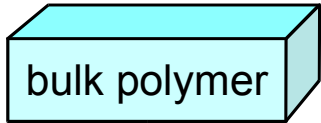


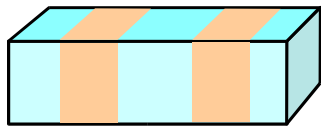
Structural Classes with Polymer Surfaces

1) as substrate:



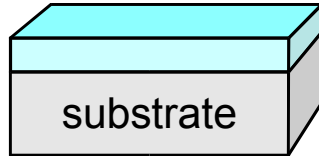
"external" surface

block copolymer



"internal" surface
→ **interface**

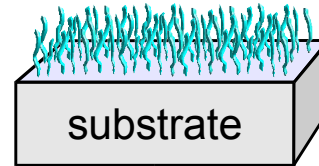
2) as surface layer:



surface & interface

(→ adhesion and cohesion important parameters)

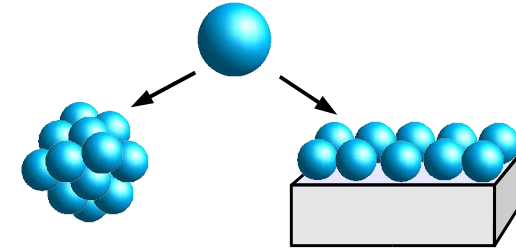
3) as surface molecules:



individual molecules share surface & interface

(→ large gradient of external influence on single molecule possible)

4) as discrete particles:



aggregate

surface layer

often very large surface-to-volume ratio

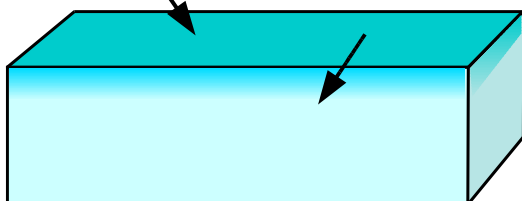
(→ substantially different behavior to bulk material)

General Modification Strategies

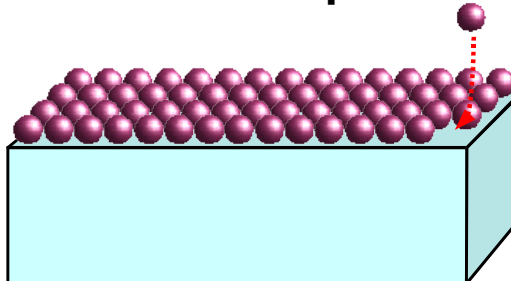
- surface transformation:

reagents
(e.g. O_2)

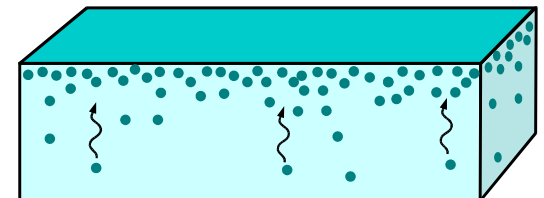
energy
(e.g. $h\nu$, γ , kT)



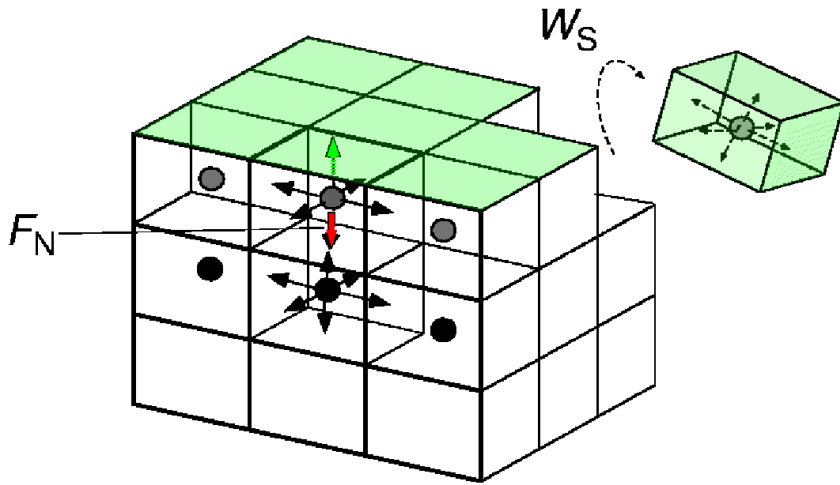
- film formation by material deposition:



- surface segregation:



