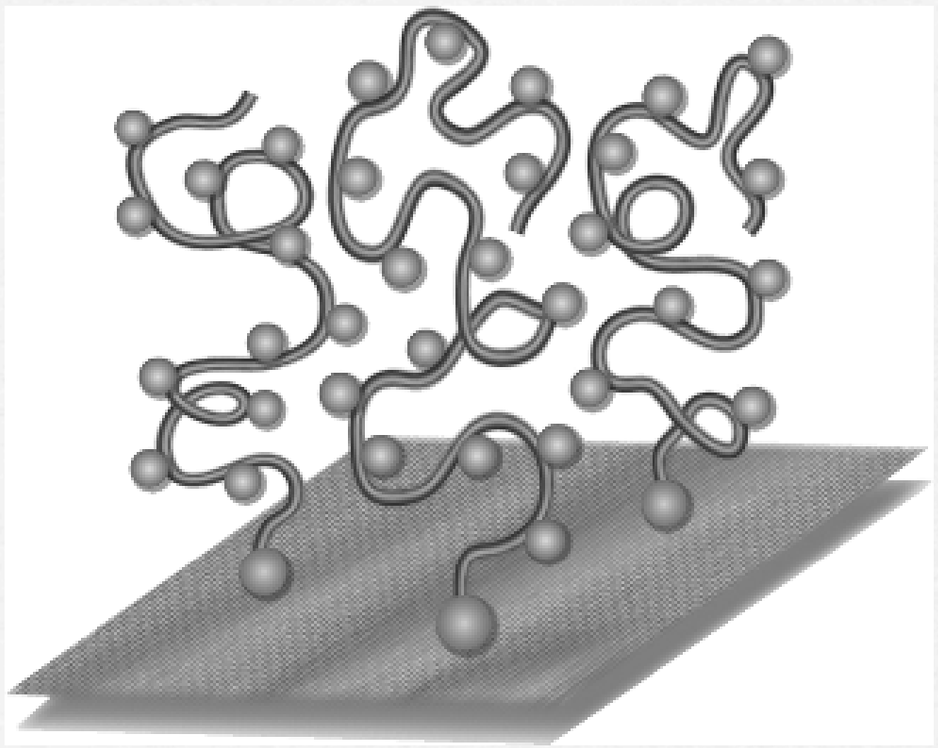
grafting polymers

polymer brushes



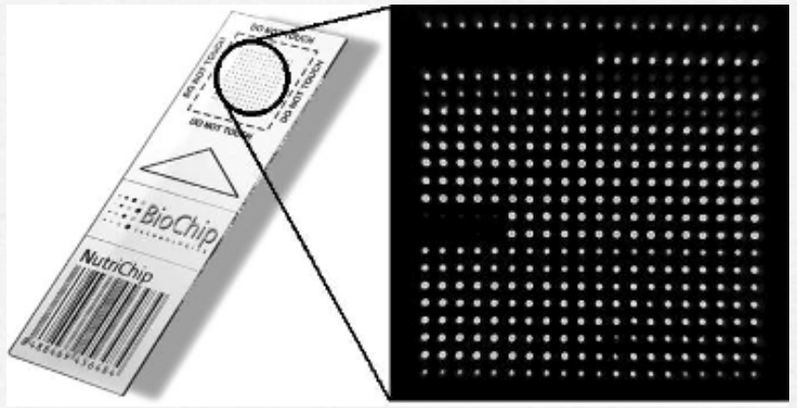




polymer brushes

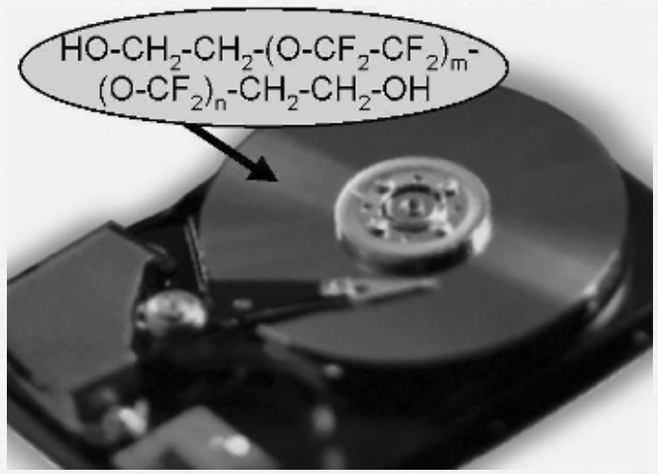
examples:

DNA-chips

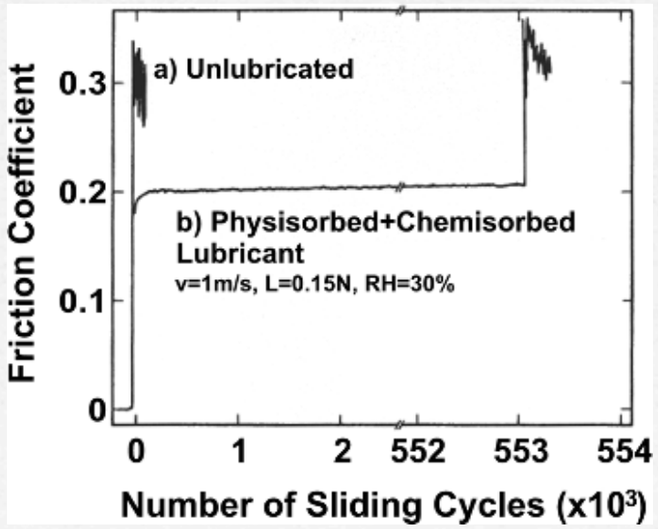


hard-drives

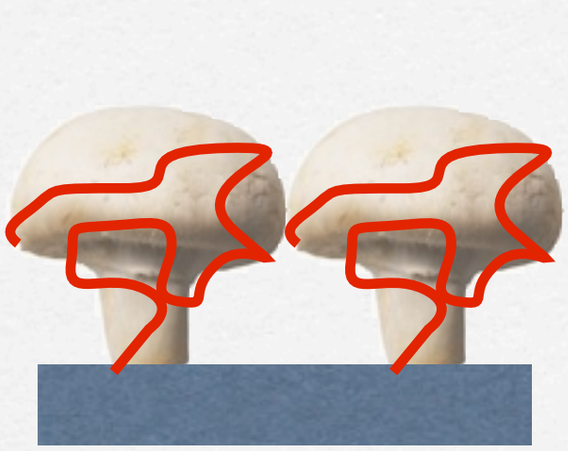
a)



b)



mushroom, pancake, brush



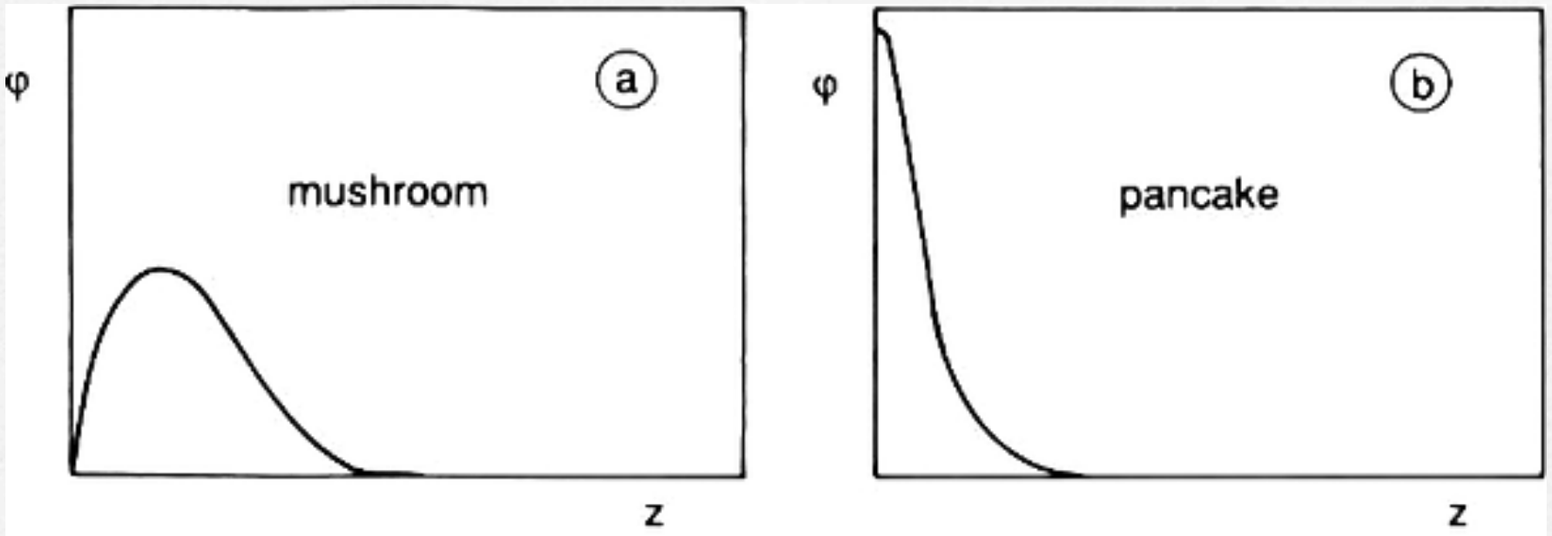
mushroom

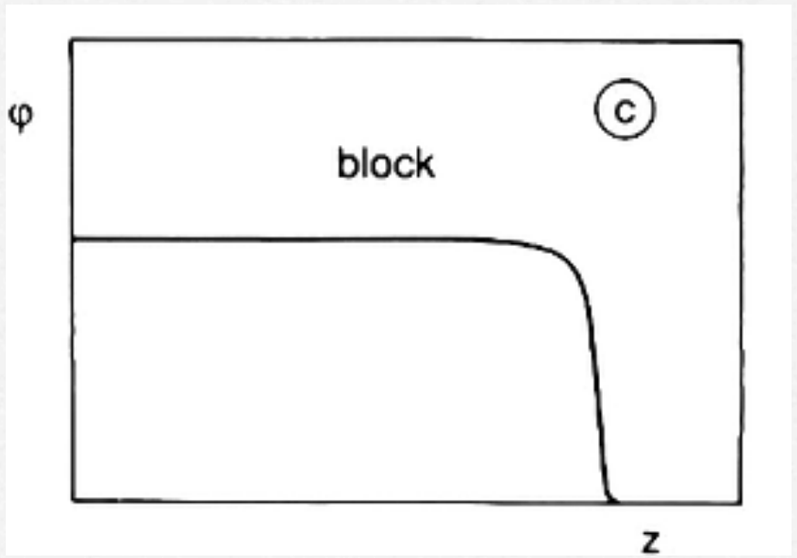
pancake

brush

mushroom, pancake, brush

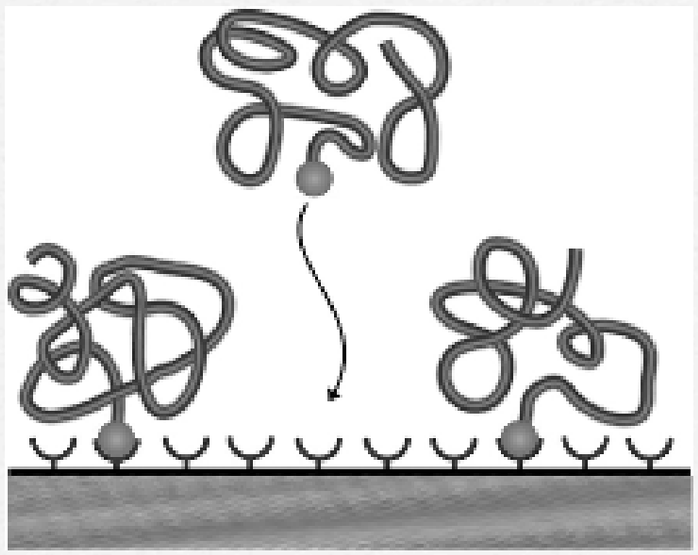
segment density profiles





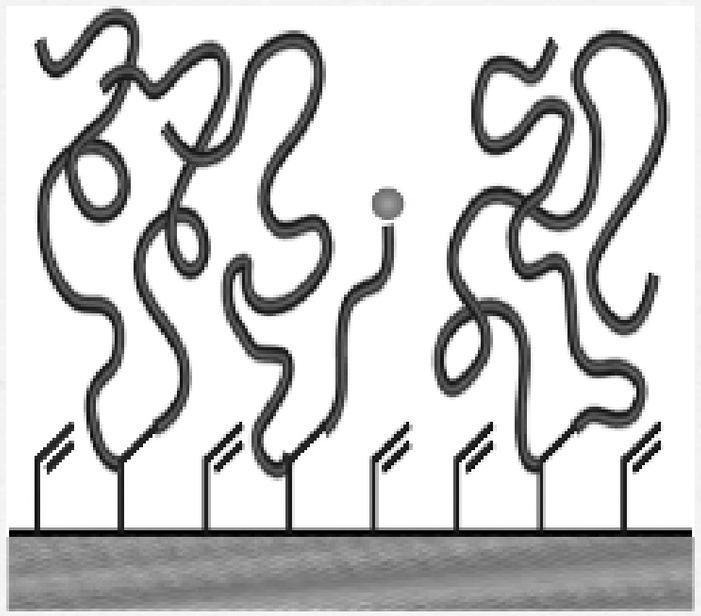
polymer brushes

a)



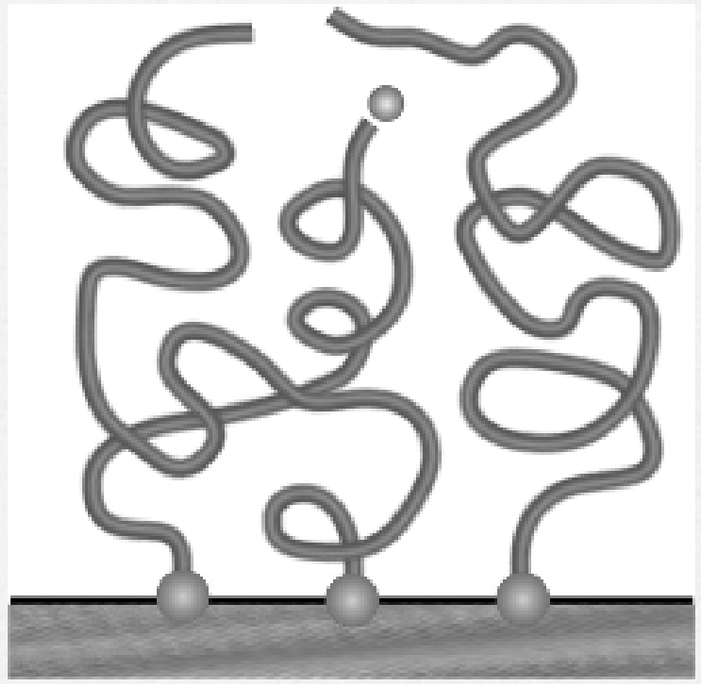
grafting to

b)



grafting via surface monomeric units

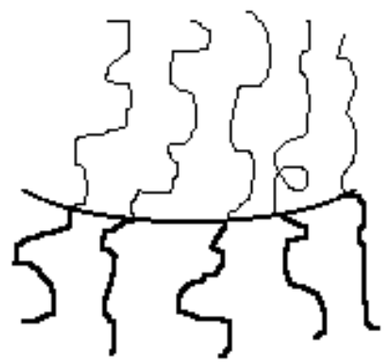
c)



grafting from

polymer brush preparation

1. LB trough -> amphiphilic block copolymer



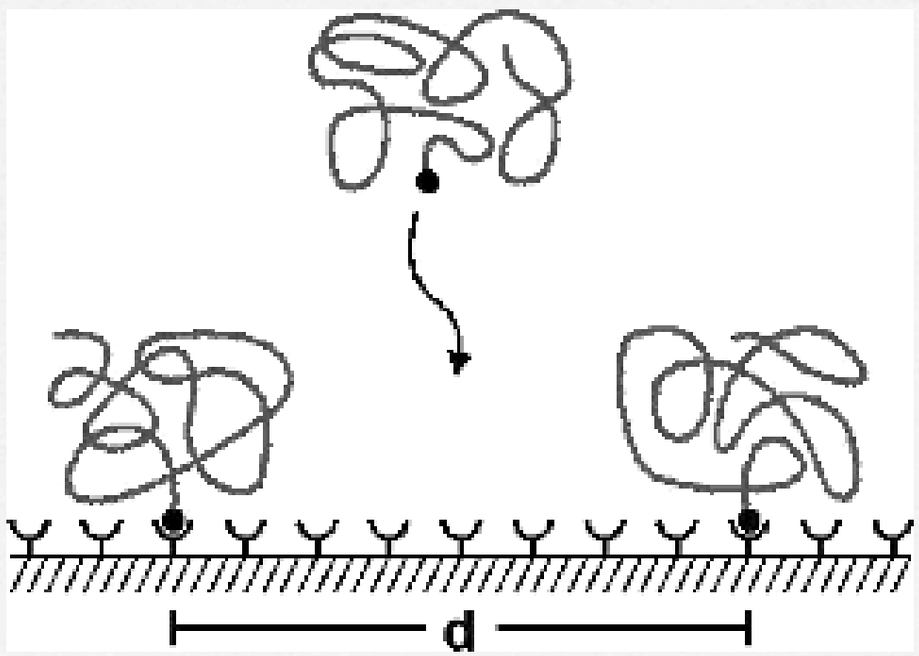
Block Copolymers at
Fluid-Fluid Interfaces

2. block or end-functionalized polymers (grafting from)

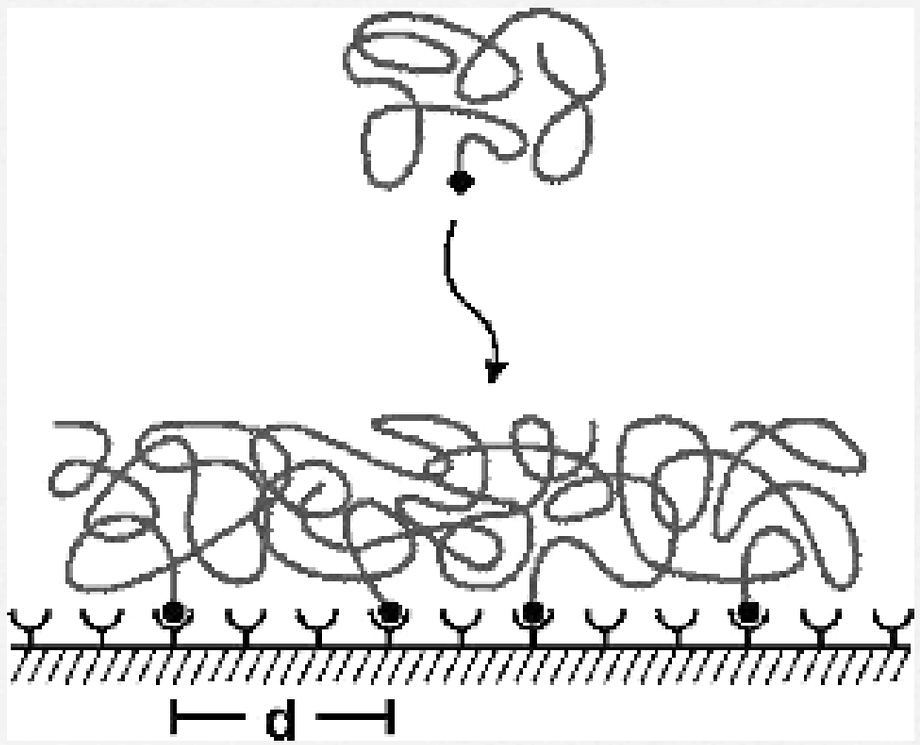
Adsorbed Block
Copolymers

grafting to: low density

a)

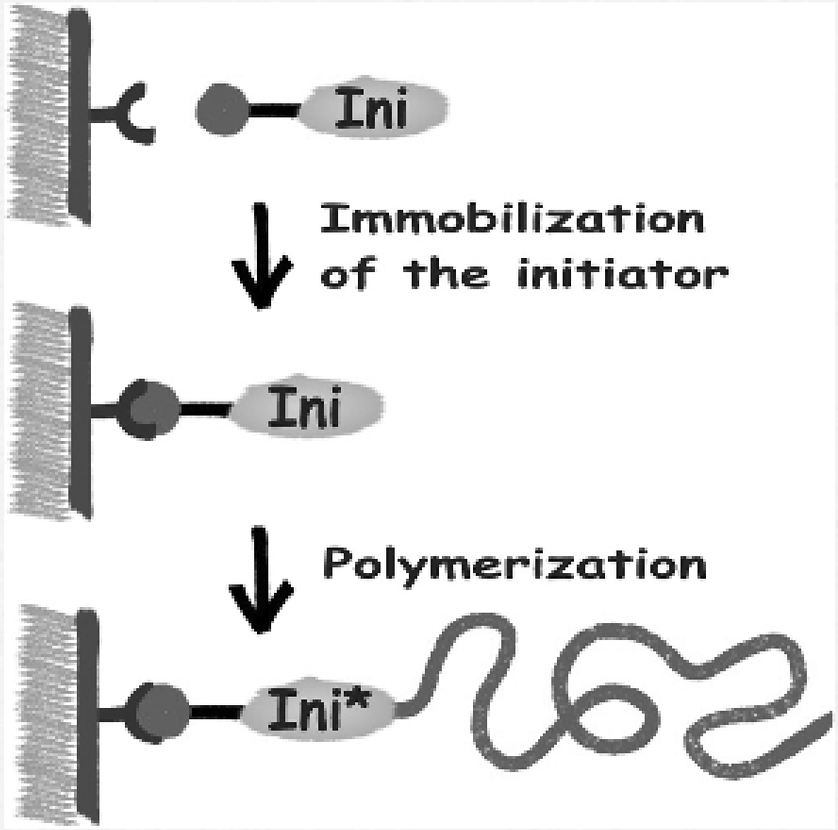


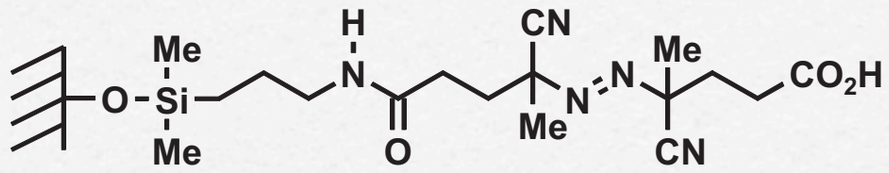
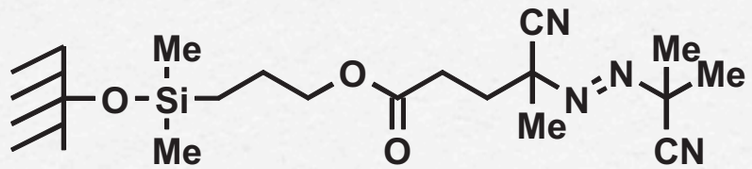
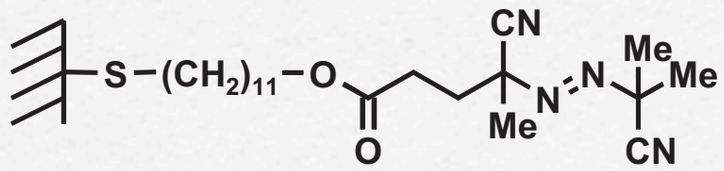
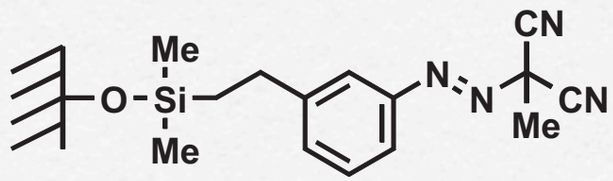
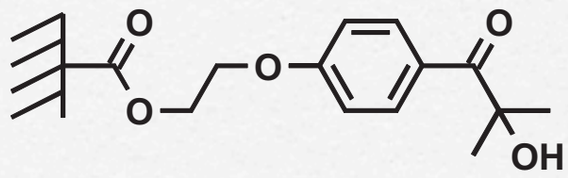
b)

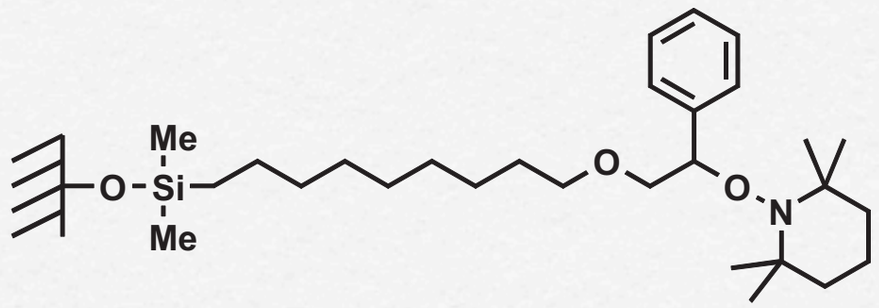
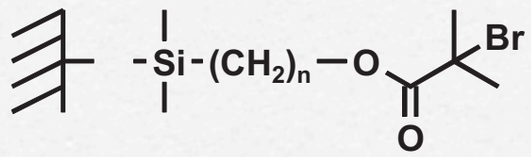
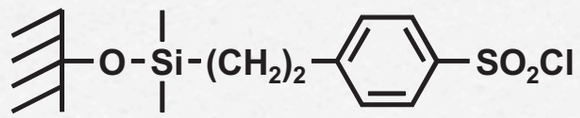
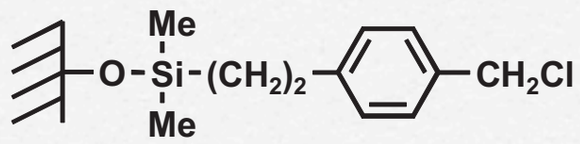
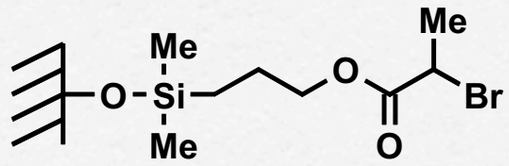


polymer brush preparation

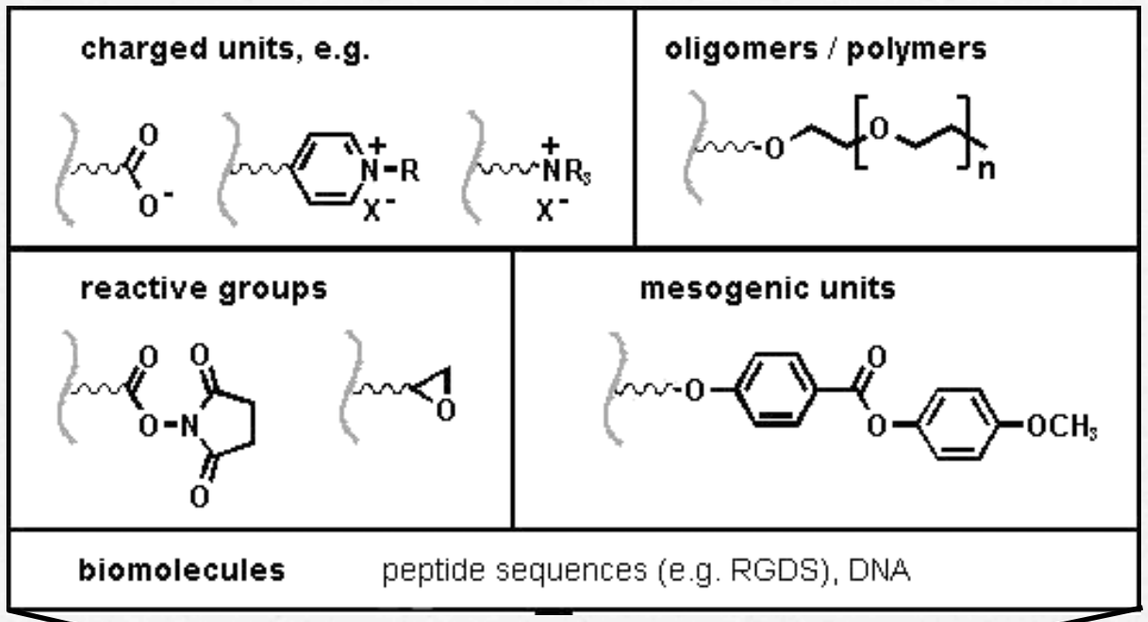
3. grafting from:

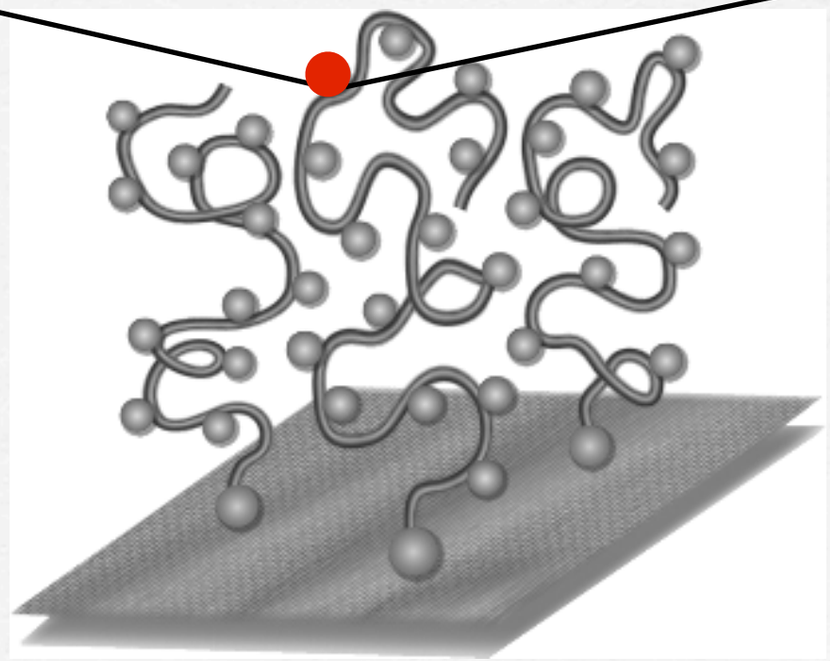


Mechanism	Initiator/initiating species	Maximum thickness (nm)	Reference(s)
Free radical		~ 100 nm	63,64
		up to 2200 nm	65–72
			
			
		n.a.	73,74

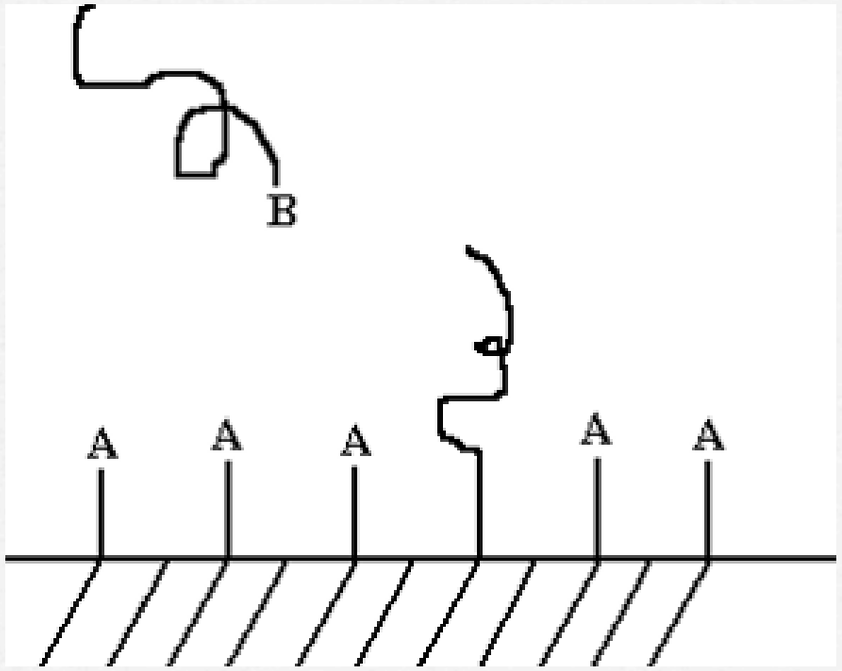
TEMPO		120 nm	75,76
ATRP		150 nm; 700 nm (water accelerated)	77–83
		100 nm	84–86
		n.a.	87–89
		< 60 nm	82,90
Others	Various systems for cationic and anionic polymerizations, RAFT and reverse ATRP	< 40 nm	91–97

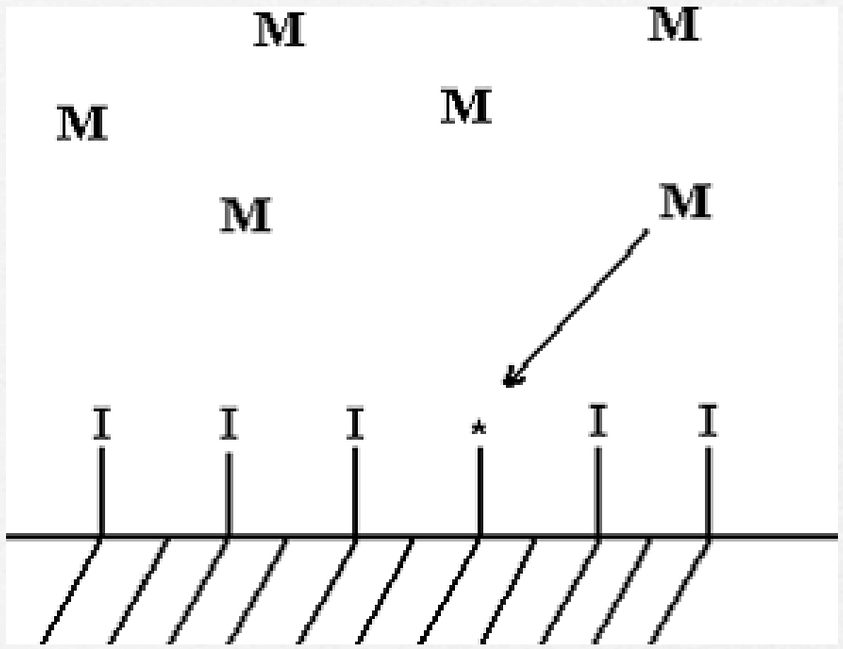
functional polymer brushes



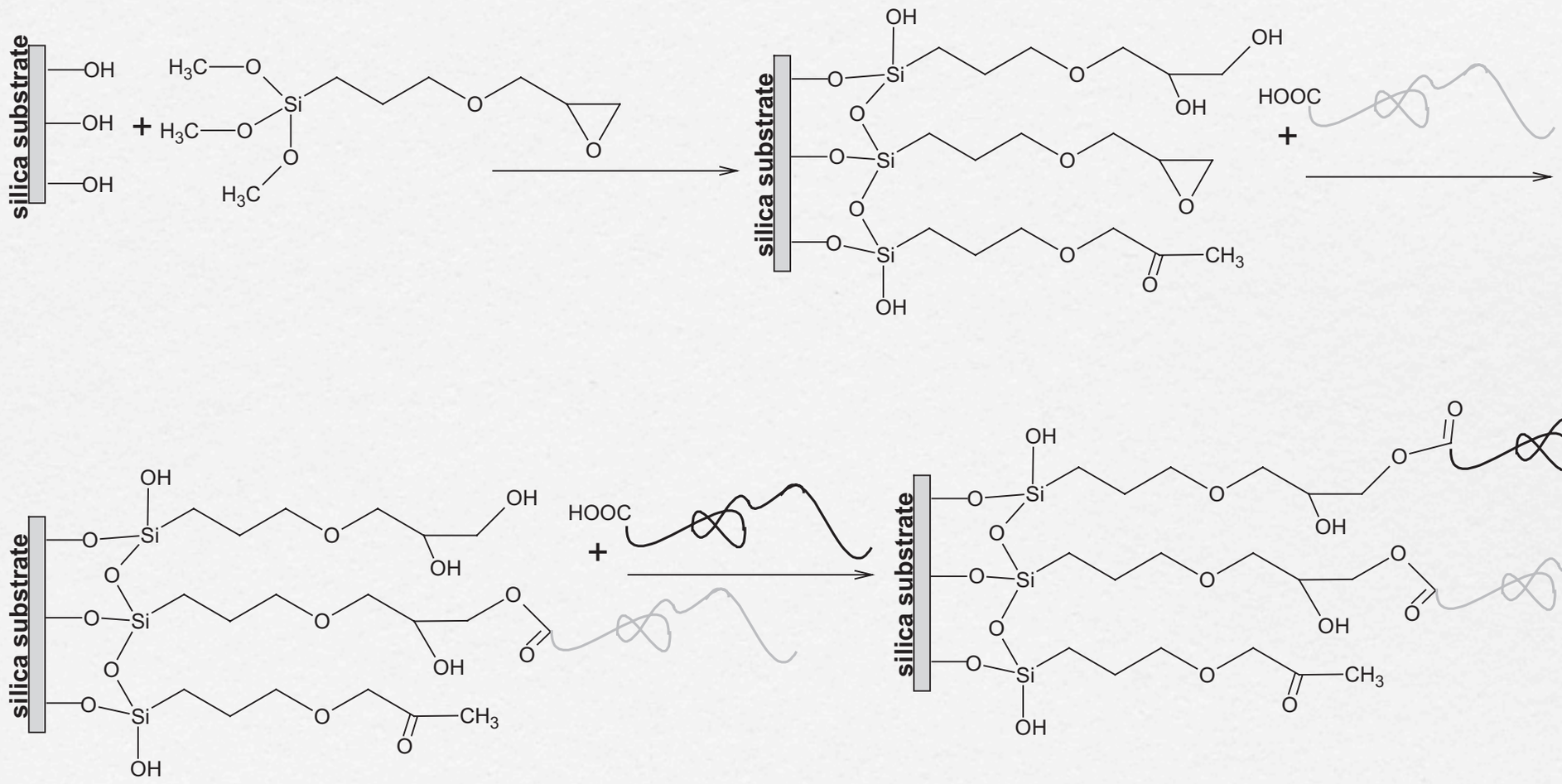


grafting to vs. grafting from

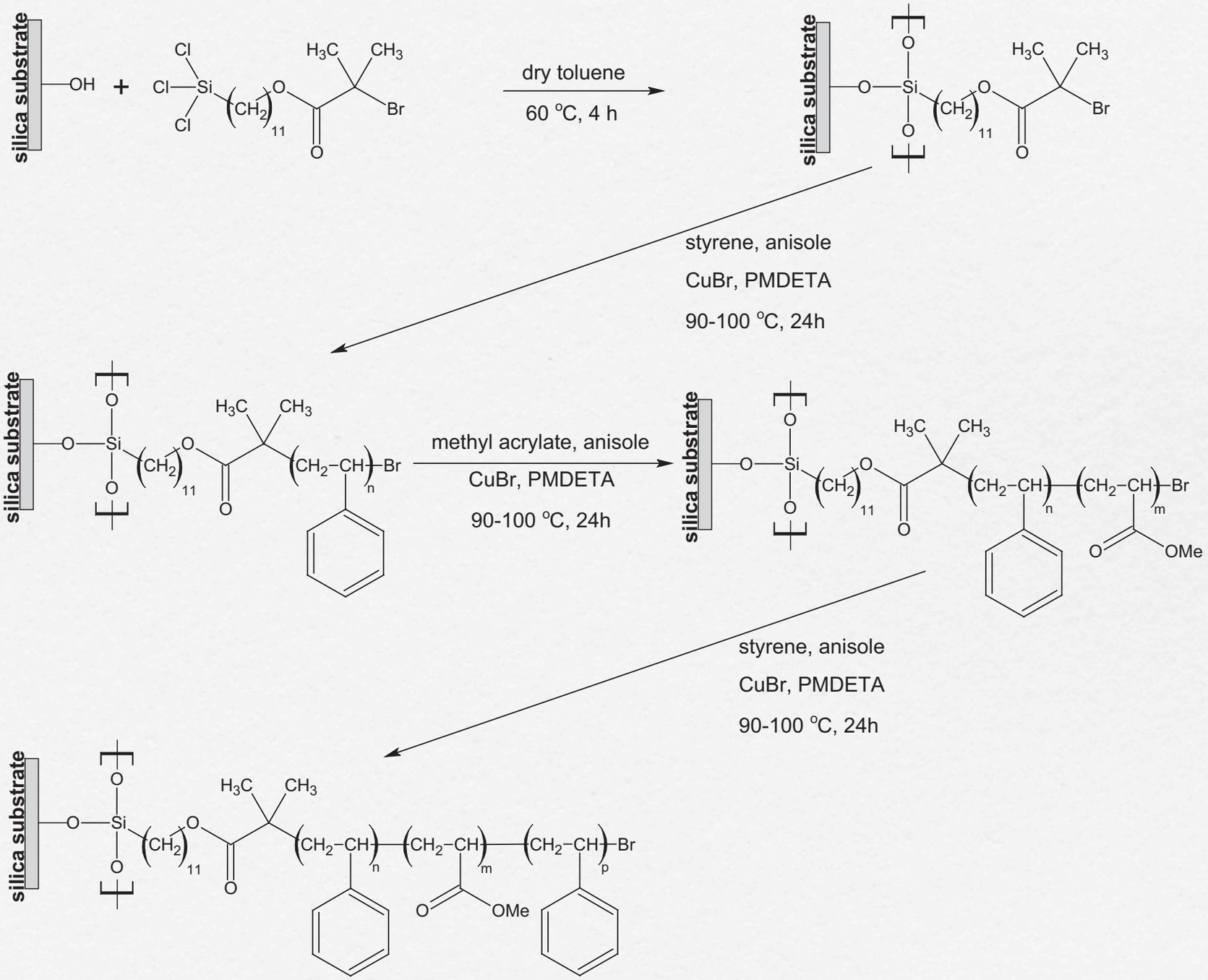




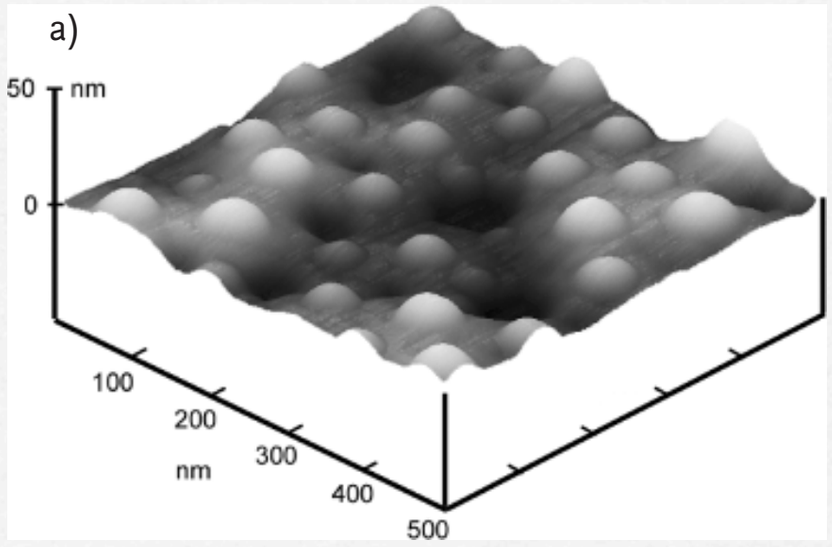
grafting to

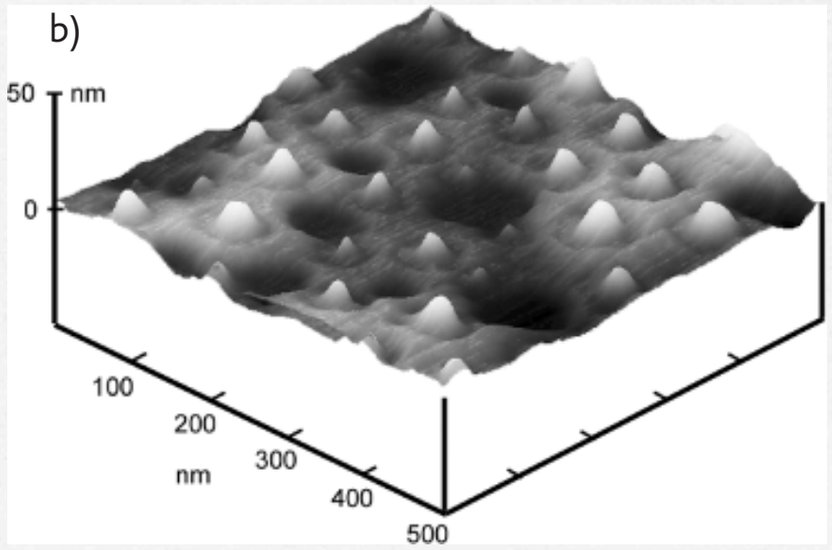

silica substrate
OH
OH
OH
+
H3C
O
Si
O
H3C
O
H3C
O
O
silica substrate
OH
Si
O
O
OH
OH
O
Si
O
O
O
Si
O
O
CH3
O
OH
HOOC
+
silica substrate
OH
Si
O
O
OH
OH
O
Si
O
O
O
Si
O
O
CH3
O
OH
HOOC
+
silica substrate
OH
Si
O
O
OH
O
O
O
Si
O
O
OH
O
O
O
Si
O
O
CH3
O
OH