Specific Differences between Surface and Bulk Properties



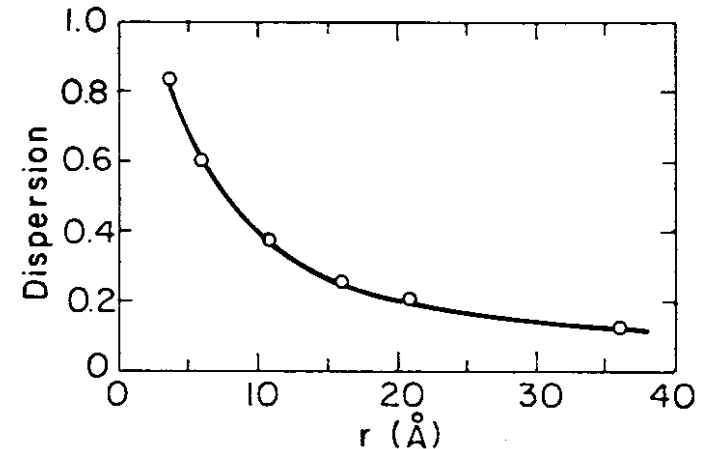
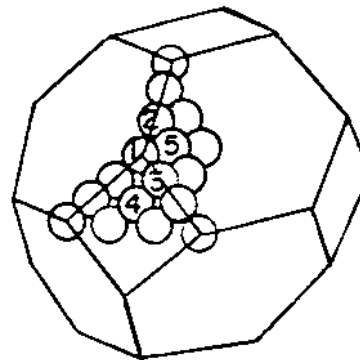
In three dimensions the structure extends to one side of the surface into the bulk.

F_N is the normal force acting onto a surface element towards the bulk, due to missing elements at the exterior.

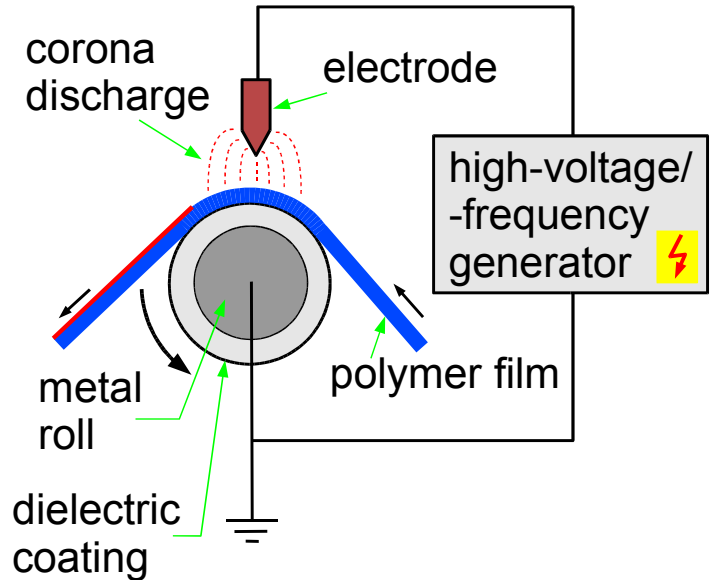
W_s is the work to transfer a surface element into the gas phase.

"dispersion": The **ratio** of the number of **surface** atoms to the **total** number of the atoms in a particle.

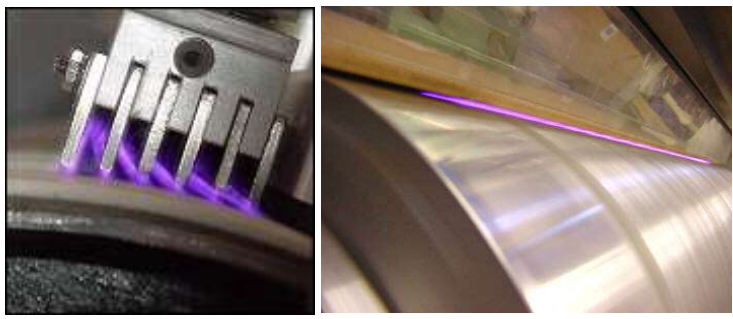
example: variation of the dispersion with particle size for close-packed cubic packing (fcc) of spherical particles



T2) Corona Discharge Treatment



corona discharge glow:



the polymer surface (often polyolefins) is treated with the products (normal pressure plasma) from a corona discharge in ambient atmosphere (about 4000-35000 J m²)

the workpiece (usually thin polymer film) is placed between an electrode and a grounded metal roll

electrons are ejected from the electrode by strong electric field

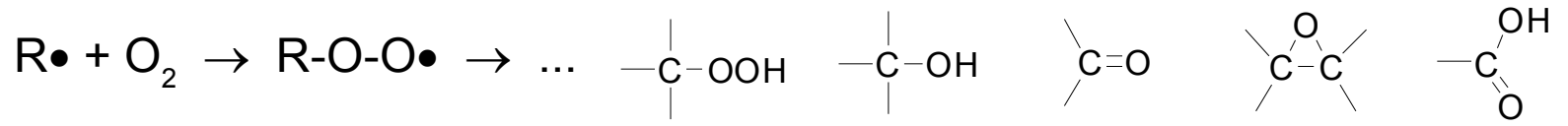
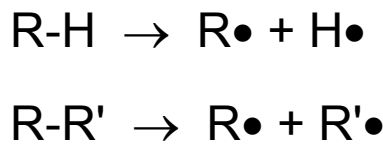
→ these electrons collide with air molecules and the polymer surface to generate **free radicals, ions, photons, excited and reactive intermediates**