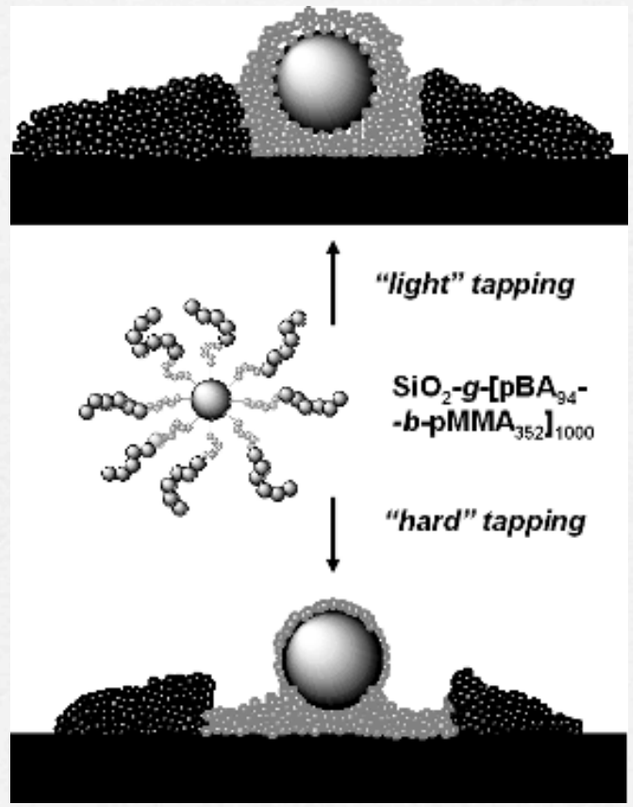
grafting from blocks



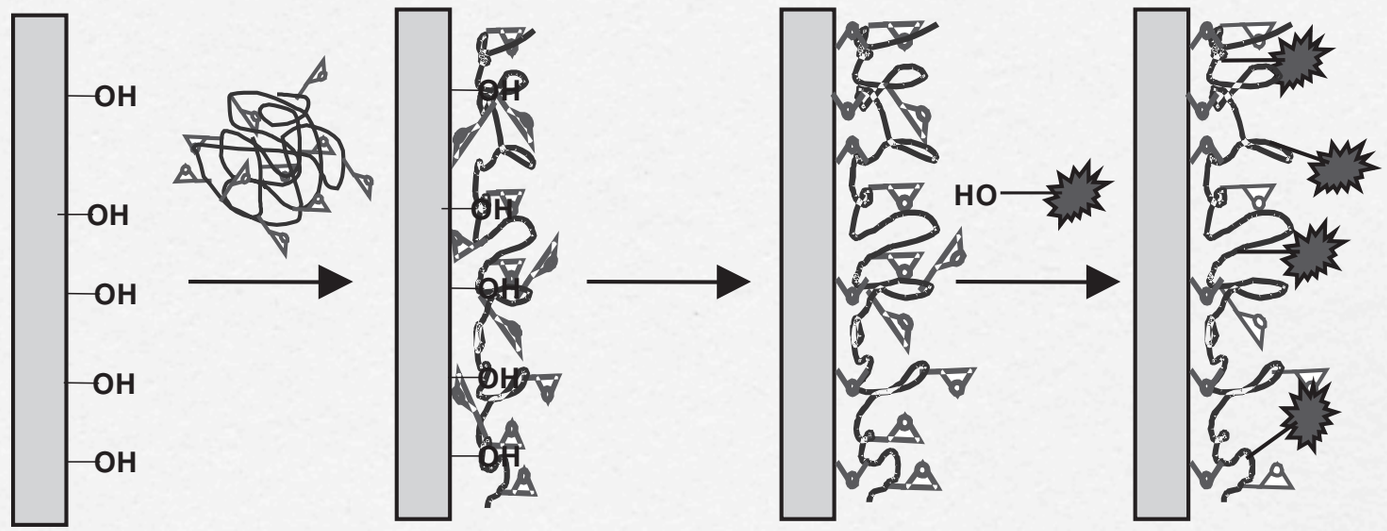
brushes on nanoparticles



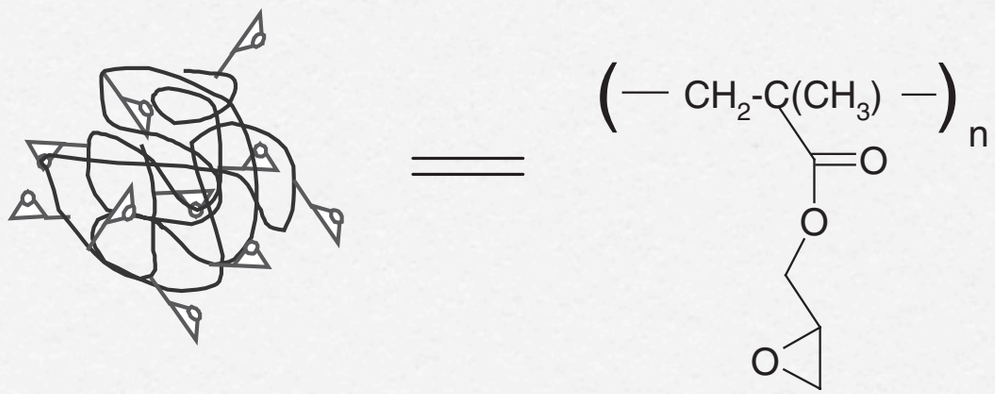




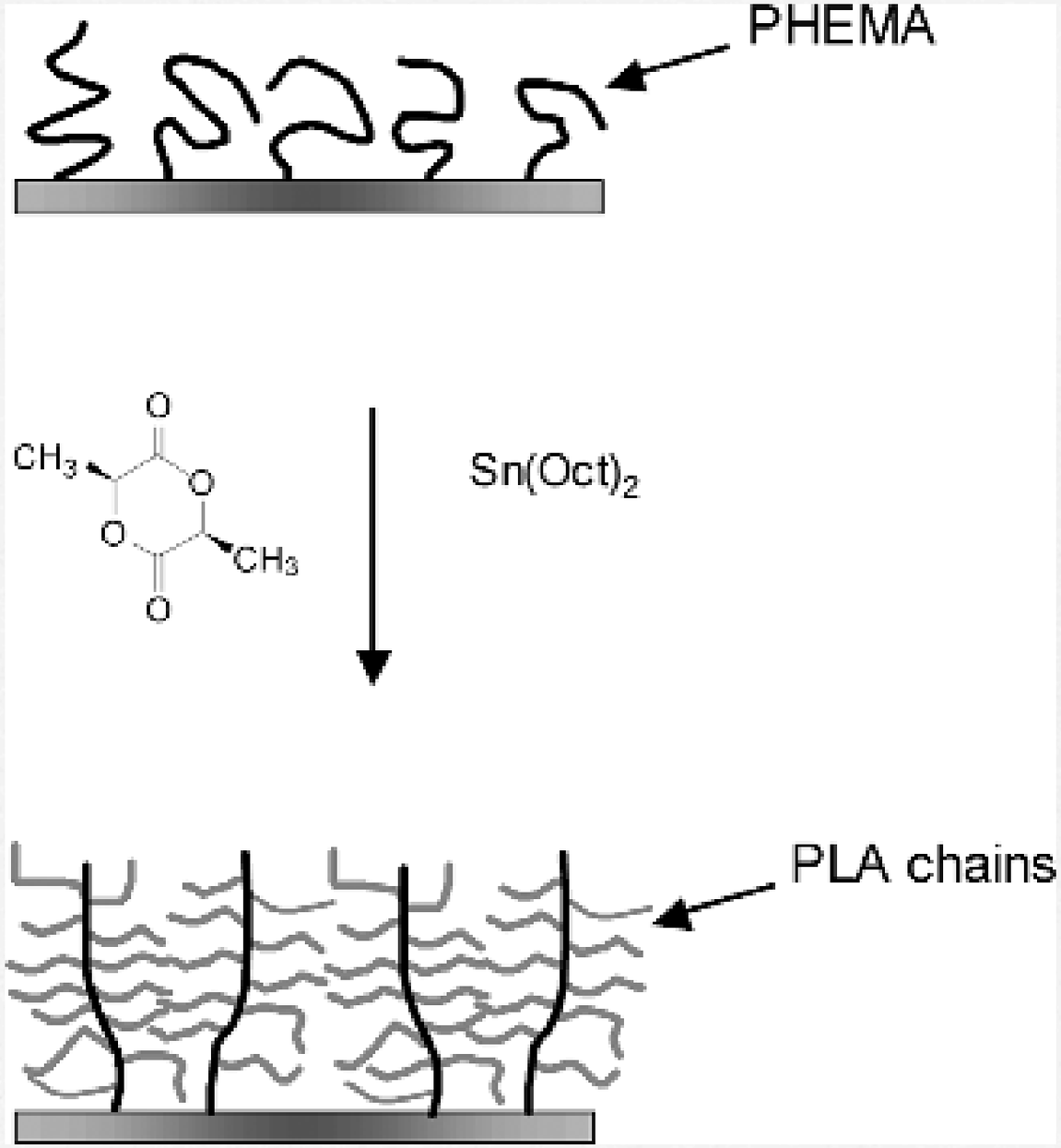
combining grafting to and from



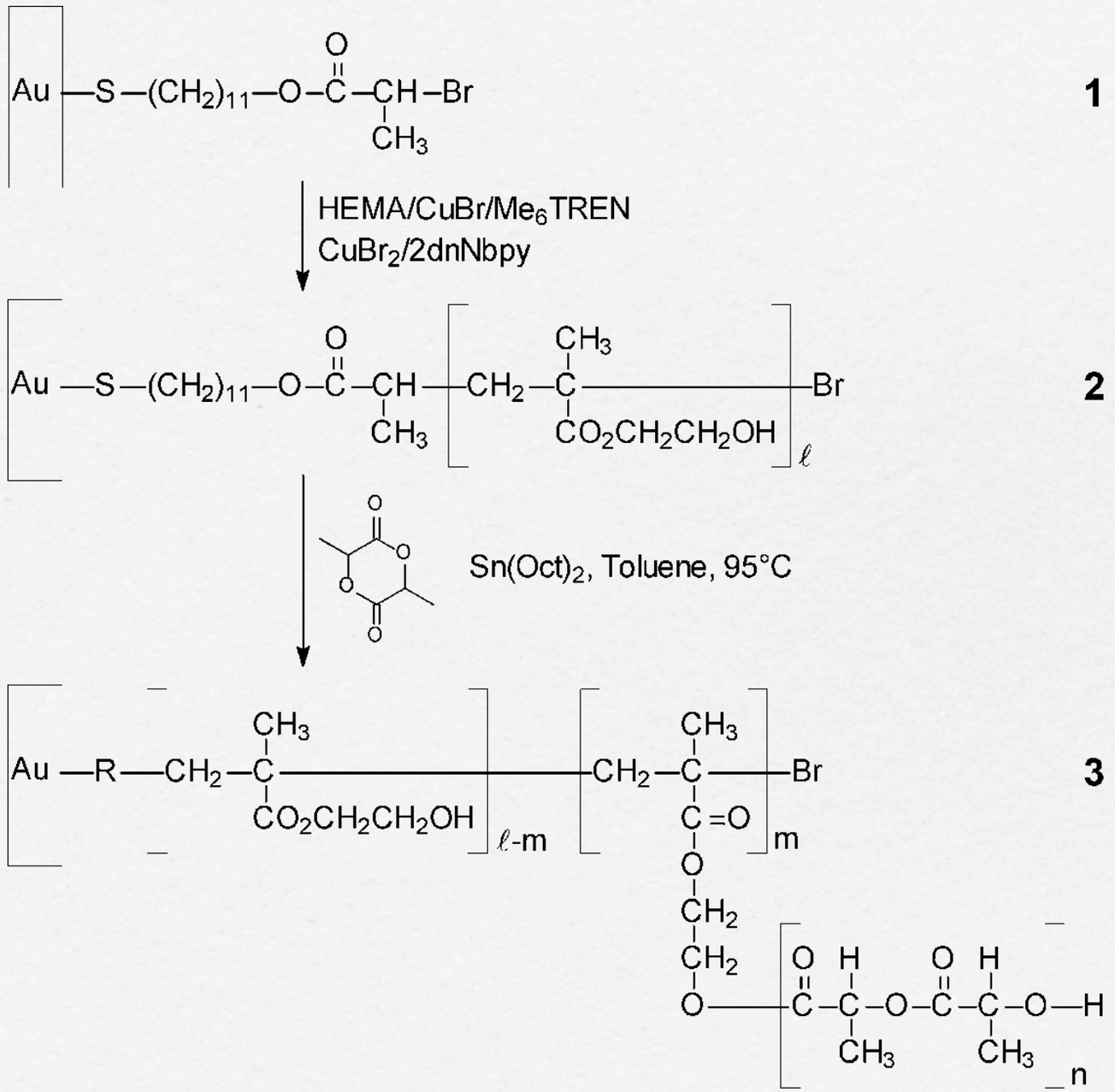
$-C(O)CR_2-Br$ R=H or CH_3



bottle brushes

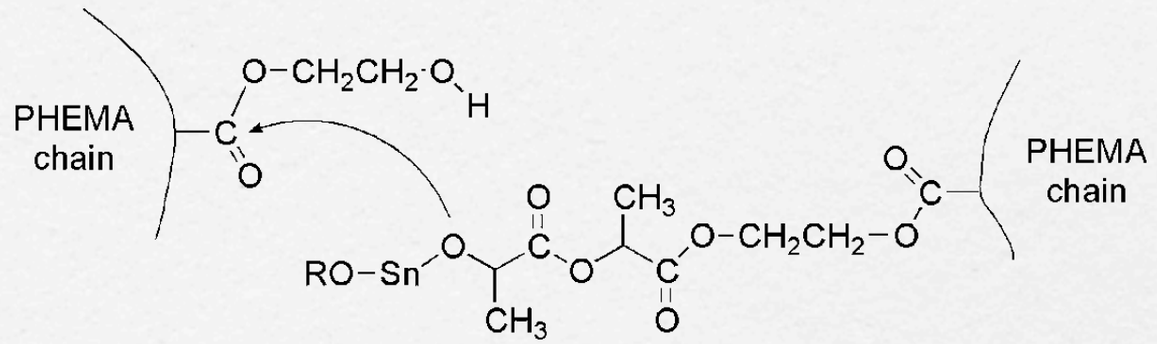


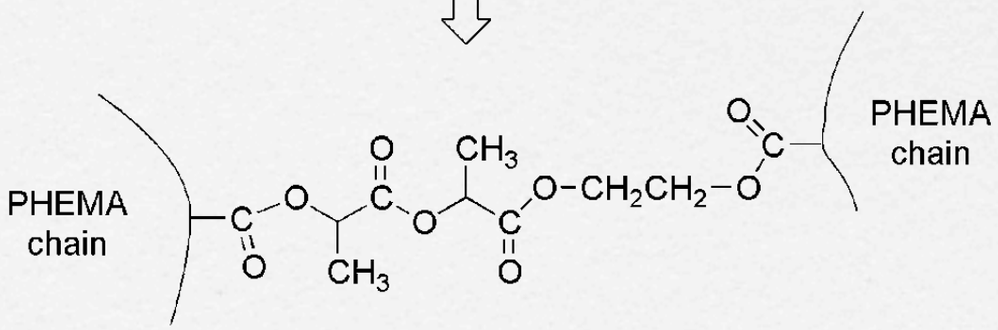
bottle brushes



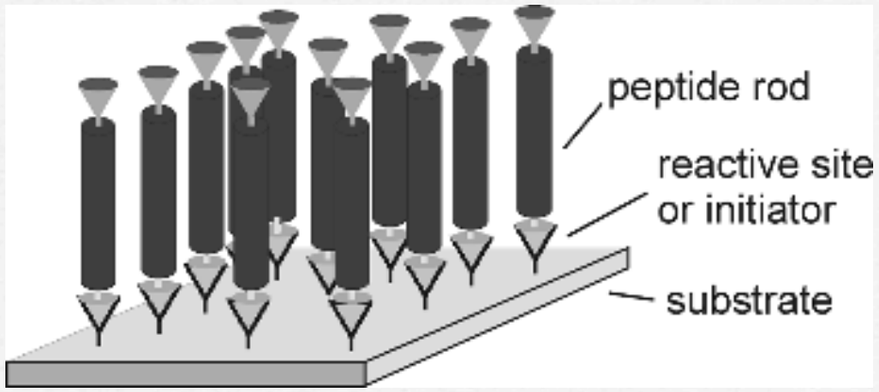
bottle brushes

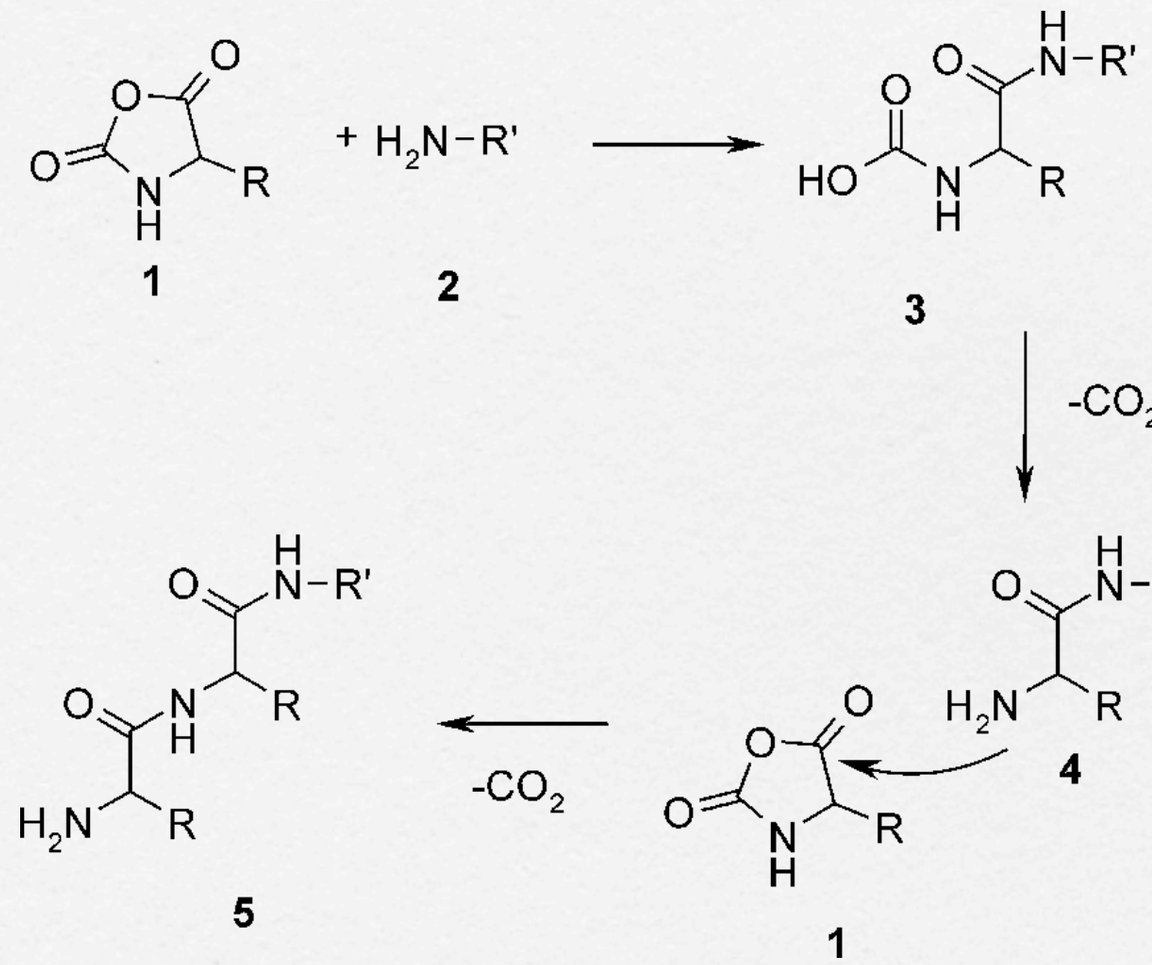
intermolecular transesterification



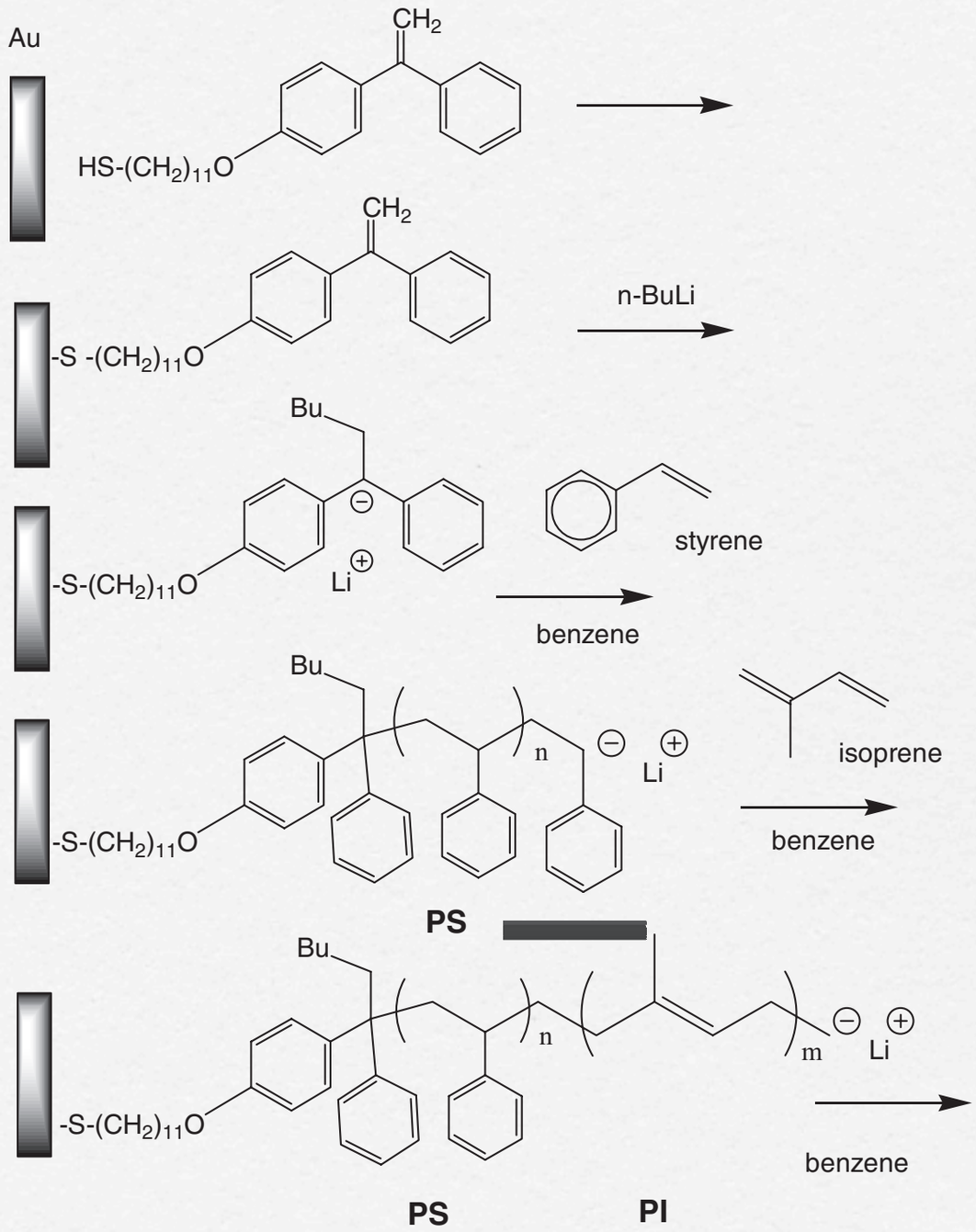


peptide brushes

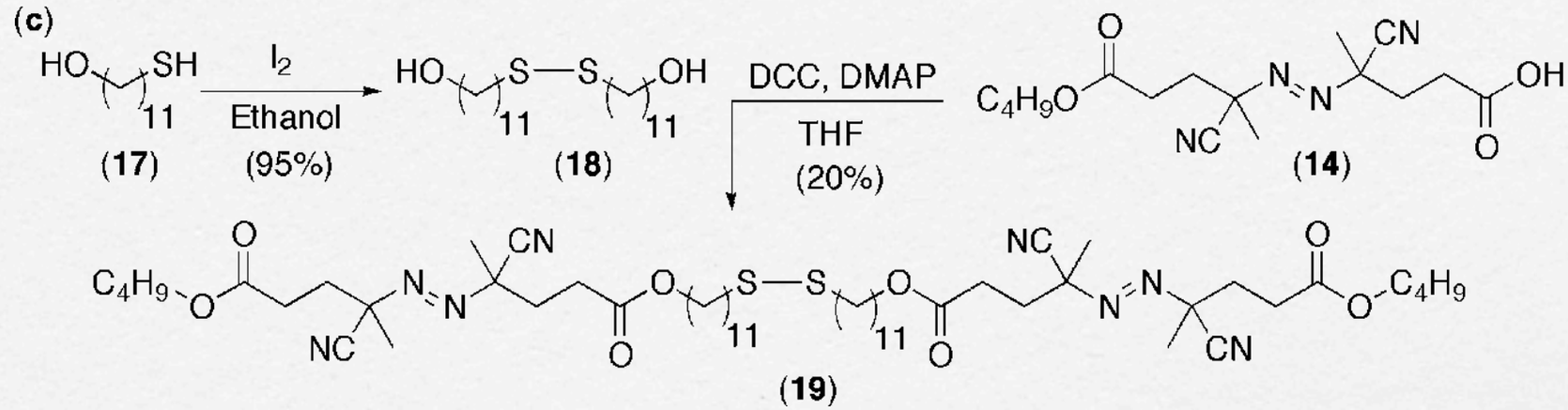


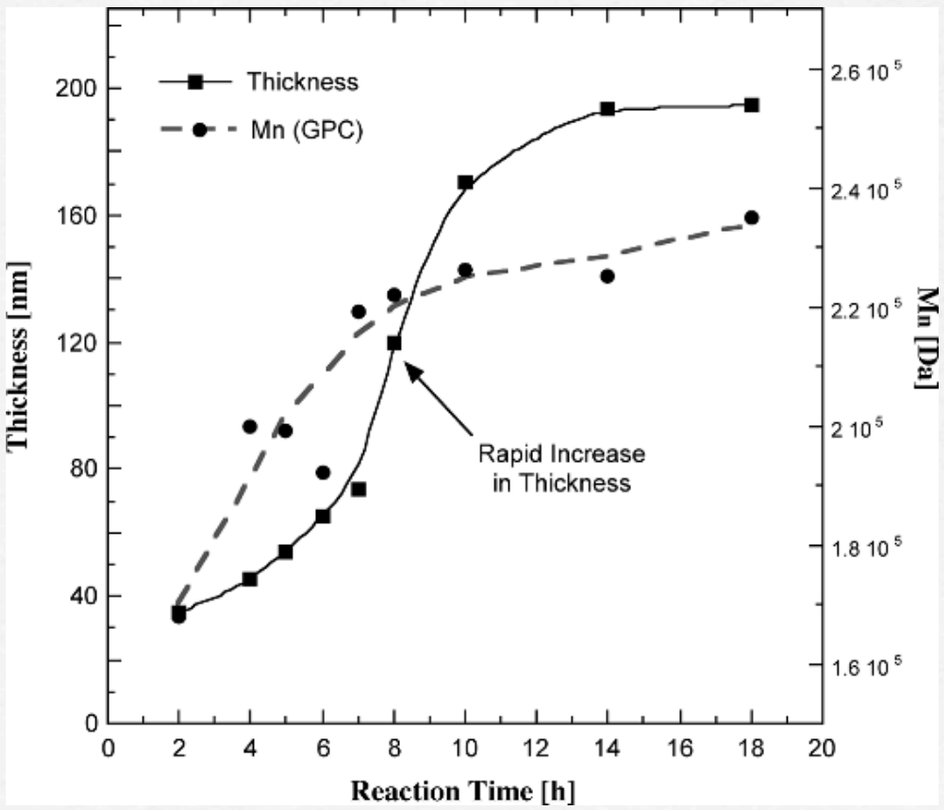


anionic polymerization



film growth, FRP





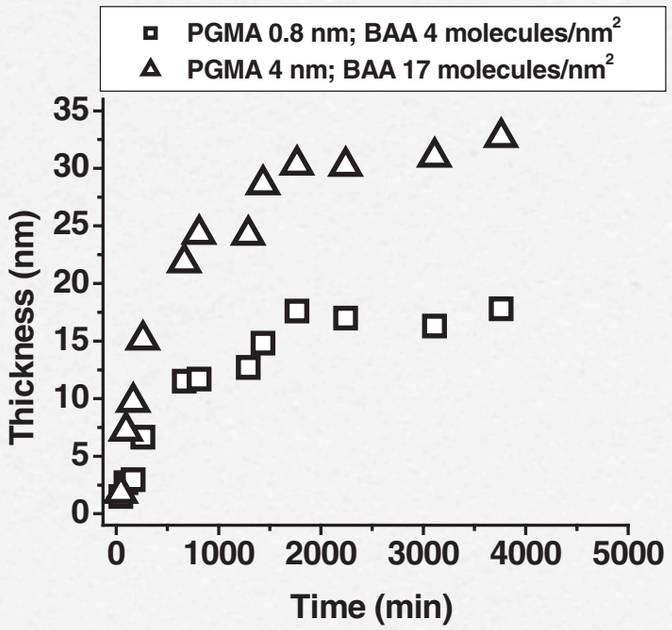
grafting from by ATRP

1. addition of persistent radical, e.g. Cu(II)

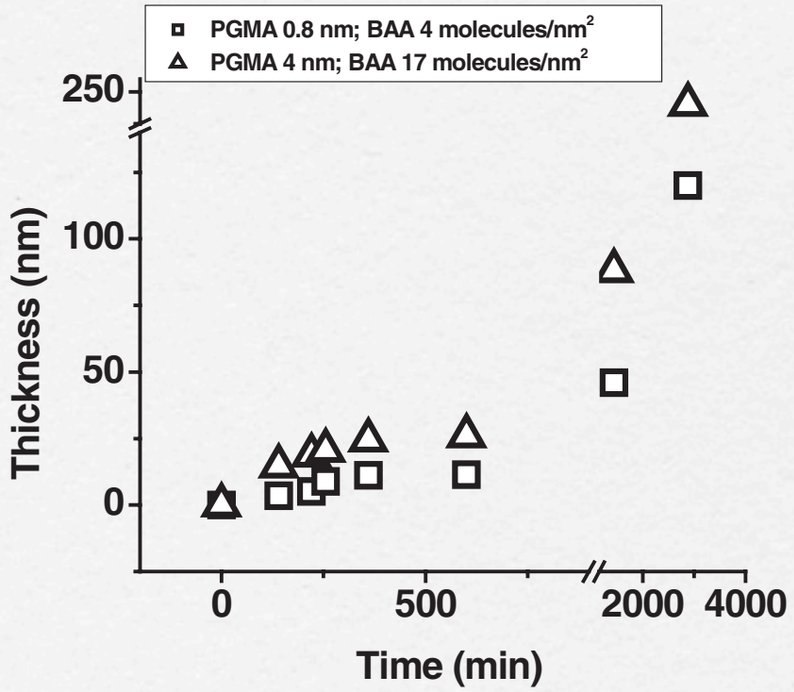
2. addition of "sacrificial initiator"

film growth, ATRP

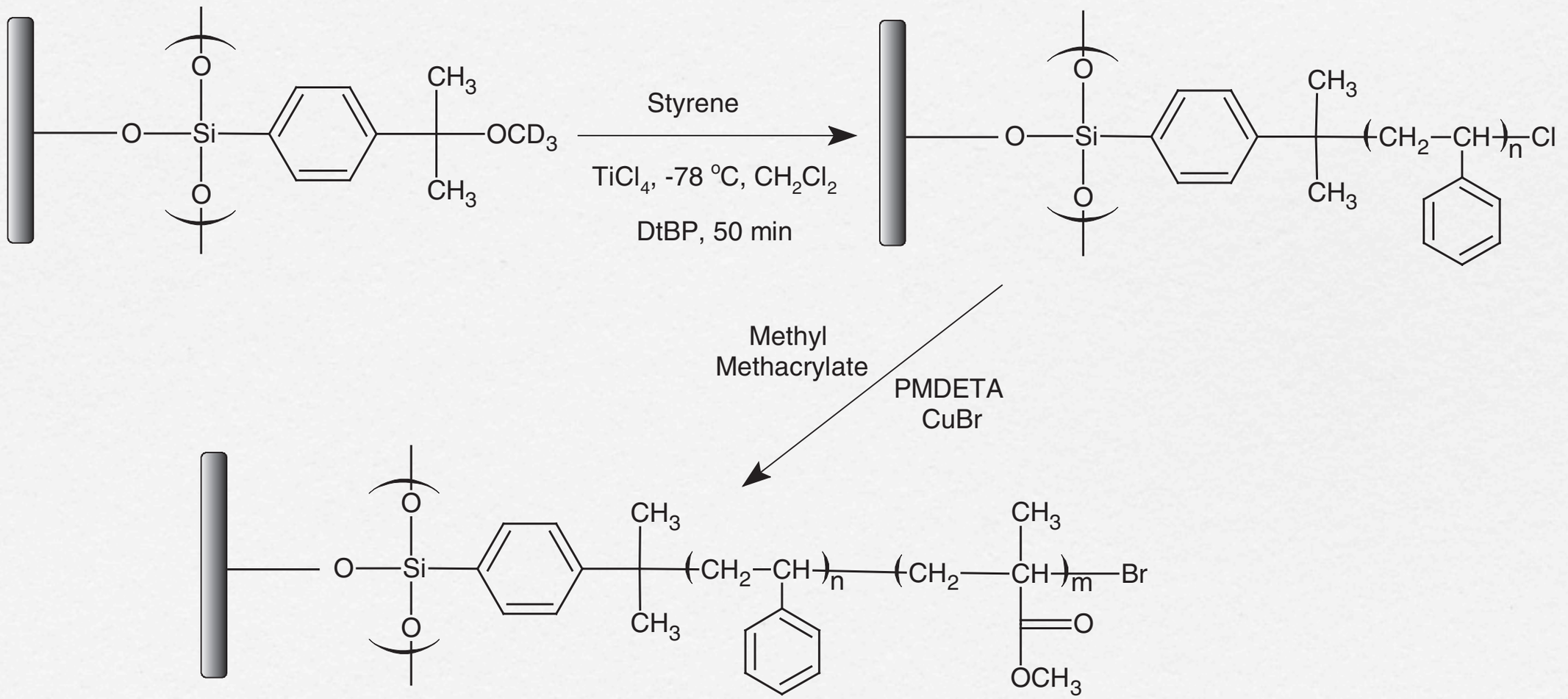
sacrifical initiator added



sacrifical initiator NOT added



combined polymerization methods

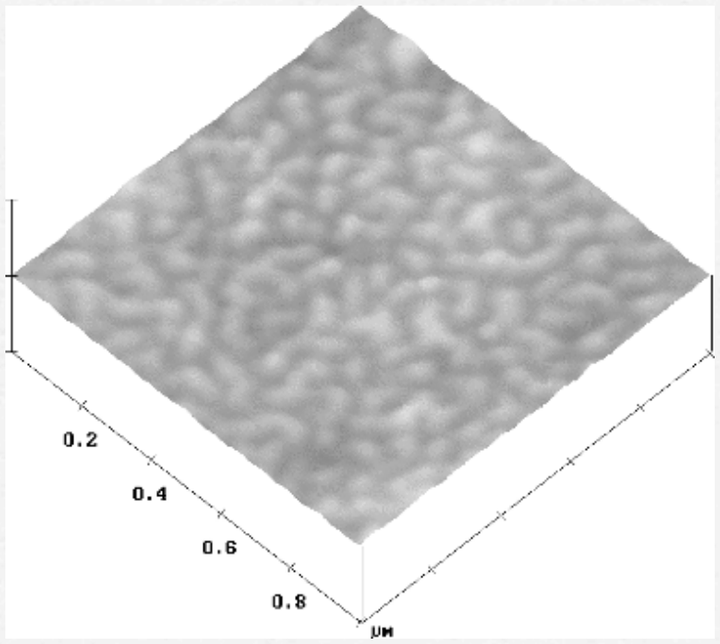


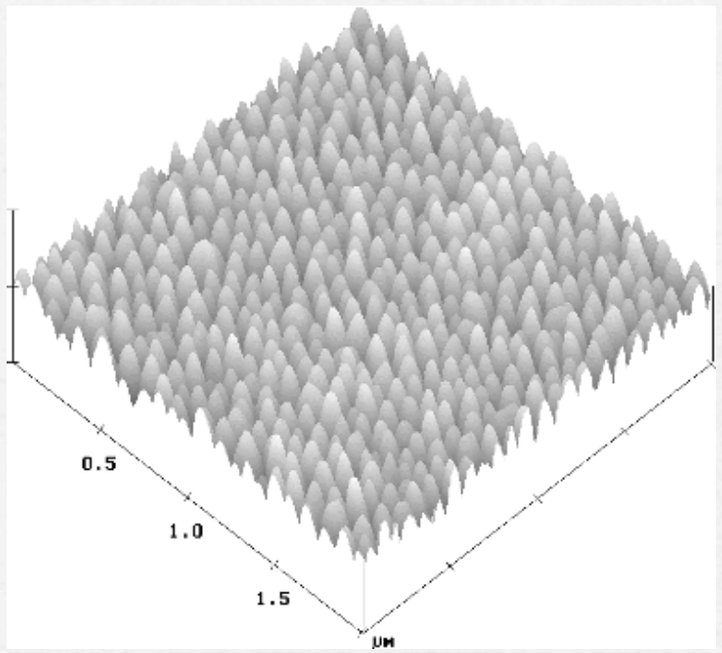
block copolymer brushes

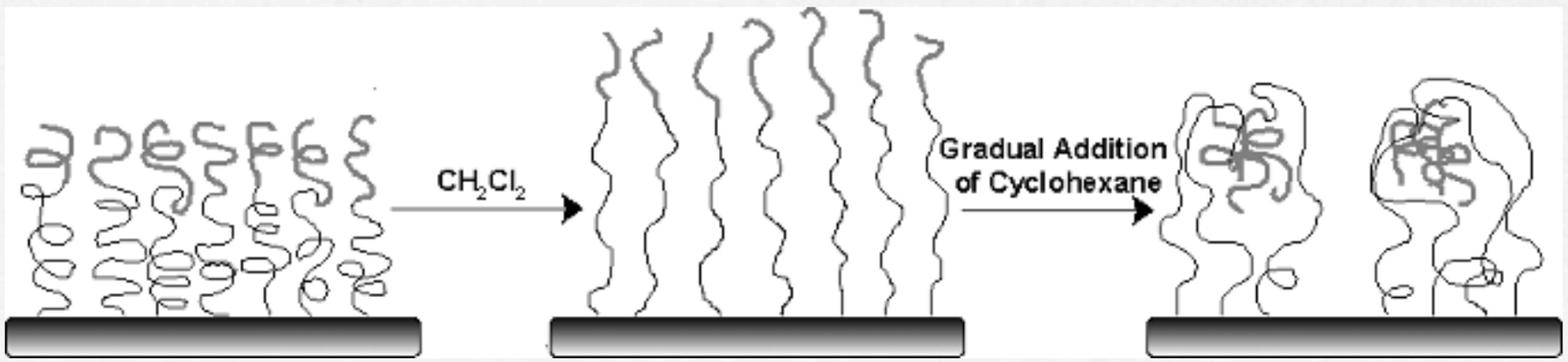
Layer	Water contact angle[b] θ_a	θ_r	Thickness[c] (nm)	Molecular weight (M_n) Calcd.[d]	Expt.[e]	PDI
PS	97	87	20	13.2×10^3	10.5×10^3	1.10
PS-*b*-PMA	73	63	18	17.9×10^3	17.2×10^3	1.23
PS-*b*-PMA-*b*-PS	88	70	3	21.7×10^3	18.6×10^3	1.07
PMA	72	59	20	15.2×10^3	13.6×10^3	1.50
PMA-*b*-PS	87	72	23	21.8×10^3	18.7×10^3	1.08
PMA-*b*-PS-*b*-PMA	73	58	15	18.4×10^3	15.5×10^3	1.23