→ reactions at the polymer surface can lead to:

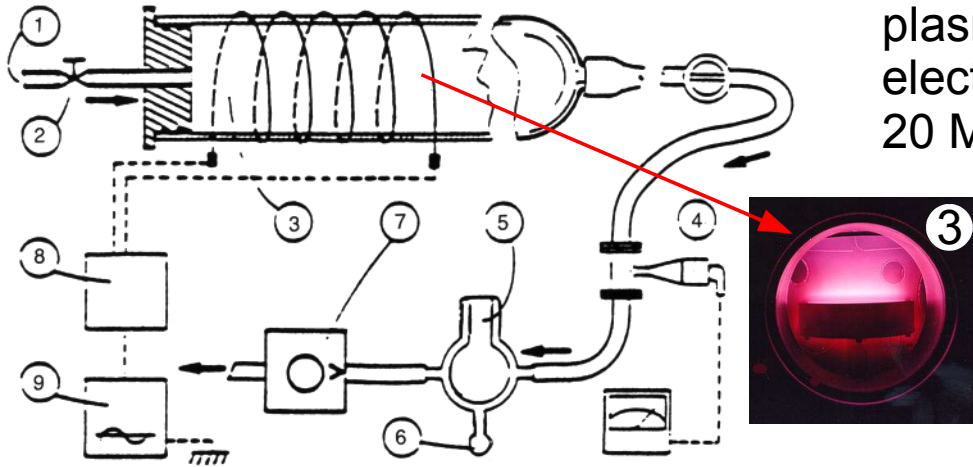
- a) **chain scission**,
- b) **cross-linking**, and
- c) introduction of **functional groups** (oxidation)

→ promotes adhesion (for gluing or printing) and wetting

chemical reactions:



T3) Plasma Treatment (Ablation / Transformation)



plasma generation in vacuum / low gas pressure via electro-magn. high frequency (RF) field (100 kHz, 10-20 MHz, 2.45 GHz) → glow discharge (RFGD)

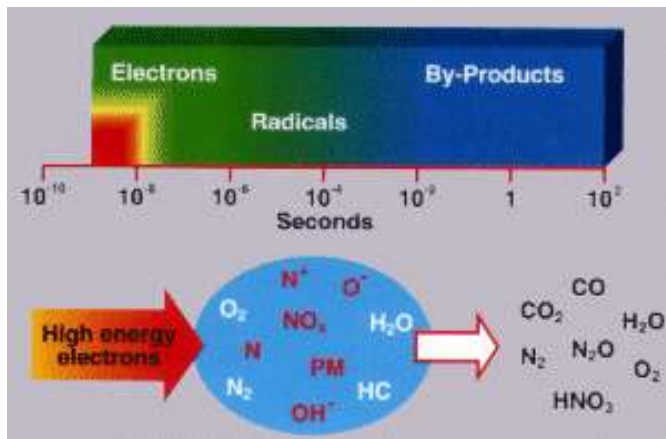
→ the generation of **functional groups** at the polymer surface can be controlled by the choice of plasma **gas** (e.g. H₂O, O₂, Ar, N₂, F₂, CO₂, NH₃)

→ free electrons, ions, radicals, and vacuum UV are reactive species (penetration depth few 10 nm)

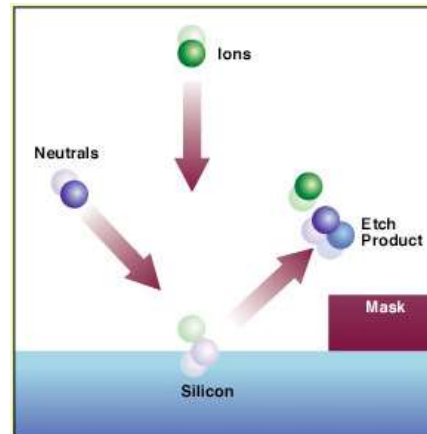
→ functional group generation, material ablation, chain scission, cross-linking

- 1) gas inlet 2) valve 3) plasma + sample
 4) pressure gauge 5) liq. N₂ 6) trap
 7) vac. pump 8,9) matching, RF gen.

reaction cascade in a pulsed normal pressure plasma



plasma ablation



process parameter:

- type of gas, pressure, flow rate,
- excitation power, exc. frequency,
- time of treatment, pulse duration / pause, temp. of substrate
- geometric factors (reactor, sample)

→ improved adhesion (metal films and printing)

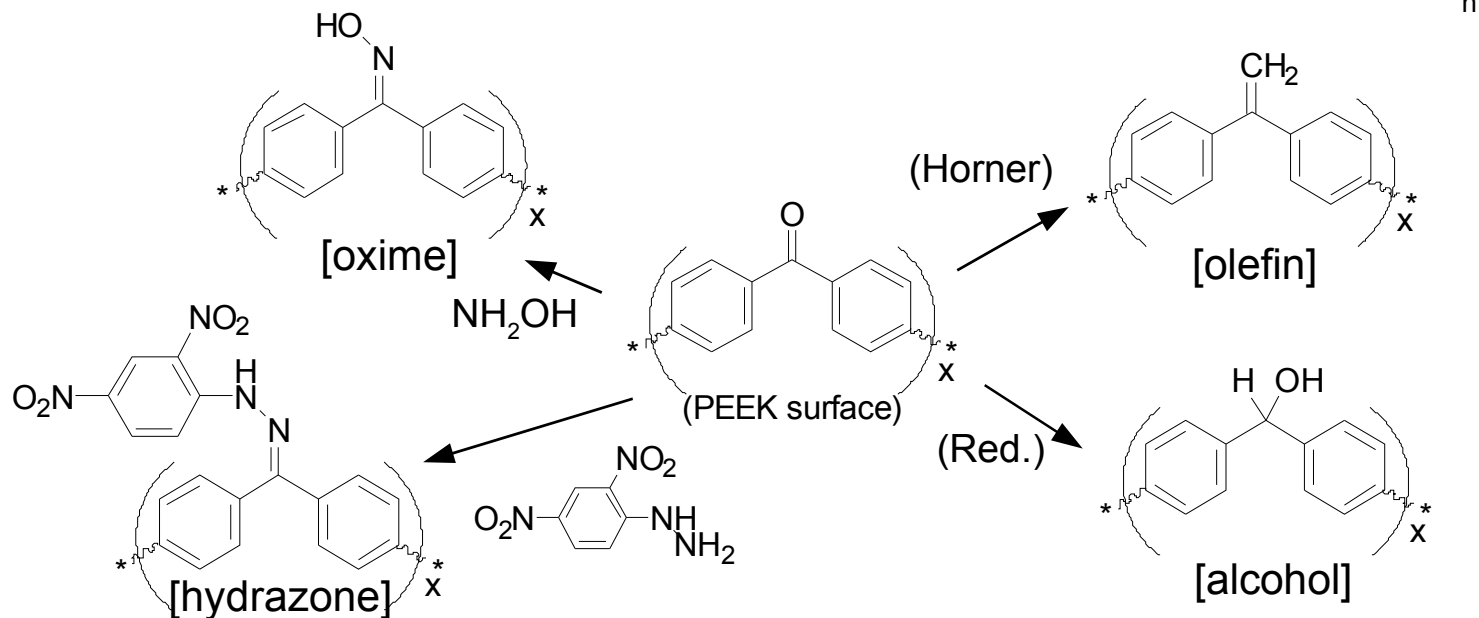
T4) (Wet) Chemical Treatment

chemical **transformation**, **etching** and **dissolution** of polymer surfaces by active reagents (often oxidizers like H_2SO_4 , $KMnO_4$, CrO_3 / H_2CrO_4 , or transformation of $-COOH$ or $-OH$ with SO_2Cl_2)

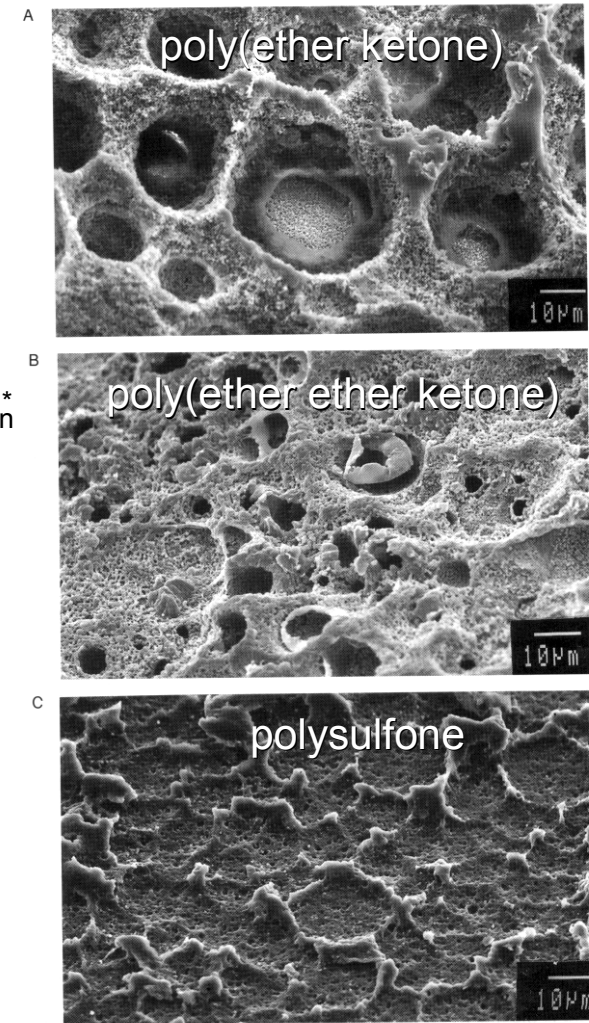
→ often differentiation between **amorphous** (more reactive) and **crystalline** (more inert) regions - enhanced by solvent treatment

→ improves roughness and adhesion of metal film in plating

example: specific chemical transformation of poly(ether ether ketone) PEEK:



modification of **surface morphology** by wet chemical etching with H_2SO_4

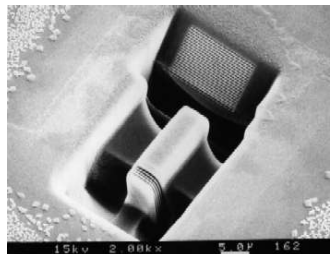


T5) Ion-Beam Modification / Etching / Milling

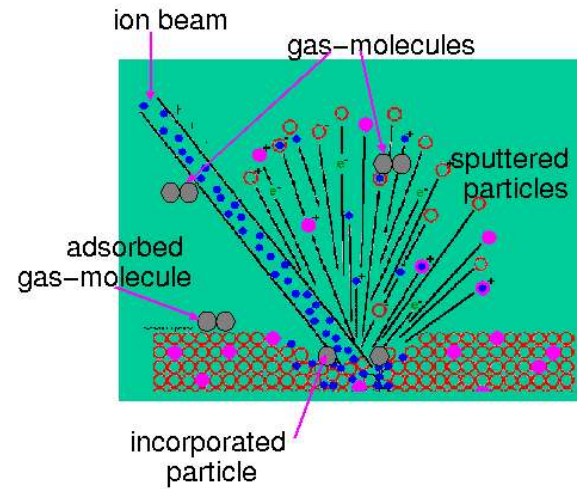
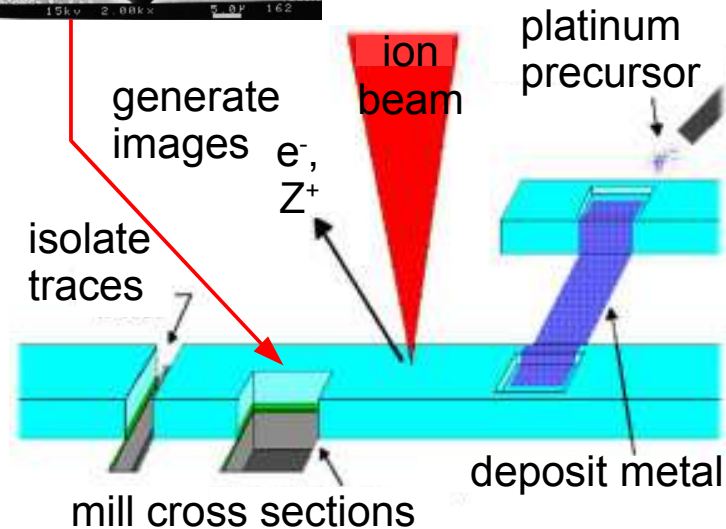
polymer surface is bombarded with **ions** (often focused as beam) to **ablate / mill** the substrate material or to **deposit** new material

→ by **scanning** the focused ion beam **3D structures** with >10 nm resolution can be generated