block copolymer brushes

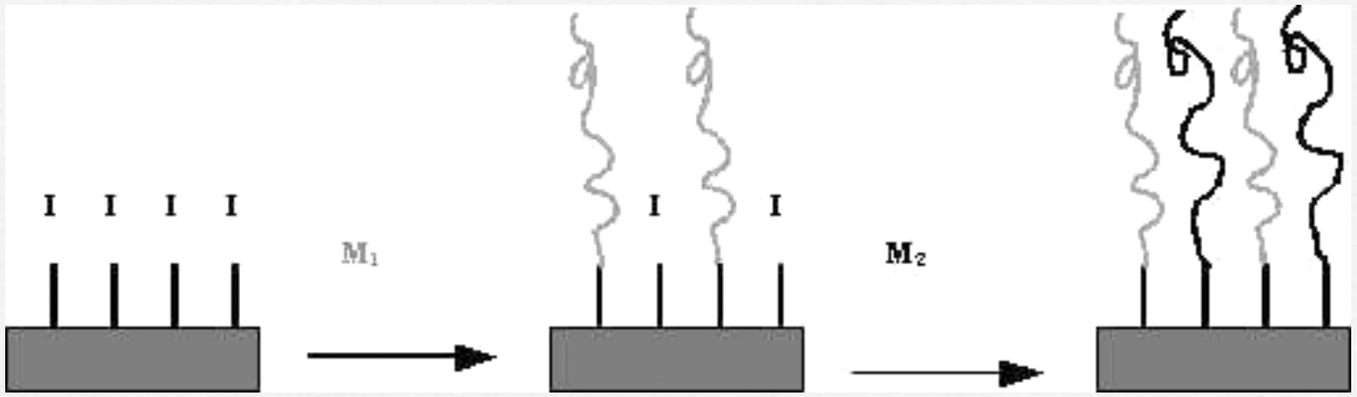
reorientation

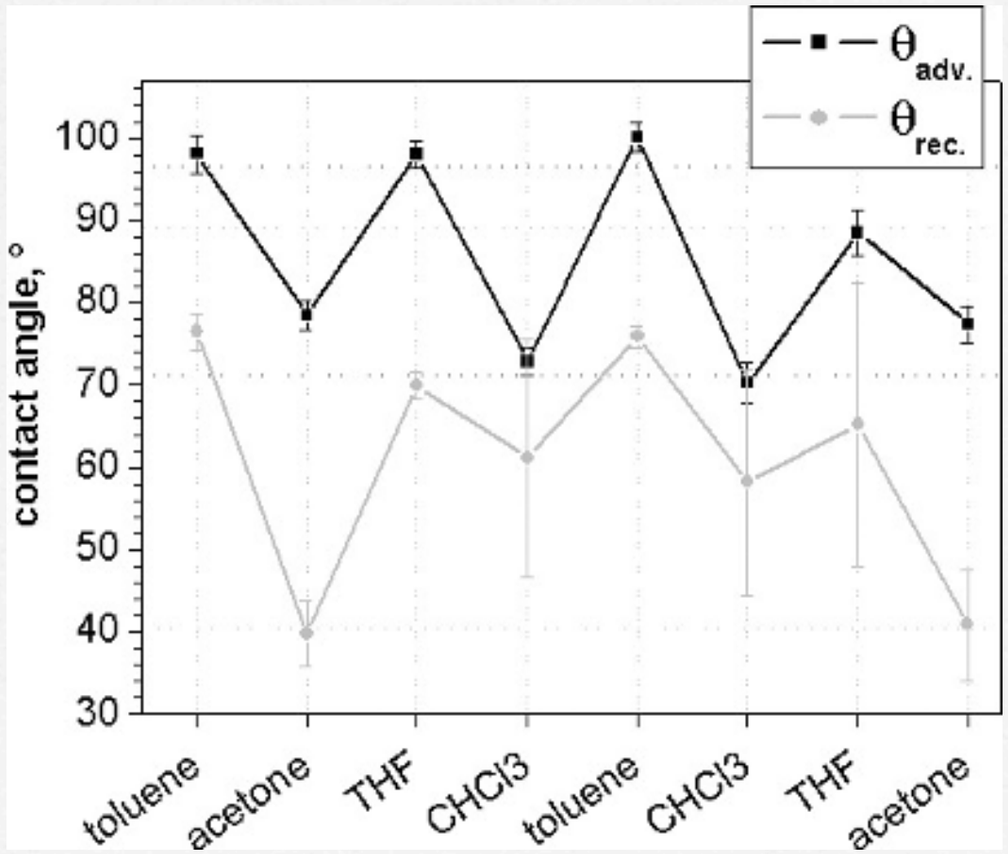




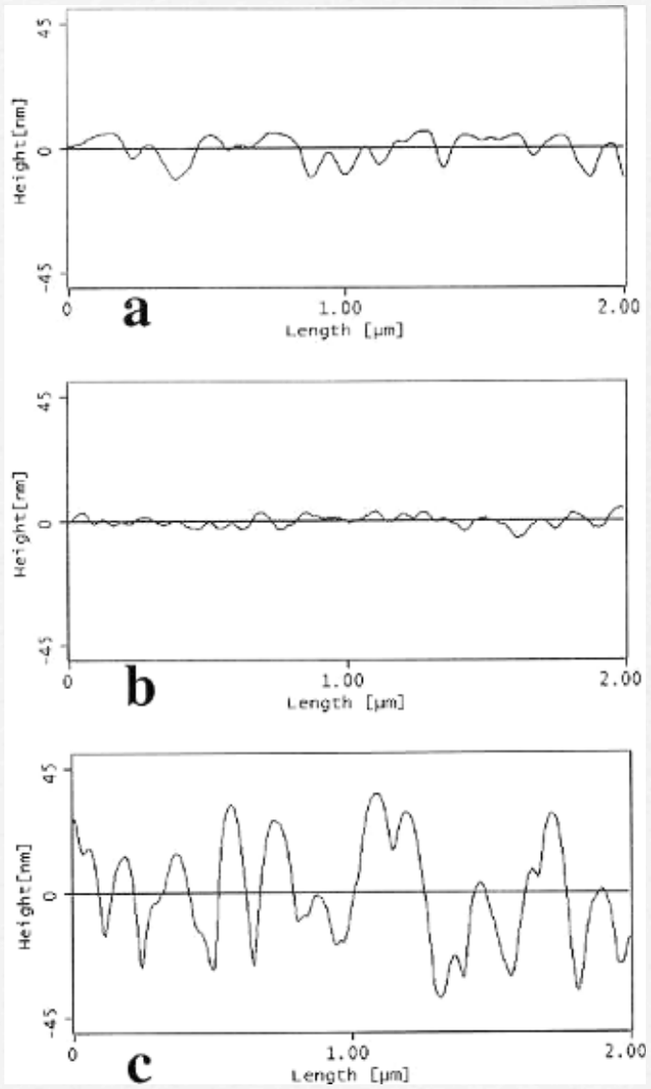


mixed polymer brushes





selective collaps



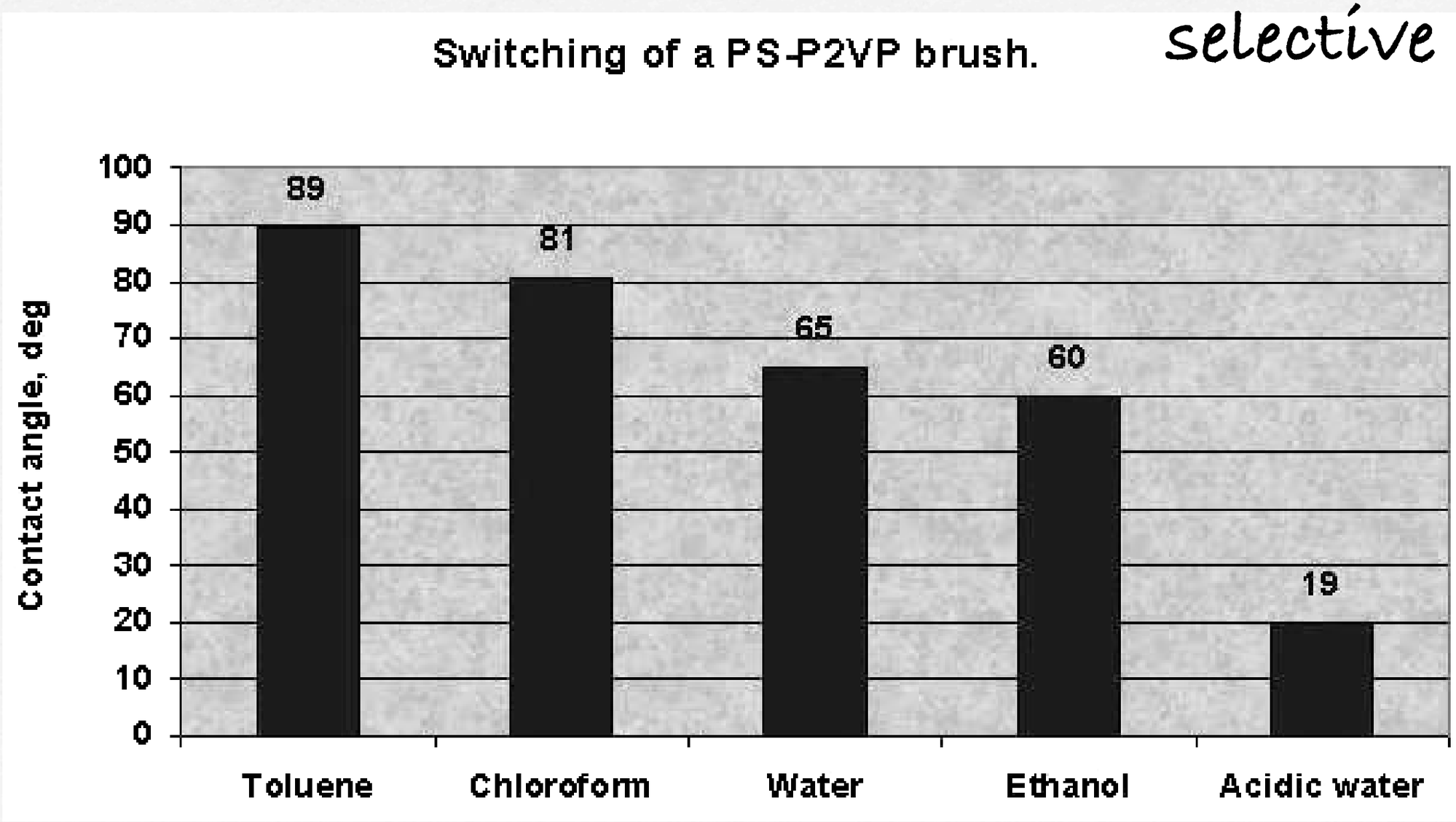
toluene

chloroform

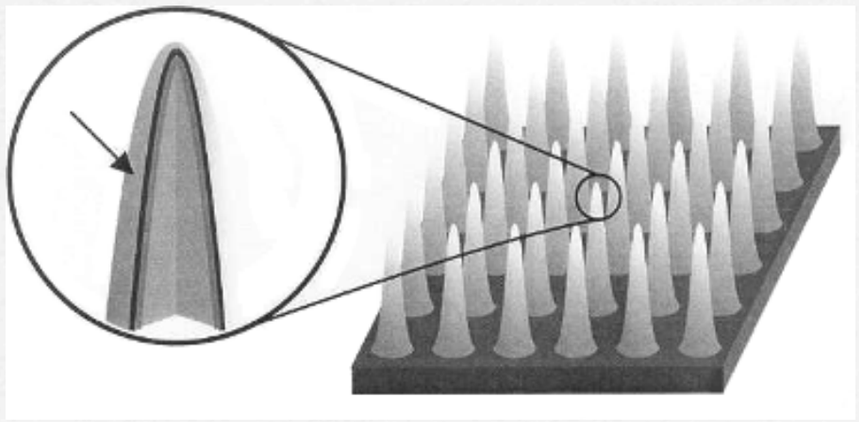
acetone

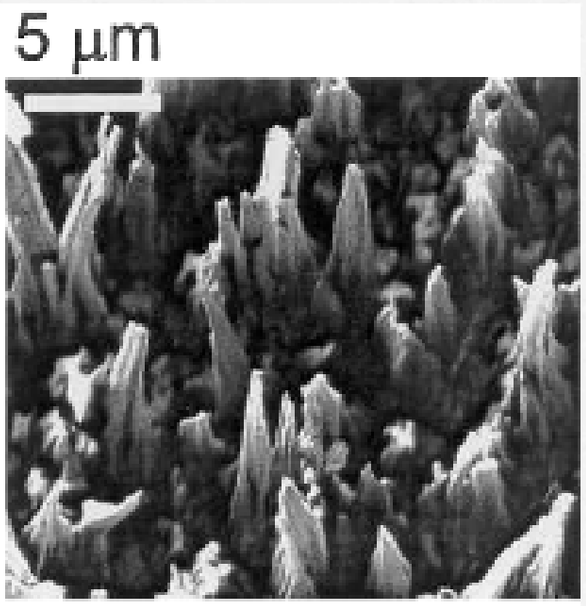
mixed polymer brushes

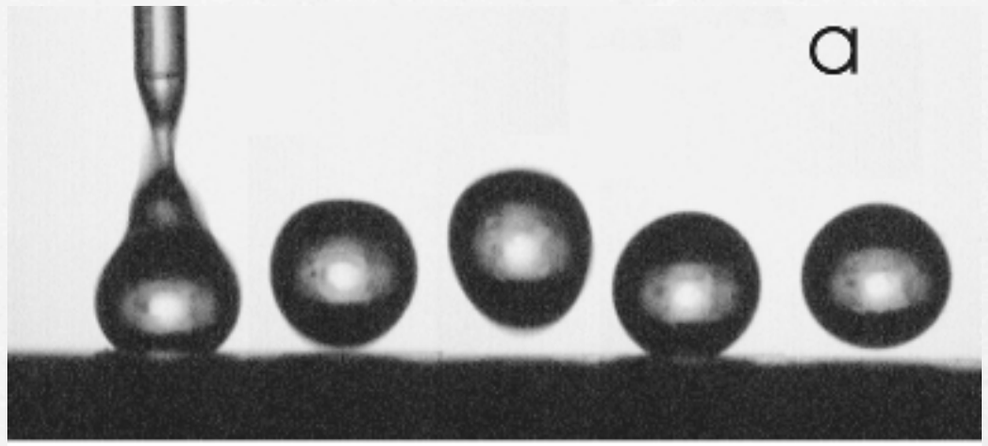
selective collaps



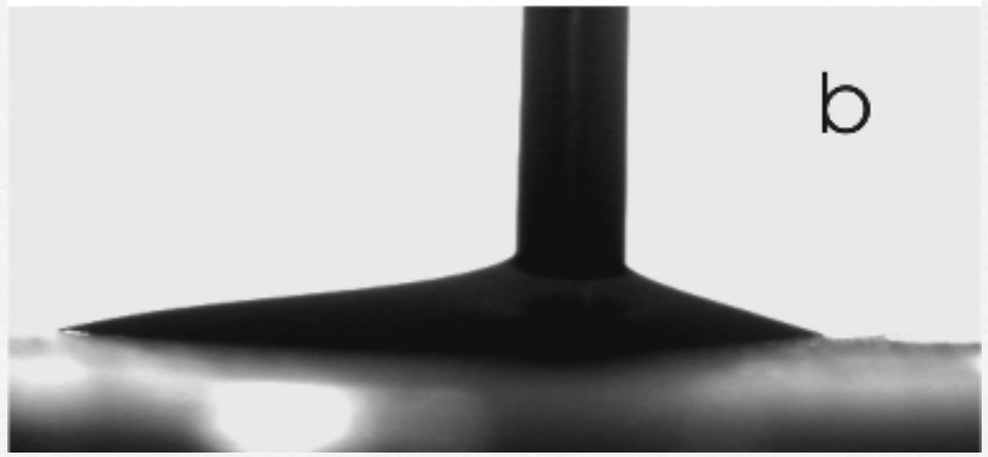
mixed polymer brushes on ripple surface





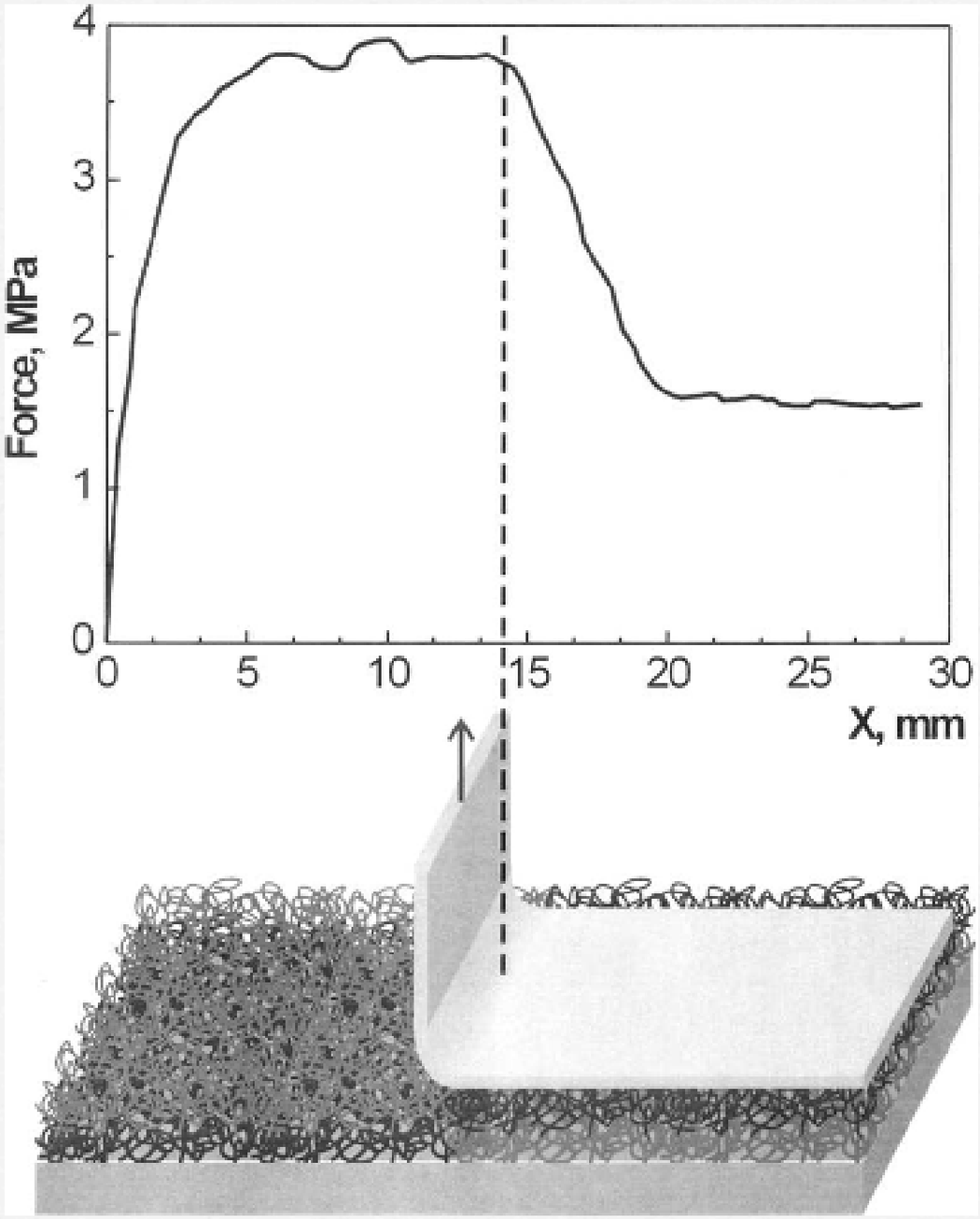


toluene



acidic water

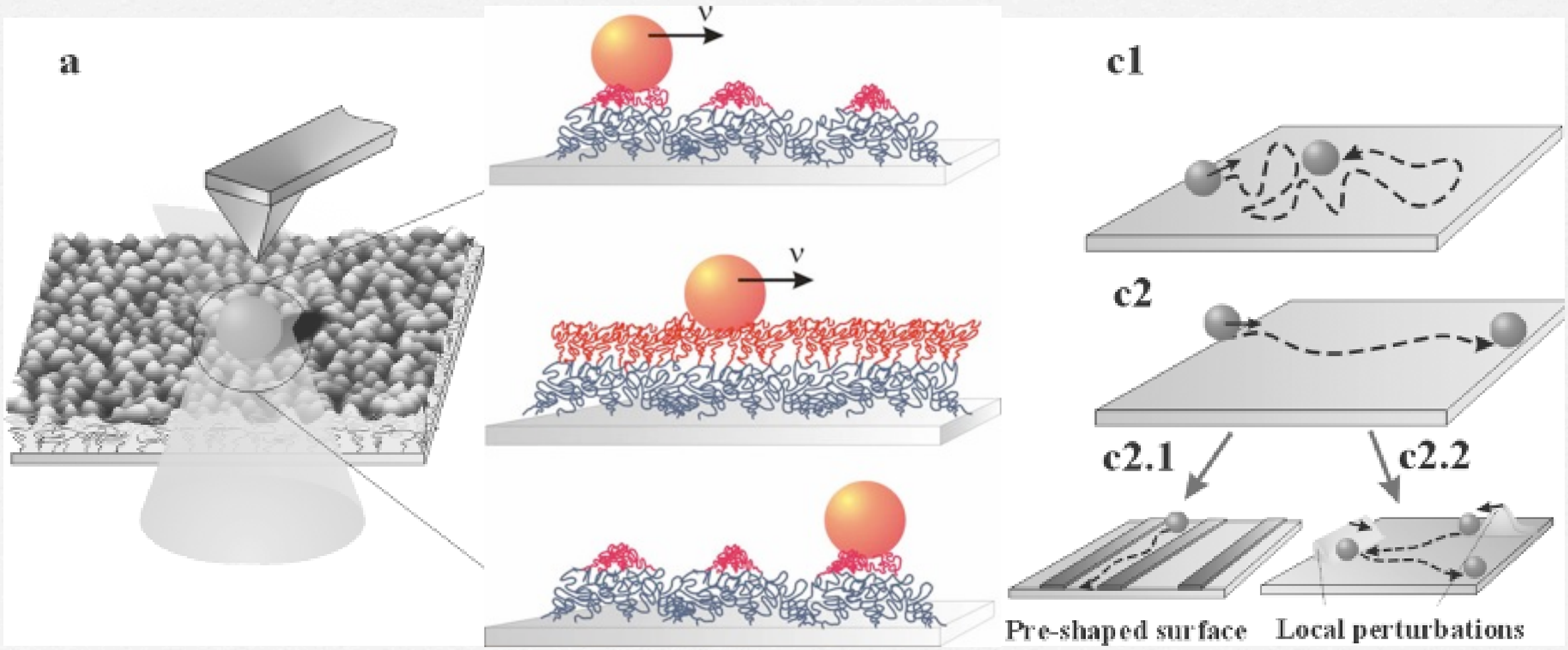
mixed polymer brushes



hydrophilic
on top

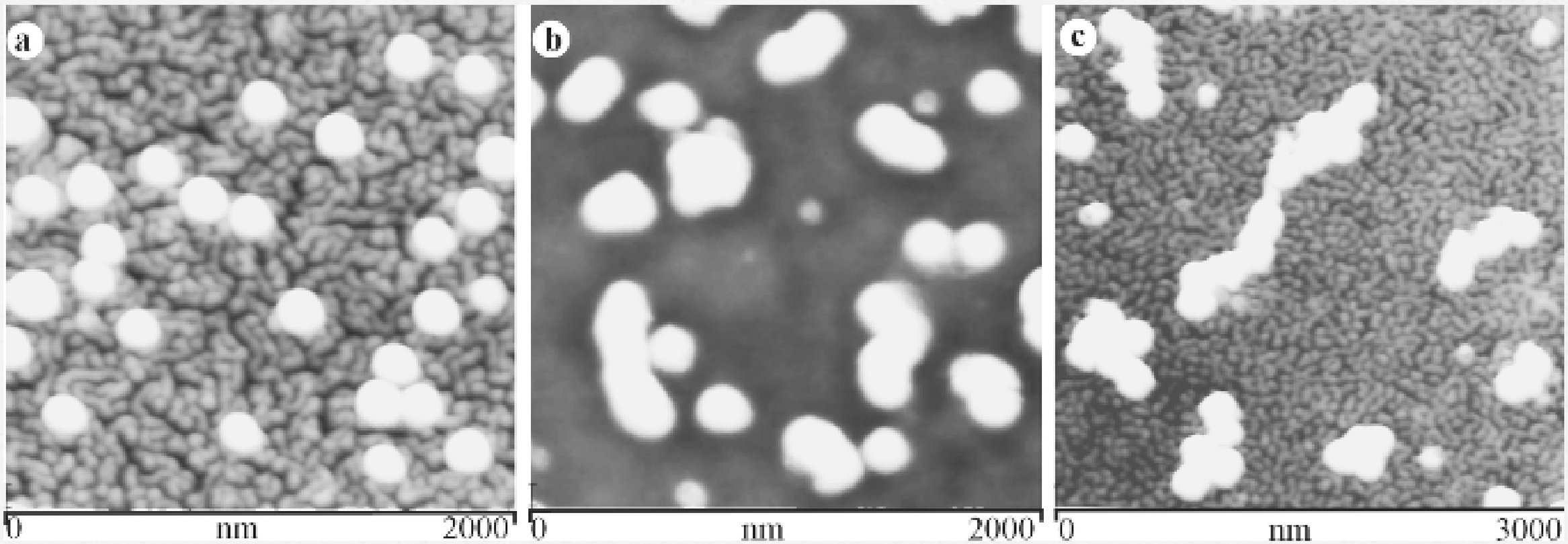
ultra-hydrophobic
on top

moving objects on block copolymer brushes



moving objects on block copolymer brushes

diblock copolymer brush p(MMA-b-GMA)

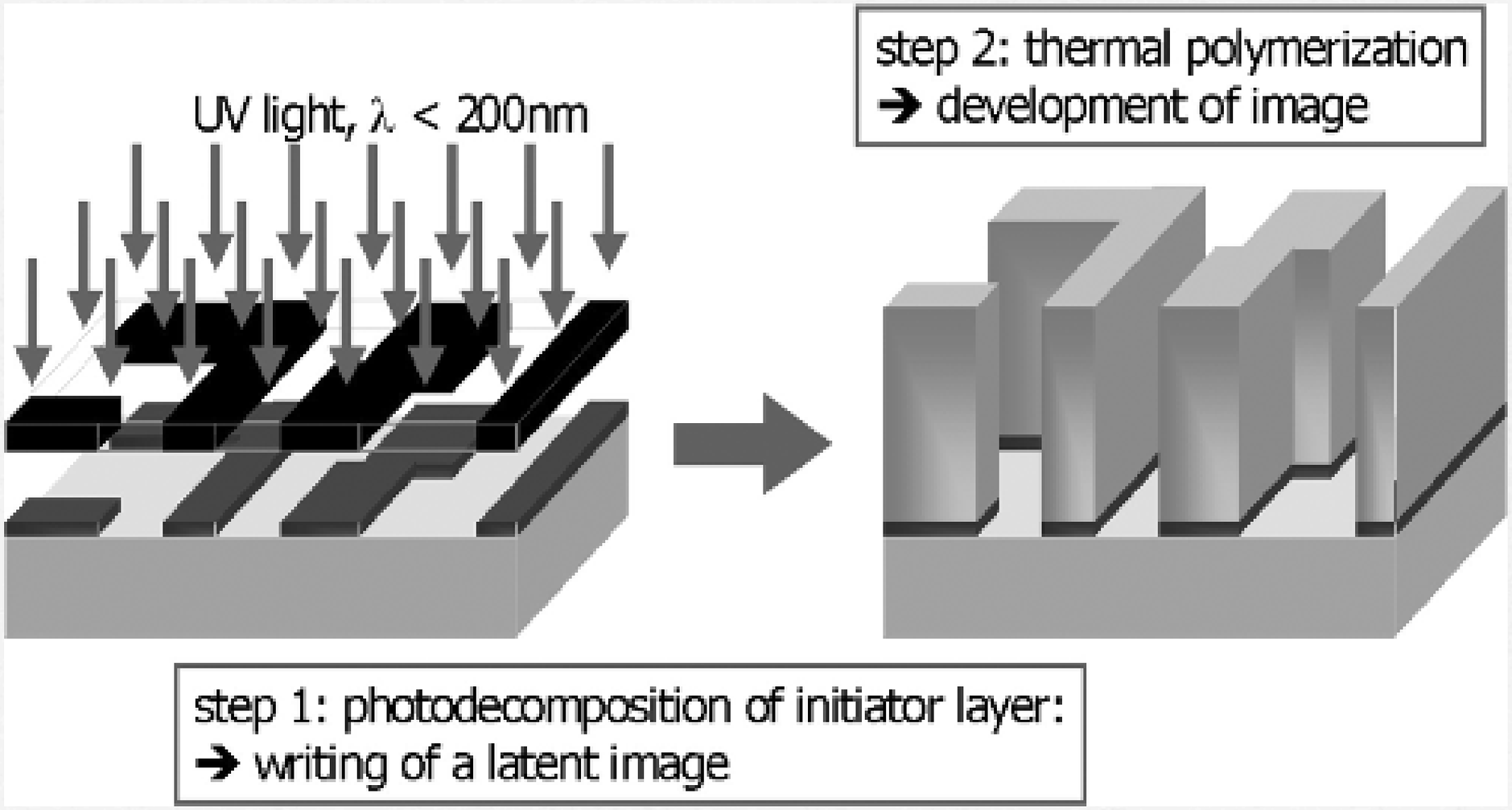


Nanoparticles adsorbed from ethanol

exposure of substrate to chloroform

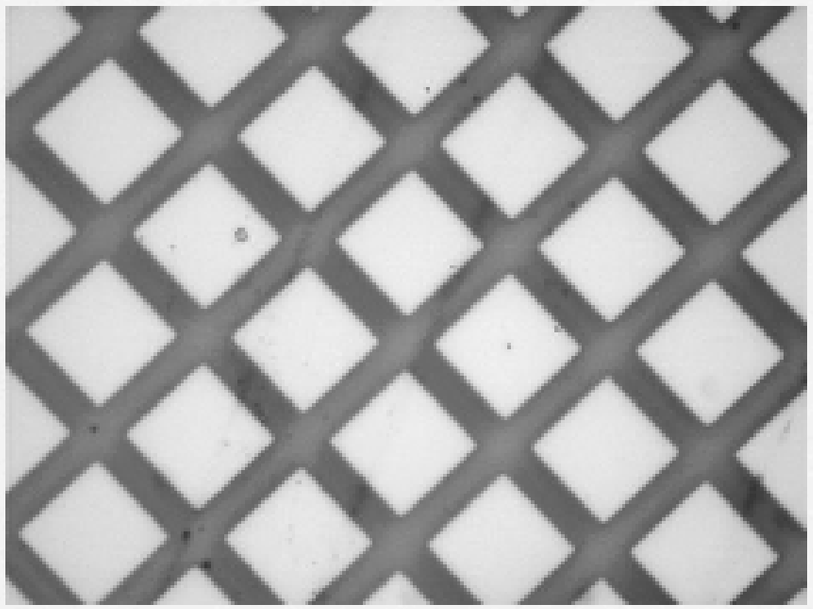
treatment of substrate with toluene (after 26 cycles)

photolithography to polymer brushes

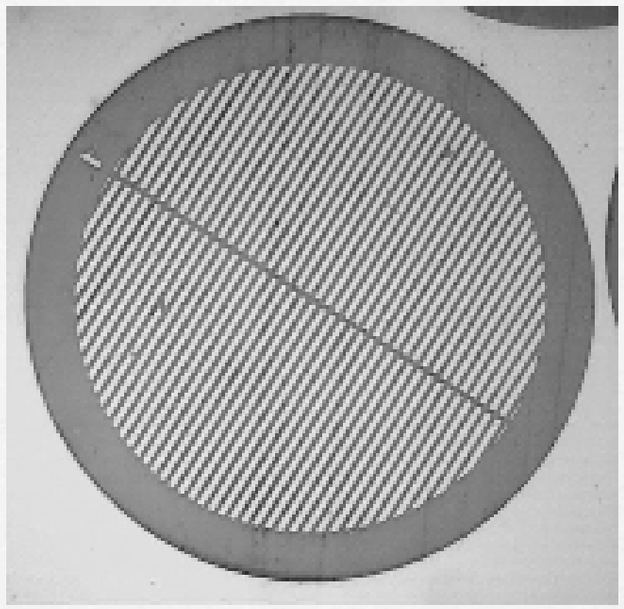


photolithography to polymer brushes

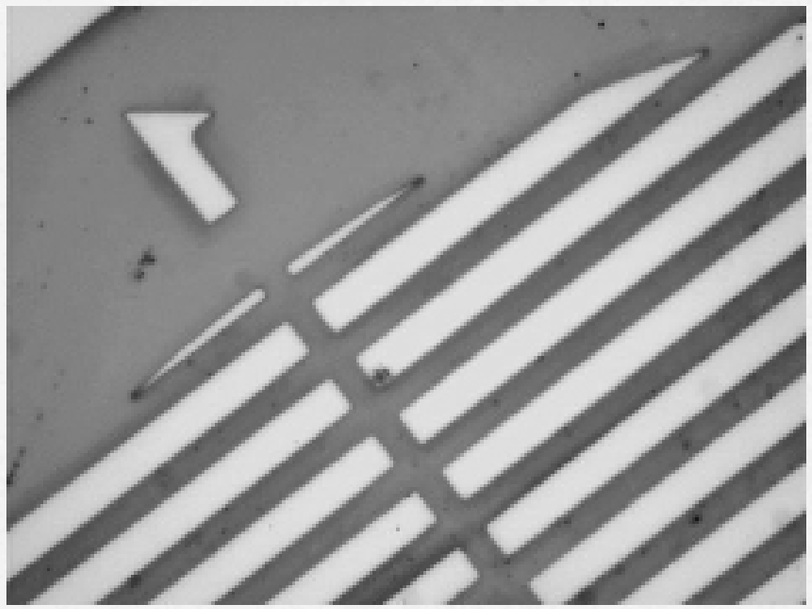
(A)



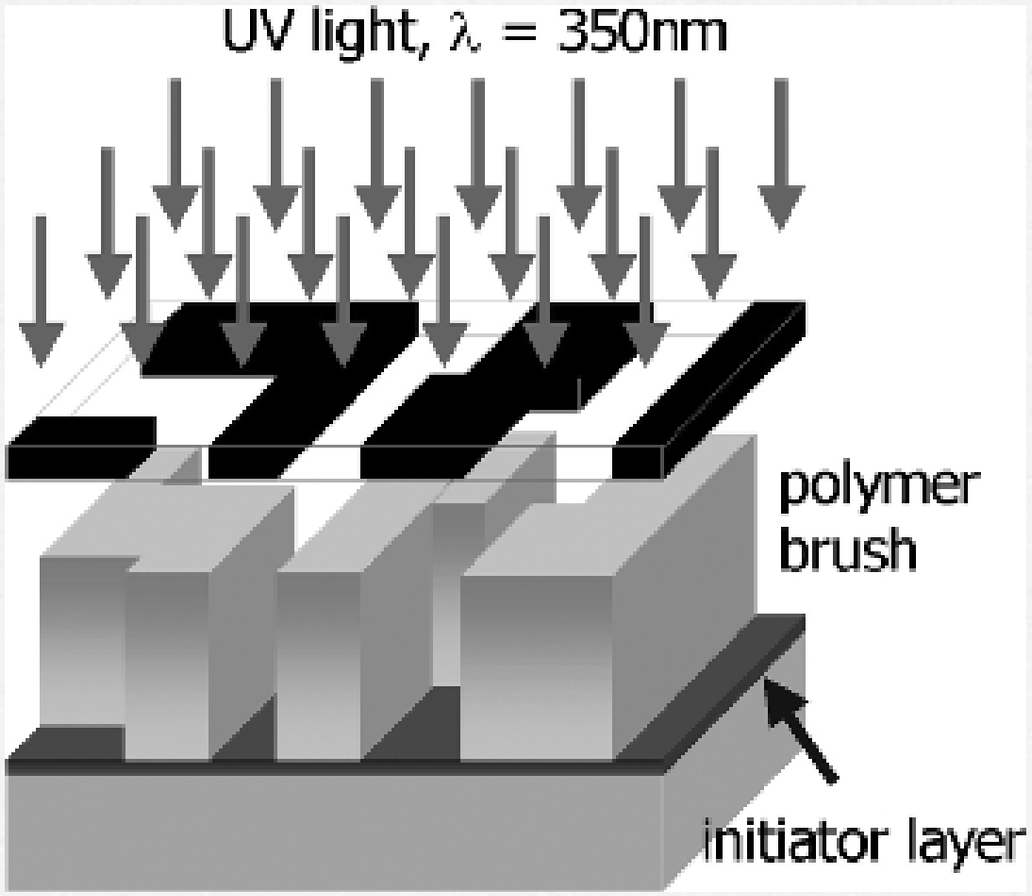
(B)

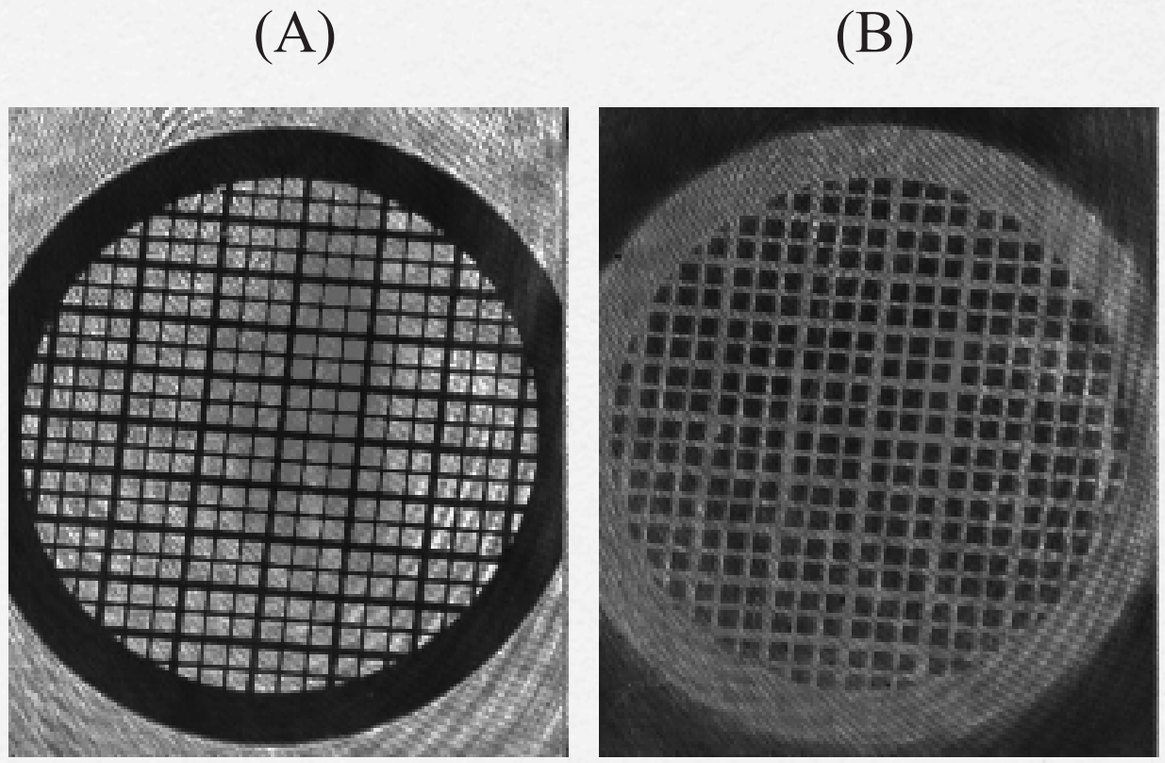


(C)

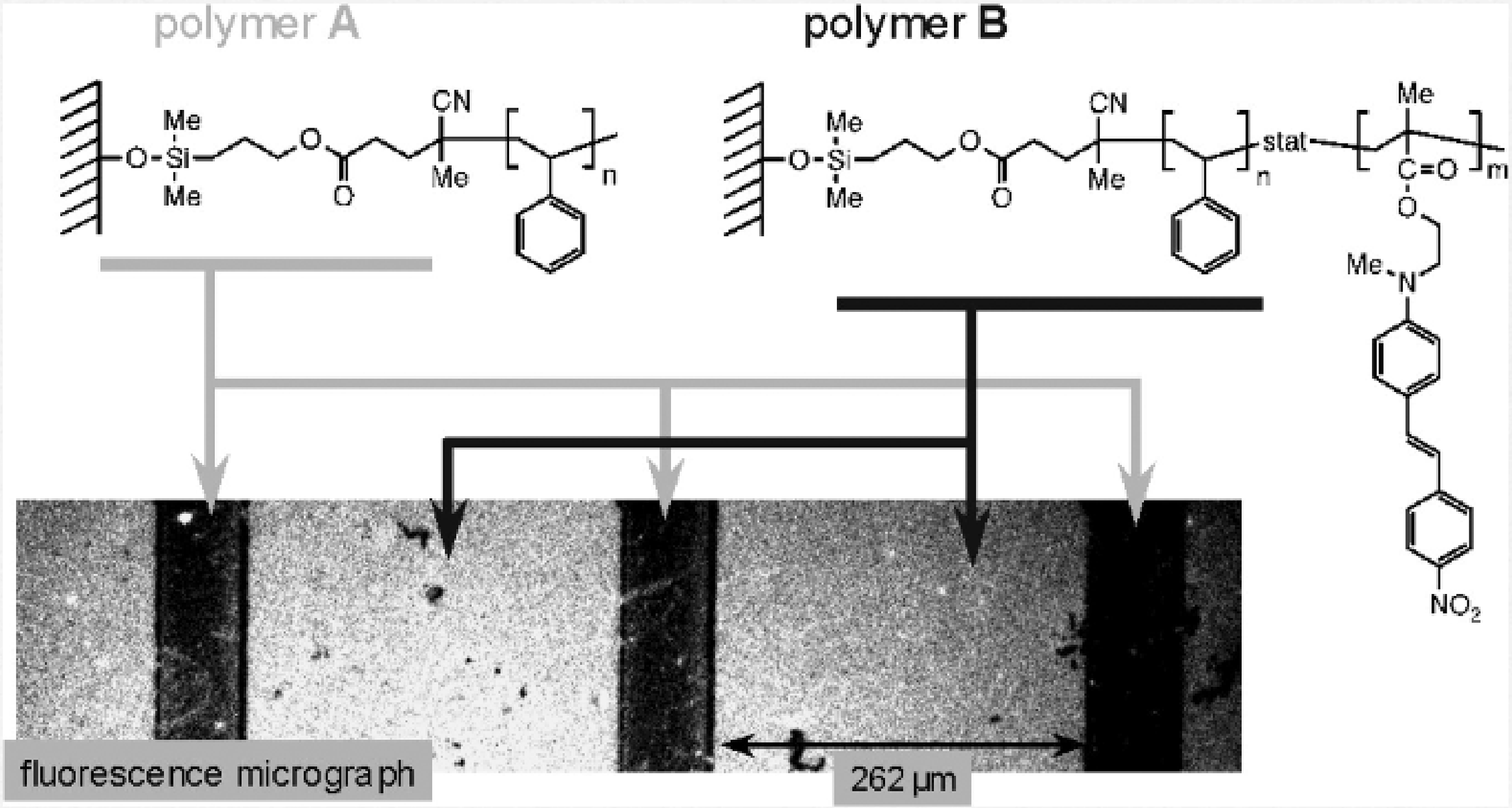


photolithography to polymer brushes



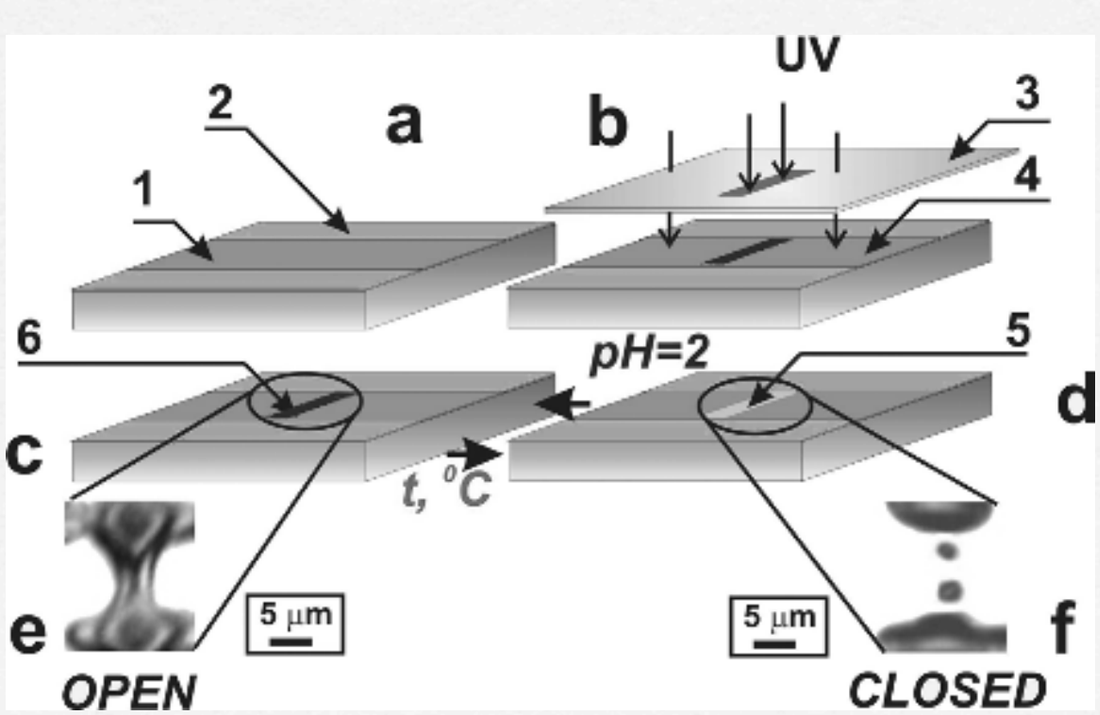


photolithography to polymer brushes

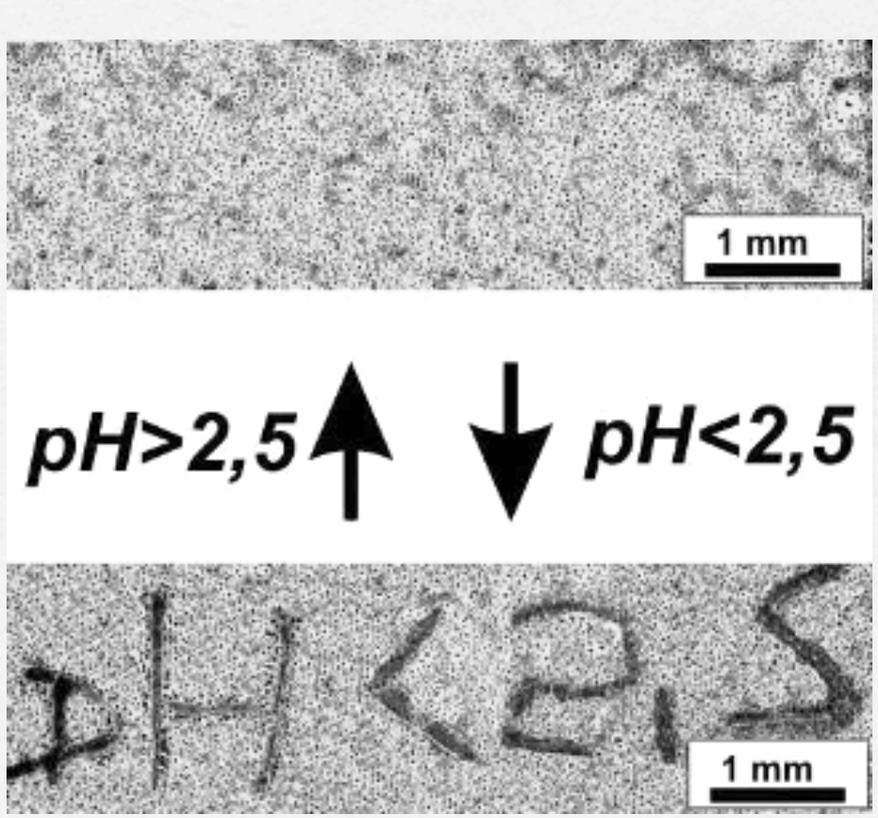


photolithography of mixed polymer brushes

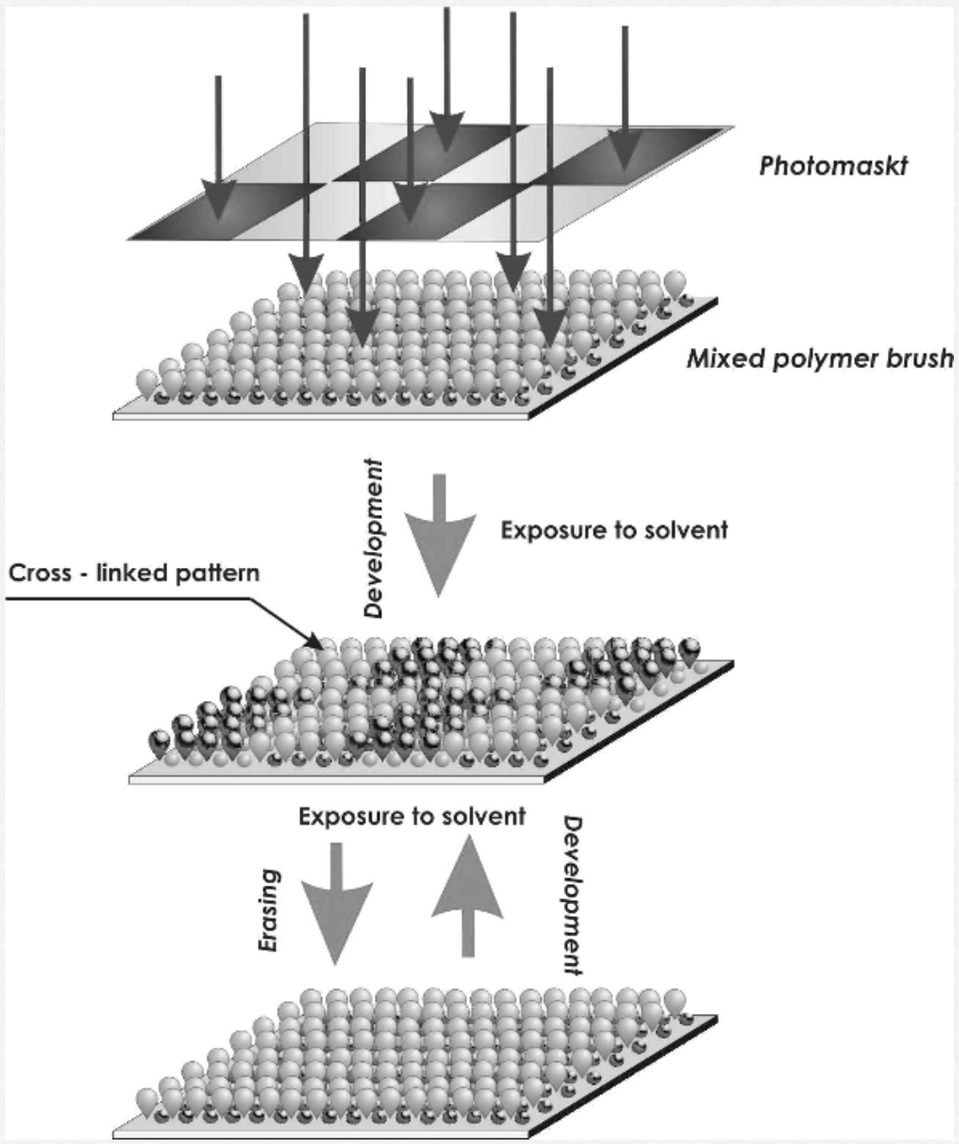
gate



pH sensor

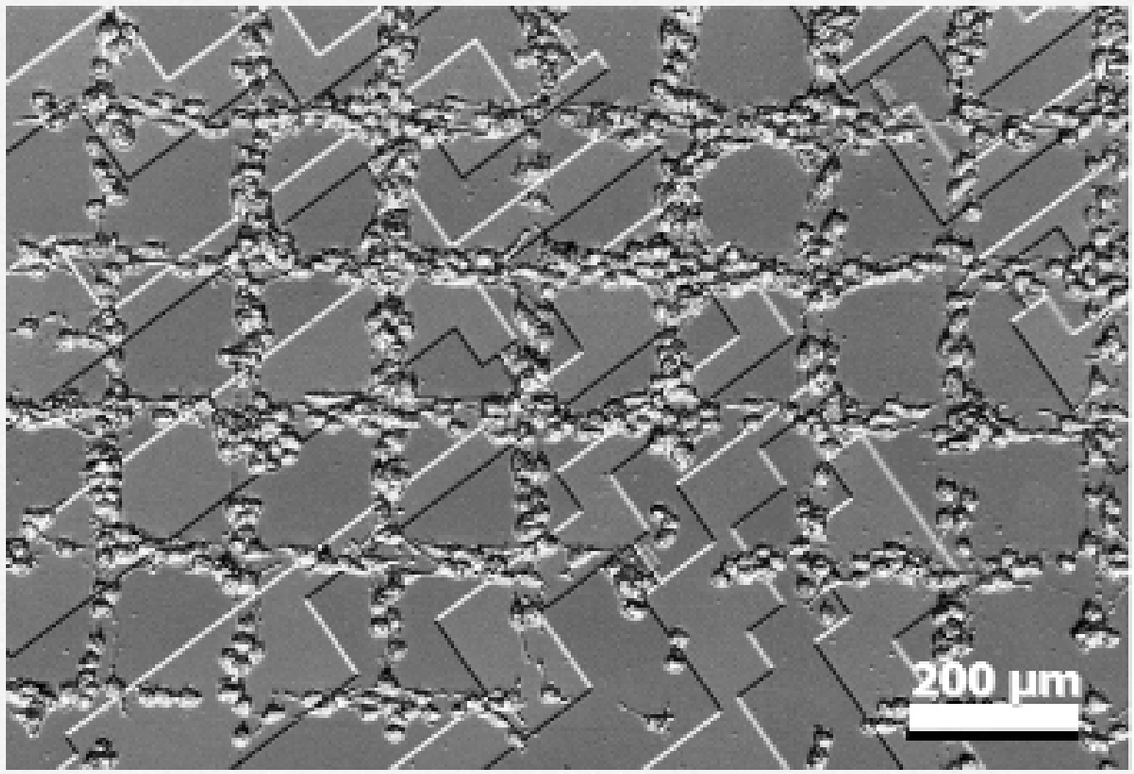


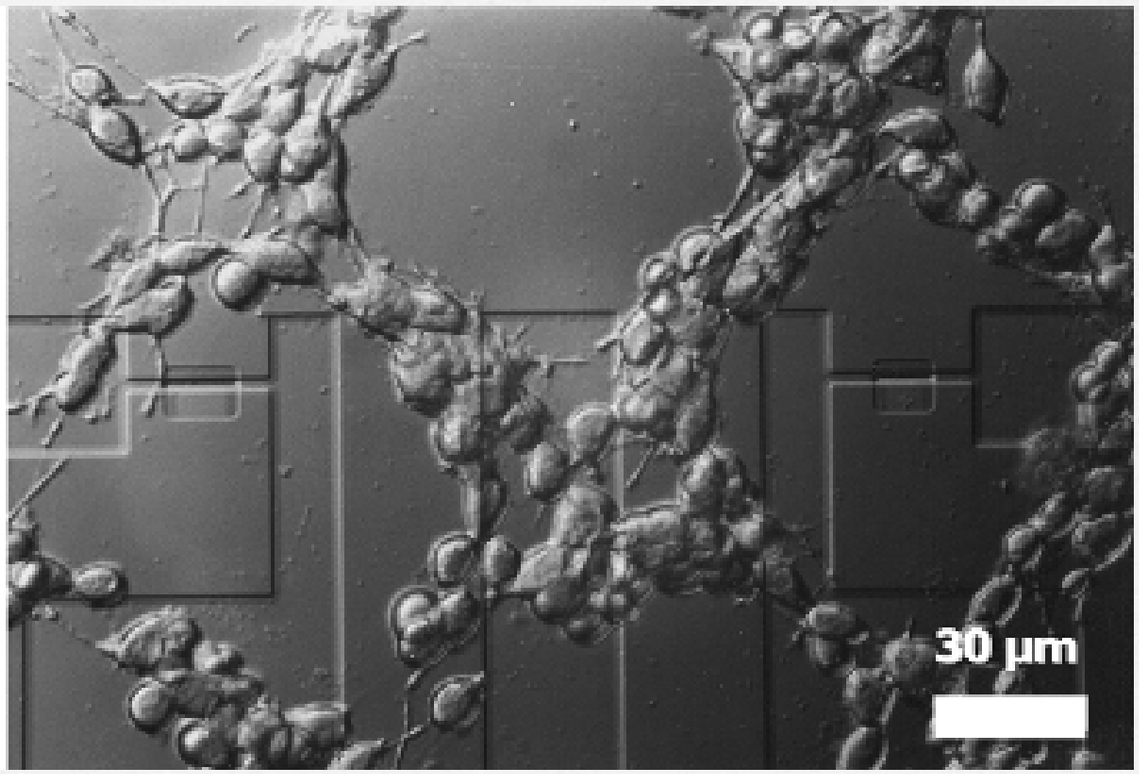
photolithography of mixed polymer brushes



mixed polymer brush, prepared from polyisoprene (PI)and P2VP

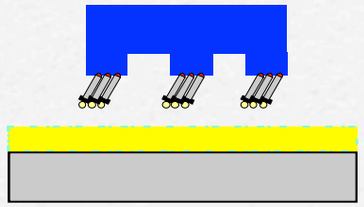
neuron cells on polymer brushes





patterning

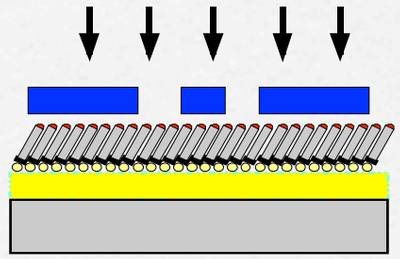
material deposition
"printing"