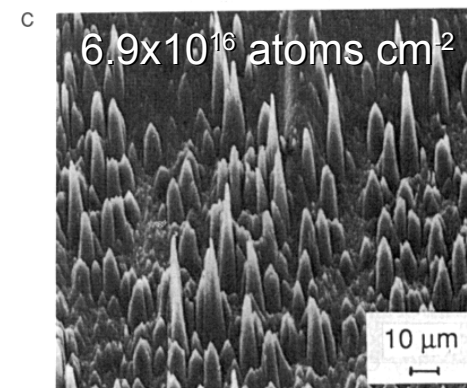
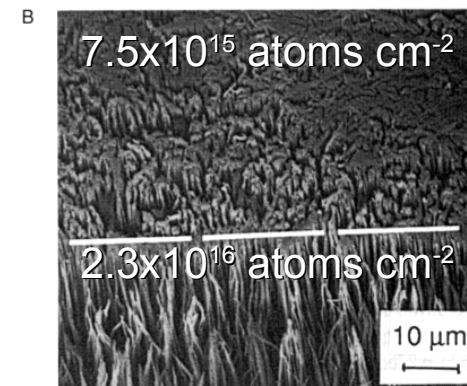
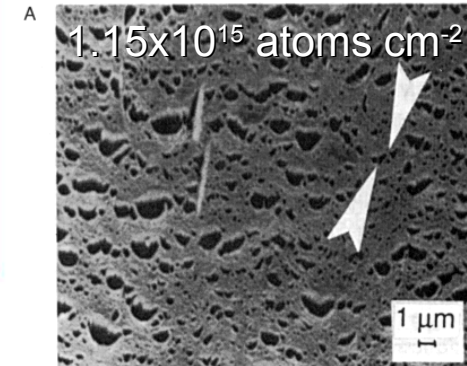
ion-milled semiconductor



→ ion bombardment of the polymer surface increases the surface **roughness**, generates new **functional groups** and may increase **conductivity**



surface morphology of PTFE after ion bombardment w/ Xe



process parameter:

type of ions, ion energy, beam dose
type of polymer

→ **reactions** at the polymer surface:

- reduction
- oxidation
- chain fragmentation
- cross-linking
- loss of heteroatoms & aromaticity

T6) UV-Irradiation



"UV cross-linker"

irradiation treatment with **short-wavelength UV** light (~180-250 nm) to **activate** polymer surfaces, or to **decompose** dirt on the surface

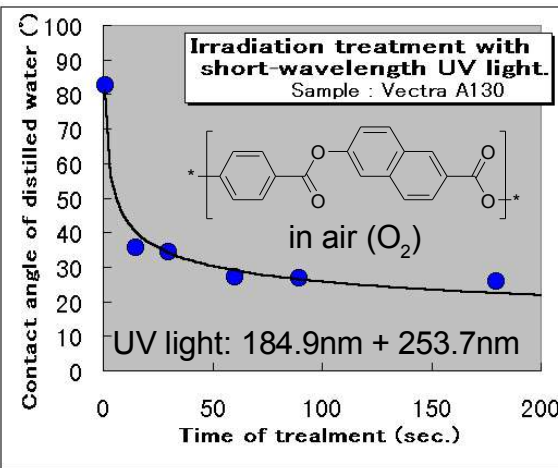
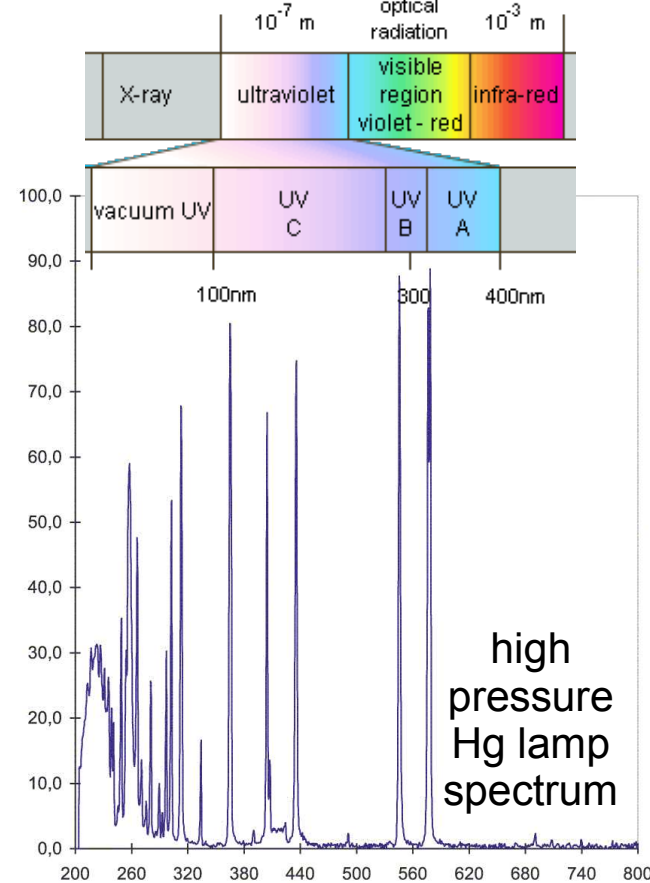
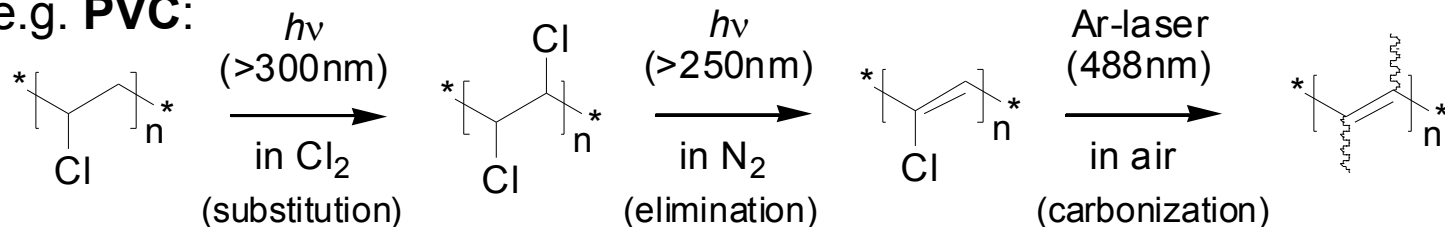
→ **energy** of light induces **chemical reaction** in and near the surface (structuring by irradiation through photomask possible)