1 mm

500 n m (40 nm)

exposure through masks:
photons, electrons, ions

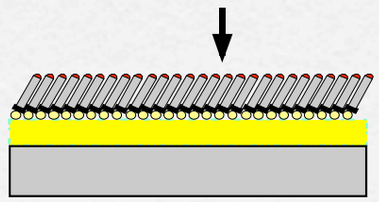


100 μm

10 n m

material modification
"lithography"

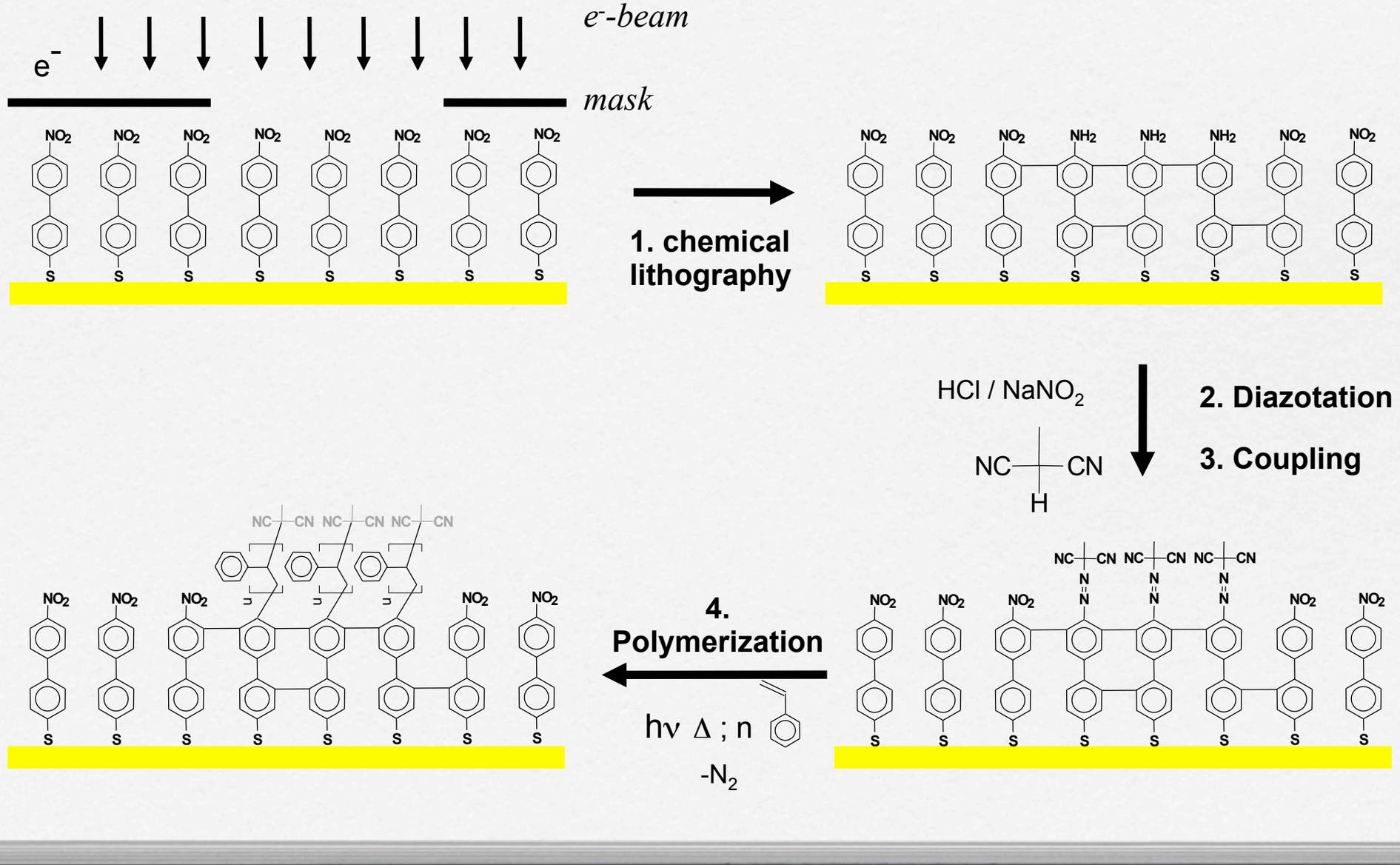
direct writing: e-beam
proximal probe (STM / AFM)



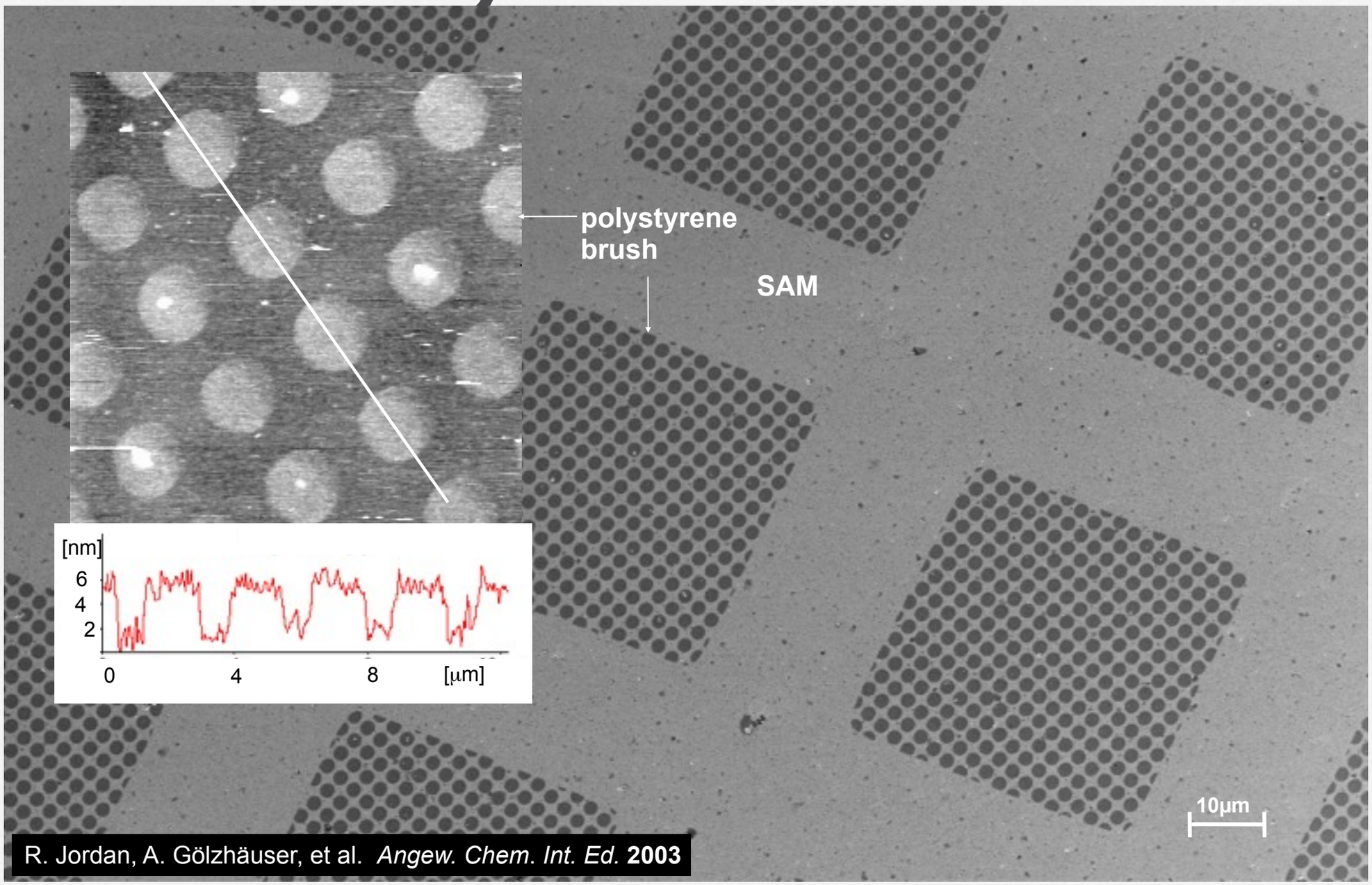
100 nm

0.1 nm

Surface-initiated Radical Polymerization

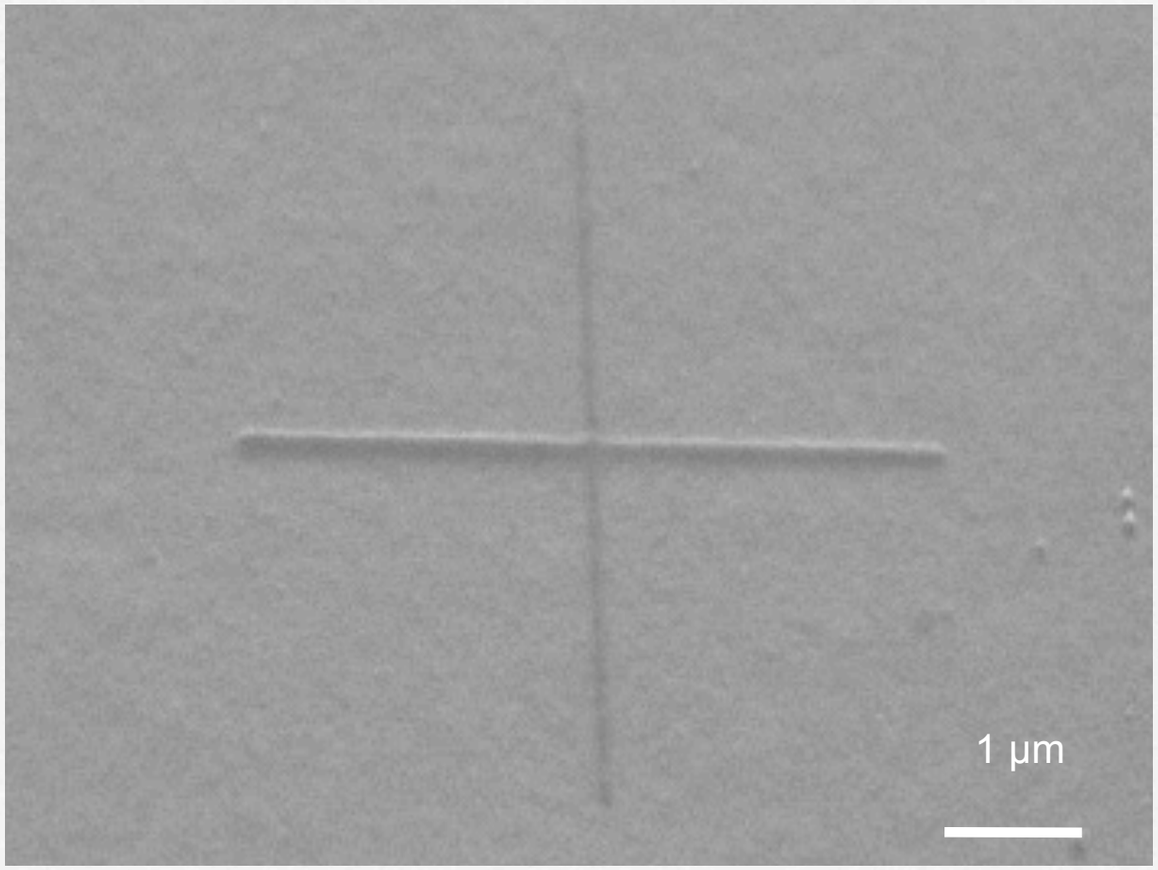


Surface-initiated Radical Polymerization



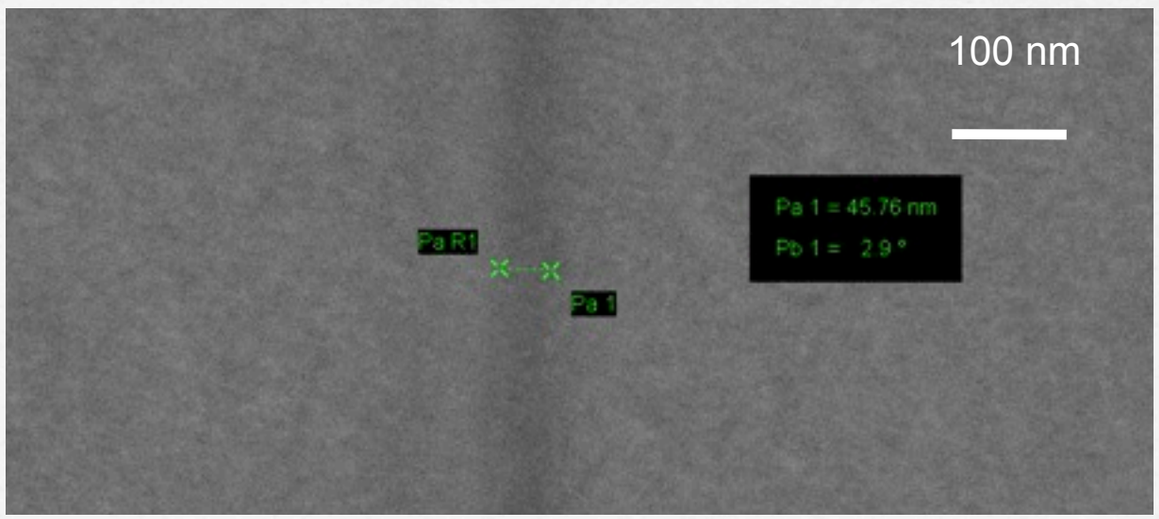
R. Jordan, A. Gölzhäuser, et al. *Angew. Chem. Int. Ed.* **2003**

Surface-initiated Radical Polymerization



height (SPM) : ~ 7 nm

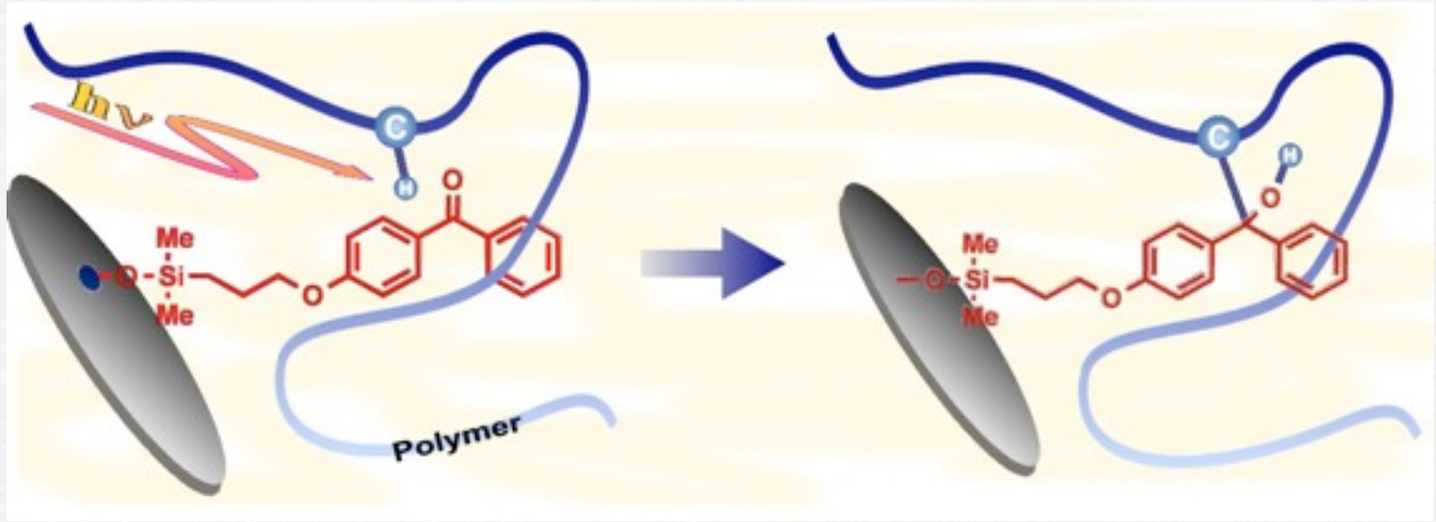
Projected linewidth : 10 nm
measured after SIP : ~45 nm



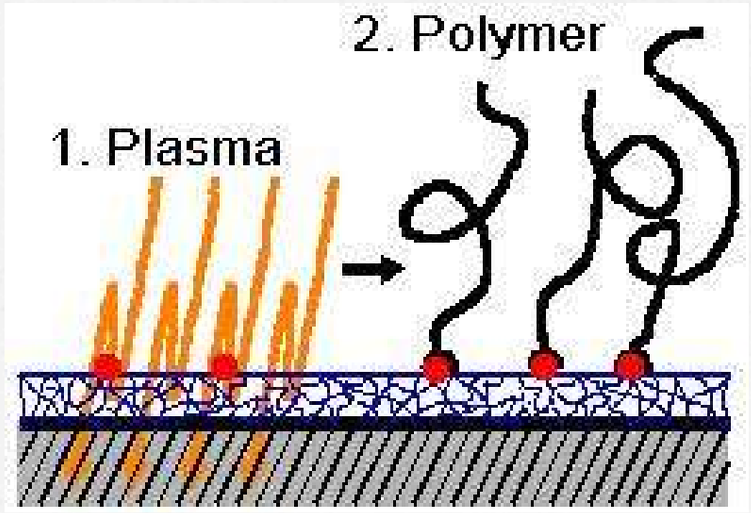
grafting onto

-> important factors determining layer structure (grafting density and thickness) are: a) anchor distance and b) polymer weight (globular conformation)

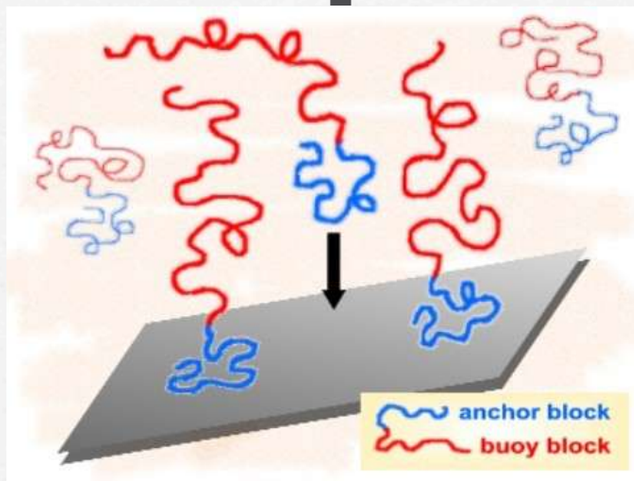
surface attachment can be achieved by
- **activation** (e.g. light) of **reactive surface groups** (e.g. benzophenones) in the presence of the polymer chains, or
- **introduction** of **functional groups** at the **surface** (e.g. plasma treatment) and reaction with **reactive polymer** chain ends



example: poly(ethyleneoxid) (PEO) surface immobilization to reduce unspecific protein adsorption and enhance biocompatibility (e.g. by introduction of amine surface groups and coupling of epoxy-modified PEG)



block copolymer adsorption



(amphiphilic) block copolymers consist of two different chain segments, which have different affinity to a substrate surface and the surrounding environment

- **anchor block**: high affinity to substrate, adsorbs to surface
- **buoy block**: high affinity to solvent, expands into medium

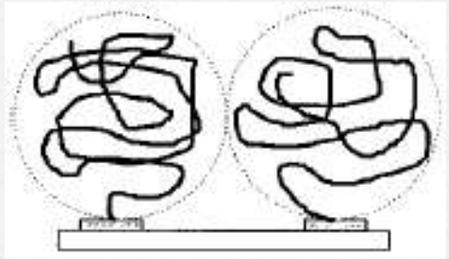
example: poly(styrene-block-ethylenoxid) PS-b-PEO
or poly(styrene-block-methylmethacrylate) PS-b-PMMA (to suppress dewetting of PS homopolymer films at SiO_2 surfaces)

important structural parameter:

- **chemical nature** of the monomers / functional groups
  (determines solubility and surface affinity)
- **relative** block lengths (ratio of buoy to anchor block)
- **overall** molecular weight (polymer conformation)

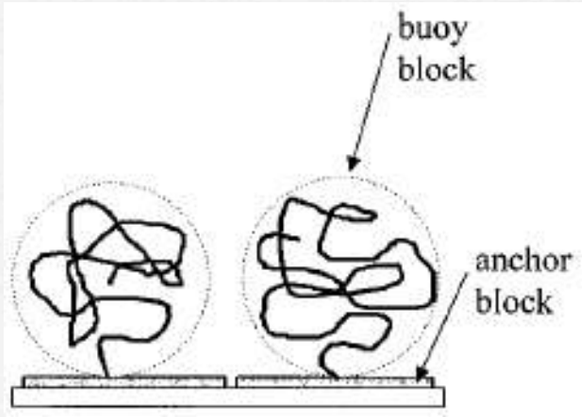
in a very simple model (first approximation) the packing density and conformation of the polymer chains is dominated either by (A) the buy block (chain stretching) or (B) the anchor block (larger separation between the buoy blocks)
in reality the behavior is more complex...

A:



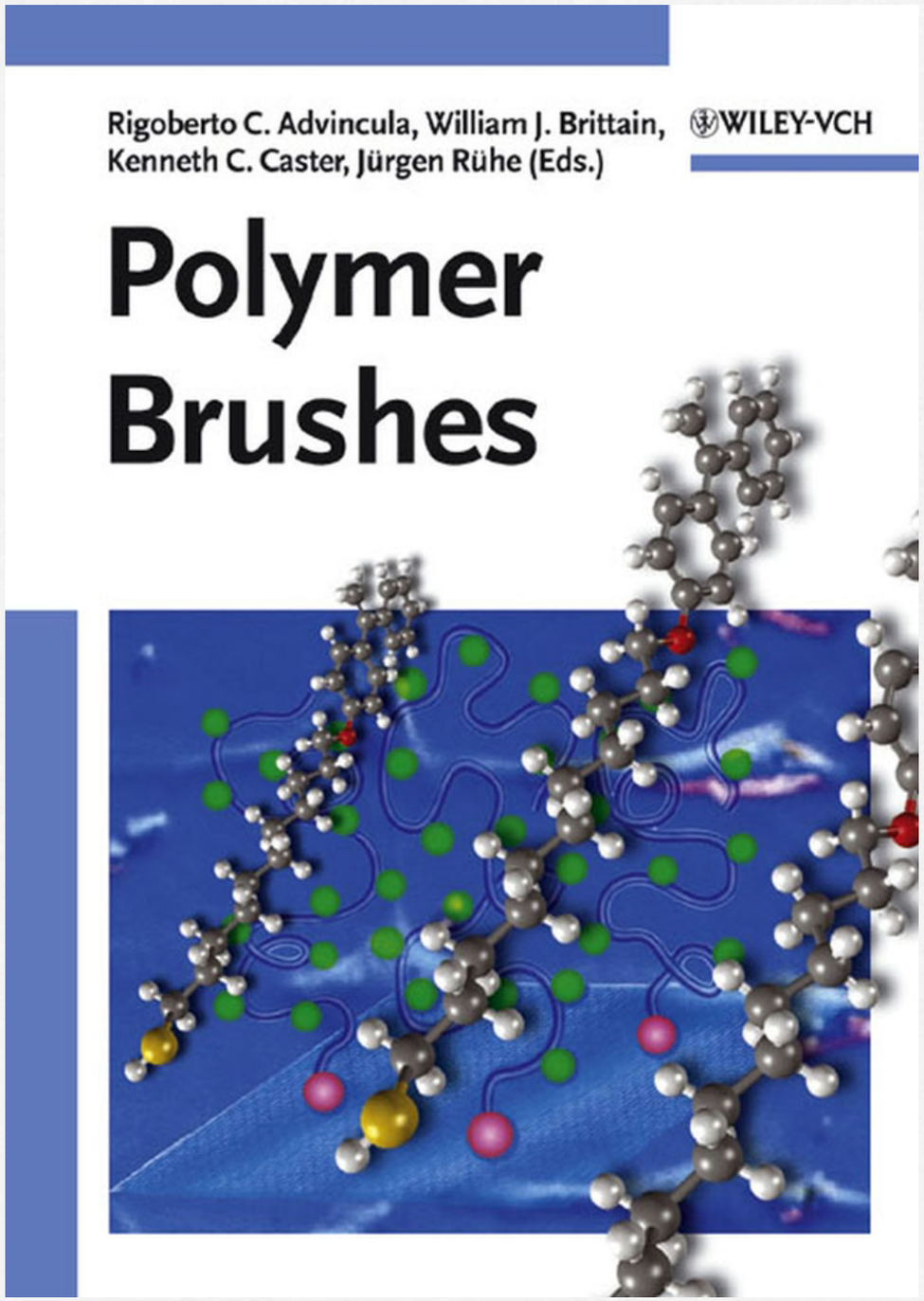
buoy-dominated packing

B:

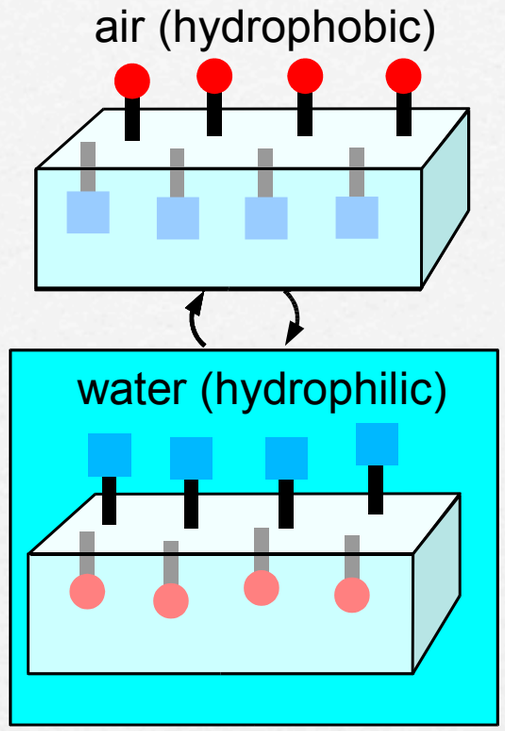


anchor-dominated packing

polymer brushes



surface segregation



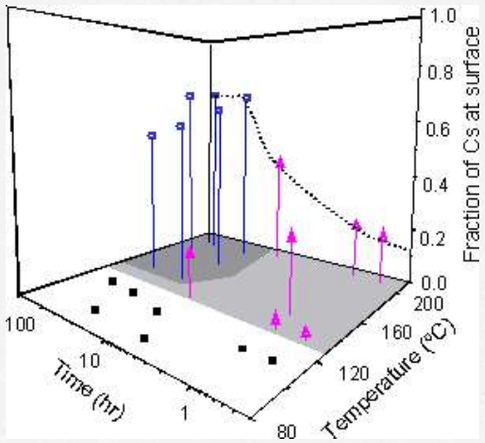
surface segregation (also "reconstruction"): at sufficient dynamics / mobility of polymer chains close to an interface

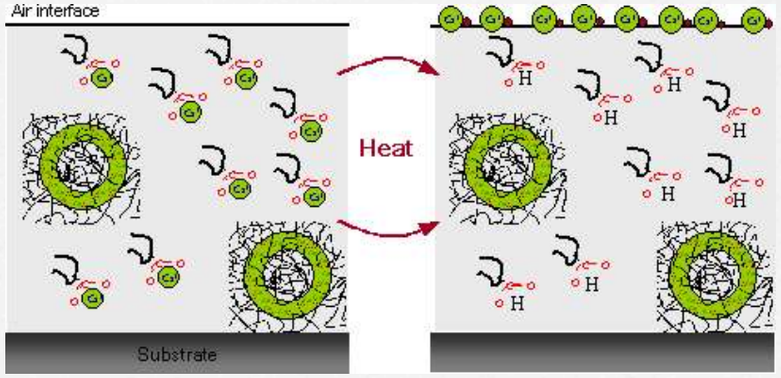
- mobile **additives** can **migrate** from the polymer bulk to the interface or

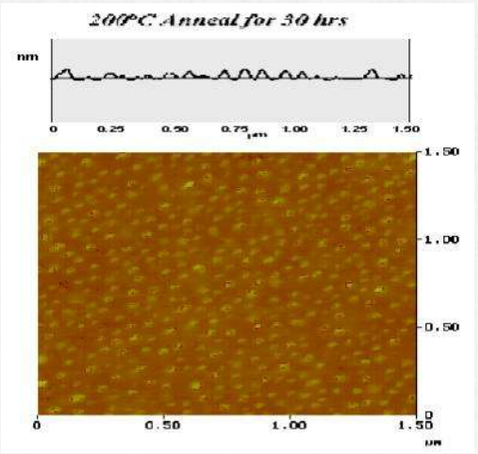
- a **reorganization** of **chain segments** and **functional groups** at the interface can occur as a **response** to the change of the **environment** (e.g. polarity change of a surrounding medium), leading to a reduction of the interfacial energy (e.g. poly(glycerol methacrylate) or surfactants in a drying dispersion paint film)

functional group: hydrophobic (e.g. -CH_3) hydrophilic (e.g. -O

example: Cs ion segregation in poly(styrene-co-methacrylic acid) films at high temperature:







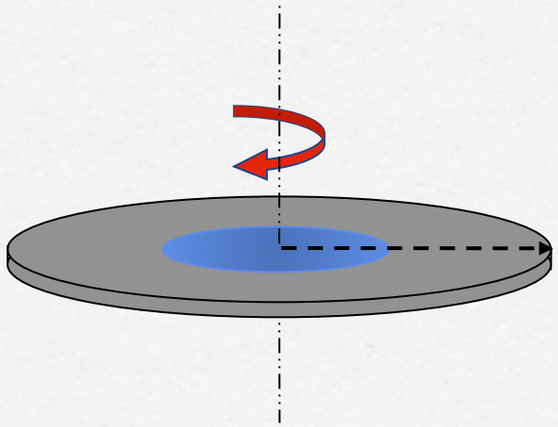
http://www.lrsm.upenn.edu/~composto/pro/sur_ion.html

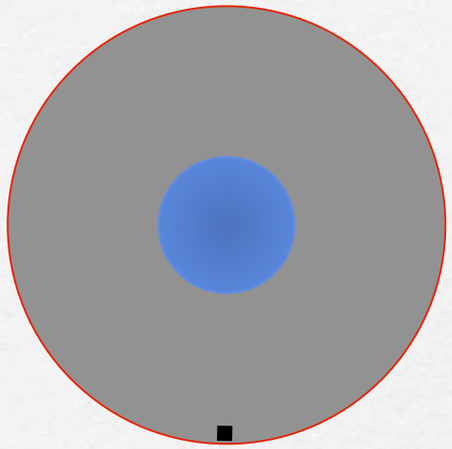
spin coating: the basics

- Spin coating was first used to apply coatings of paint and pitch around seventy years ago.
- In 1958 Emslie et. al. developed the first spin coating model.
- This model has been used as a basis for future more specific or complicated models.

spin coating: the basics

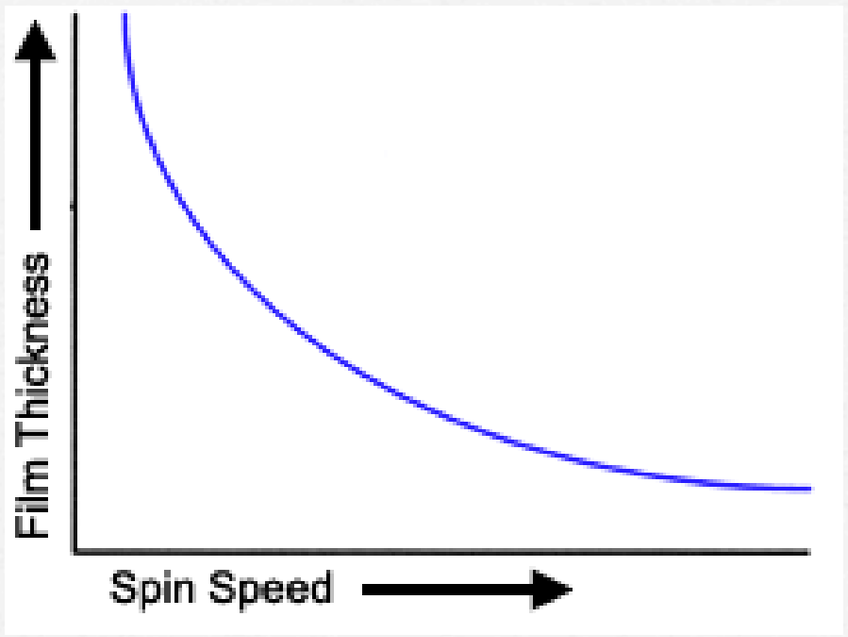
- Centripetal force is responsible for the spread of liquid across the wafer.

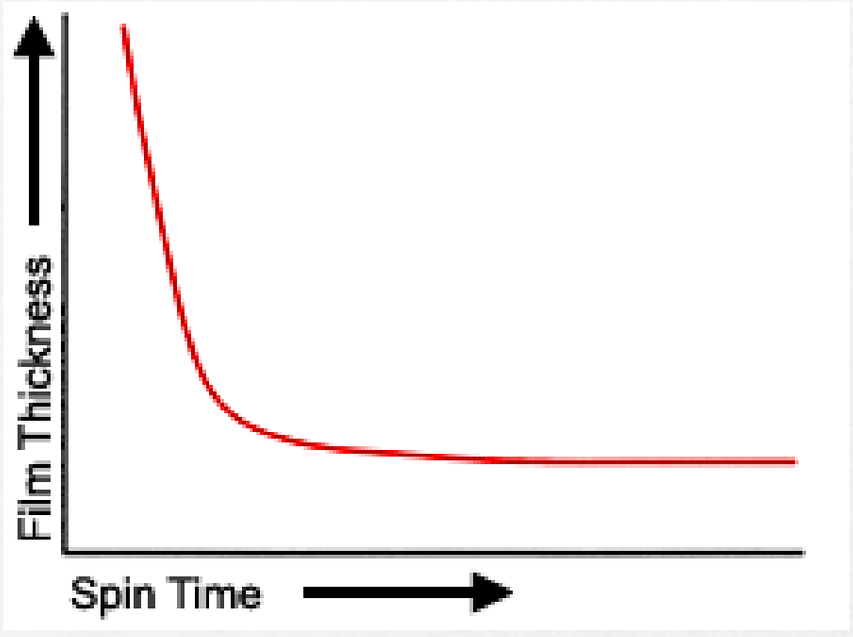


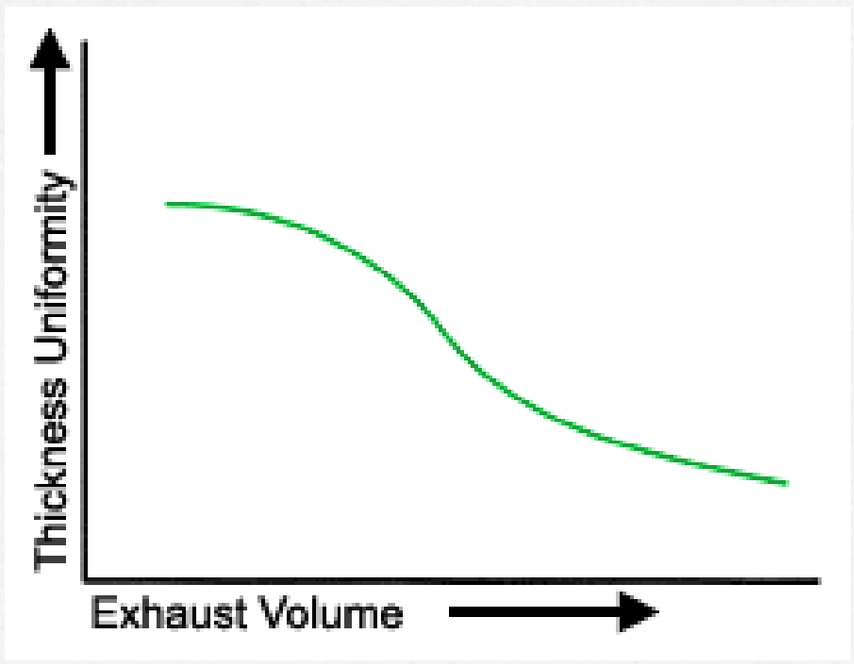


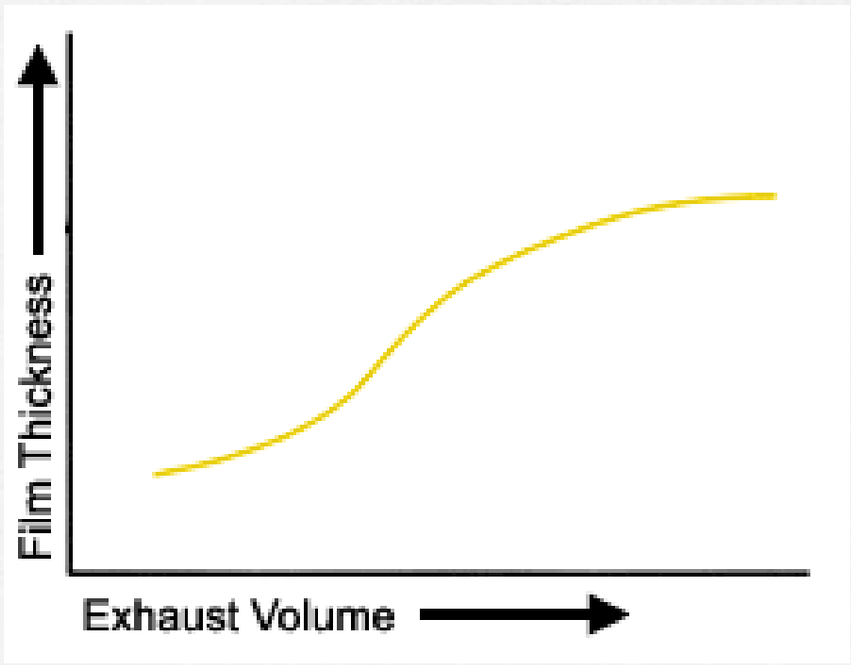
- At long times the fluid will flow only negligibly, resulting in a lower limit of the final thickness.

spin coating: the basics



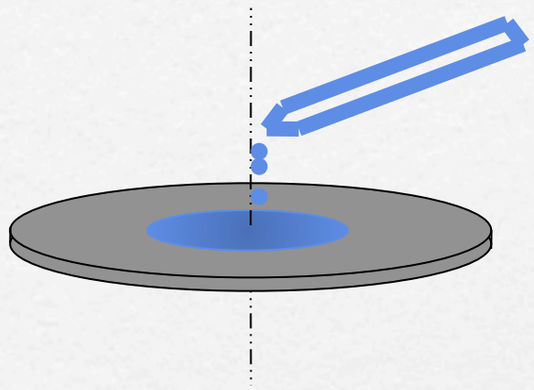






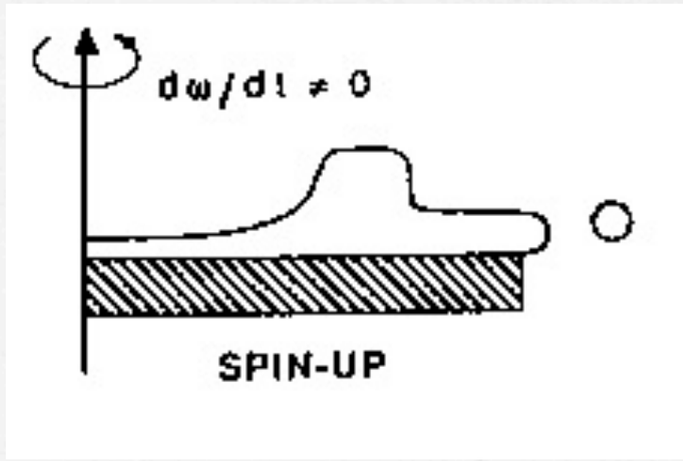
spin coating: the process

- Four main processing steps:



- Step 1: Deposit fluid onto substrate.

- Step 2: Accelerate wafer to final radial velocity.

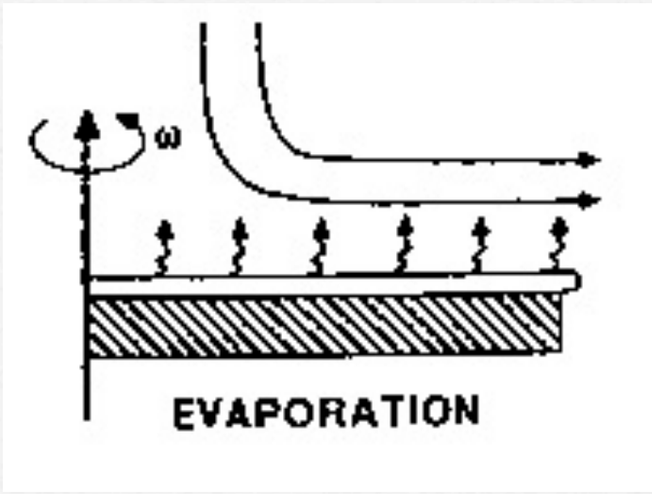


spin coating: the process

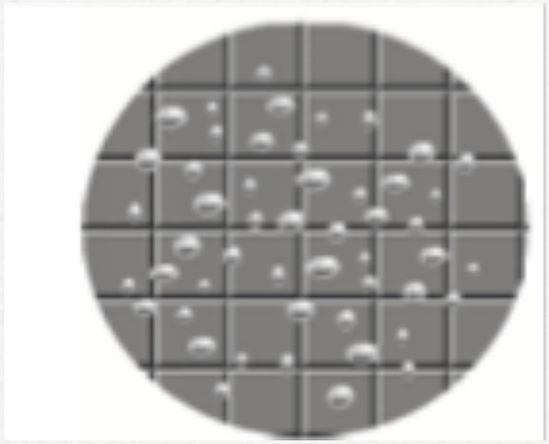
- Four main processing steps:

- Step 3: The coating thins at a rate that depends on the velocity at which the wafer is spinning and the viscosity of the fluid.

- Step 4: Solvent is evaporated from the film, resulting in further thinning.



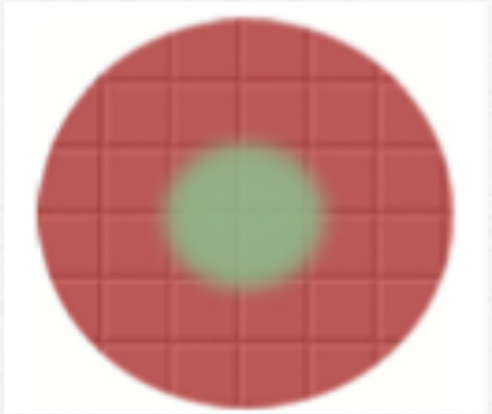
spin coating: defects



- Bubbles on the surface of the coated wafer.
- This occurs when fluid is deposited as the wafer is spinning, and may be caused by a faulty dispense tip.

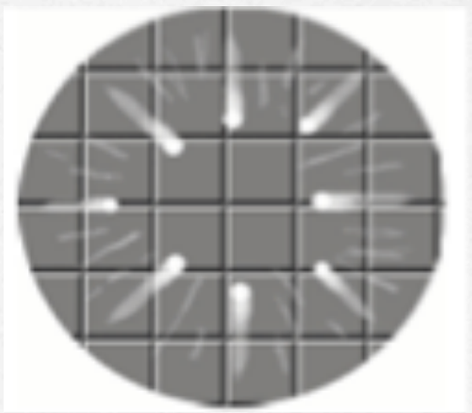
- A swirling pattern may be observed.
- Causes:
  - Fluid deposited off center
  - Acceleration too high
  - Spin time to short
  - Exhaust rate too high

spin coating: defects

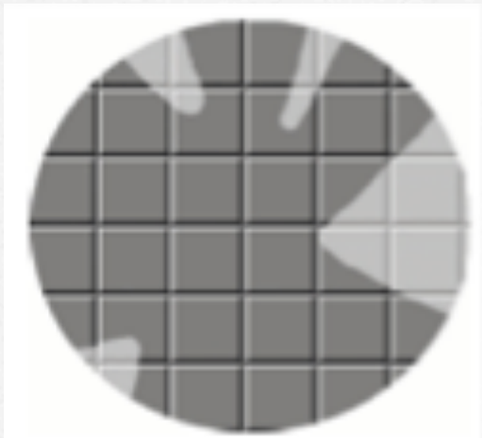


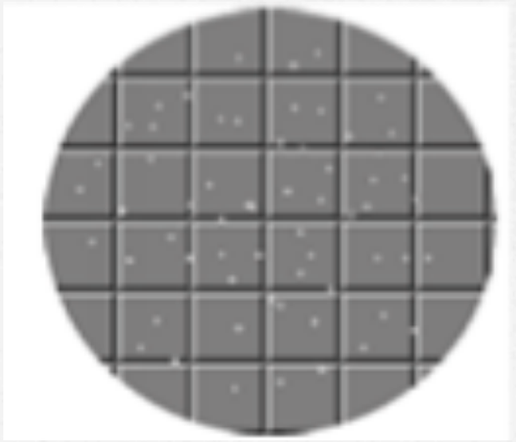
- A mark or circle in the center of the wafer could indicate a chuck mark.
- If a chuck mark occurs the type of chuck should be changed.

- Streaks can occur on the wafer for a number of reasons including:
  - Acceleration too high
  - Fluid deposited off center
  - Particles on surface prior to spin



spin coating: defects



- Uncoated areas on wafer occur when to little fluid is deposited on the wafer.

- Pinhole defects can be caused by:
  - Air bubbles
  - Particles in fluid
  - Particles on substrate.