process parameter:
wavelength (photon energy), dosis (energy per area), surrounding species / medium

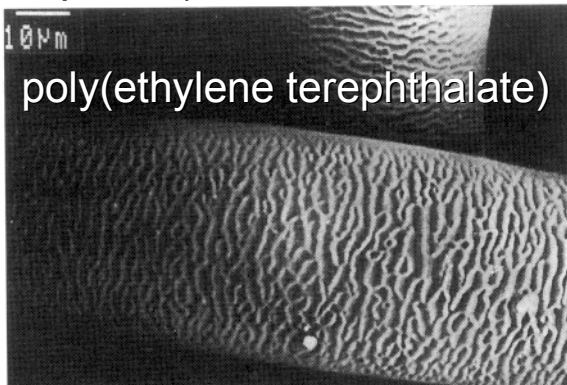
→ possible **reactions:**

- ablation (e.g. activation of oxygen to ozone → volatile ox. prod.)
- surface group transformation (e.g. elimination)
- introduction of functional groups by photochemical reaction with species from the environment / medium (e.g. -COOH by ox.)

e.g. **PVC:**



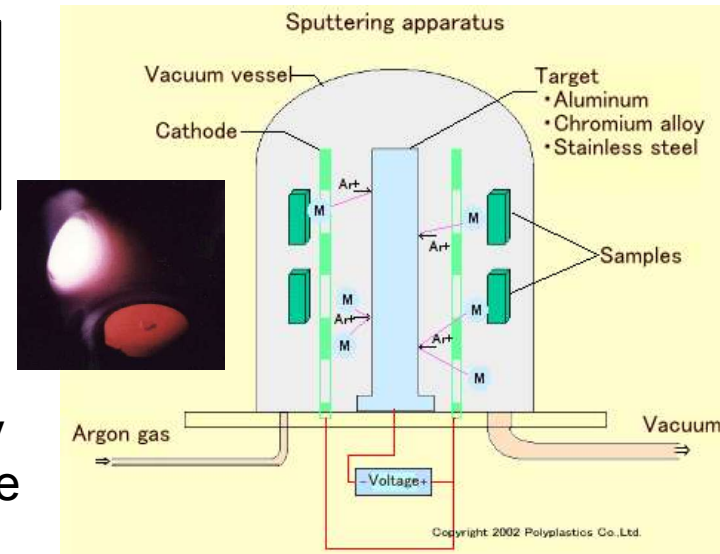
UV laser (248 nm, 60 mJ cm⁻², 10 pulses)



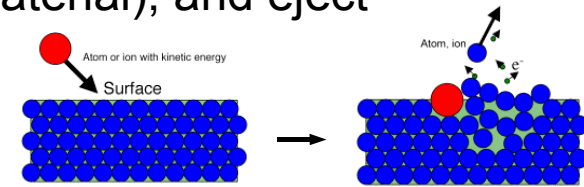
Material Deposition: D1) Metalization

a) metal evaporation and sputtering:

metal evaporation in vacuum by heat, e⁻-beam, or glow discharge

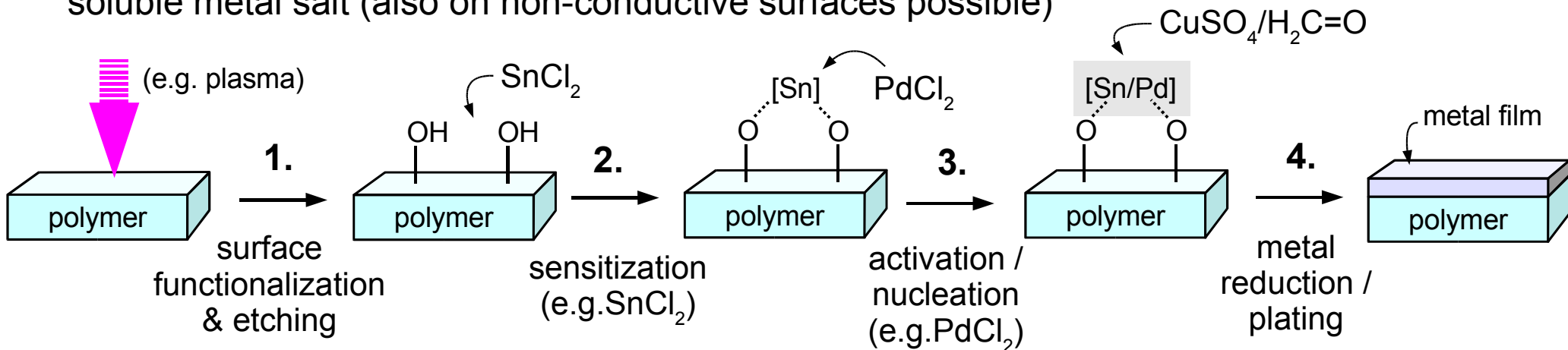


"sputtering": high voltage across a low-pressure gas (e.g. Ar, 5 millitorr) creates plasma (glow discharge), energized plasma ions strike "target" (coating material), and eject atoms from target which travel to and bond with the substrate



b) electroless / chemical metal deposition (plating):

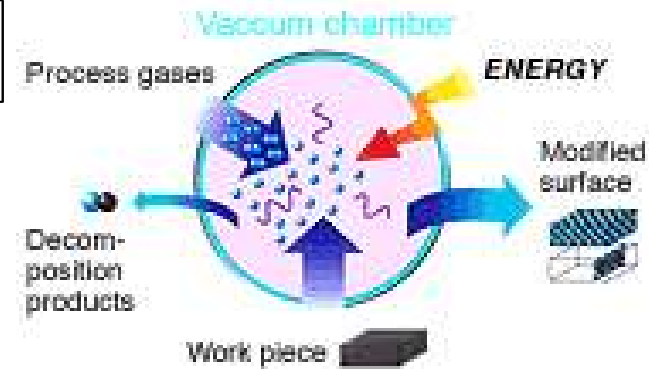
usually deposition of a metal film (e.g. Cu, Ni, Co, Au, Ag, Pd, Pt) by chemical reduction of a soluble metal salt (also on non-conductive surfaces possible)



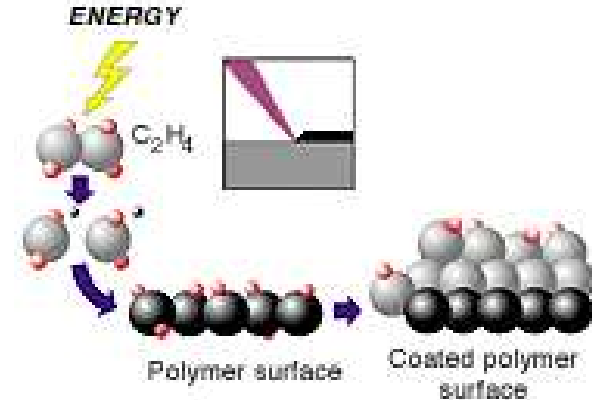
D2) Plasma Polymerization

plasma polymerization or plasma enhanced chemical vapor deposition (PECVD) utilizes a similar setup as shown in T3) "Plasma Treatment", but **addition of monomer** through gas phase to generate a **polymer film** at the **substrate surface**

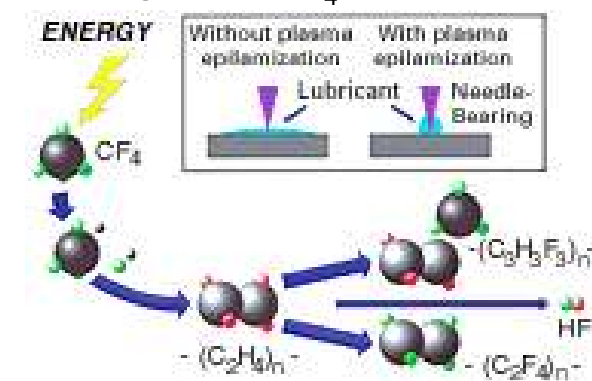
- **CAP-mechanism** (competitive ablation and polymerization: **parallel** processes of **ablation** (material removal) and **polymerization** (material deposition) in plasma of monomer at low gas pressure
- can generate **homogeneous**, highly **cross-linked** polymer films with thicknesses of up to $1\ \mu\text{m}$ ($\sim 10\ \text{nm min}^{-1}$)



generation of **diamond-like** coating from C_2H_2

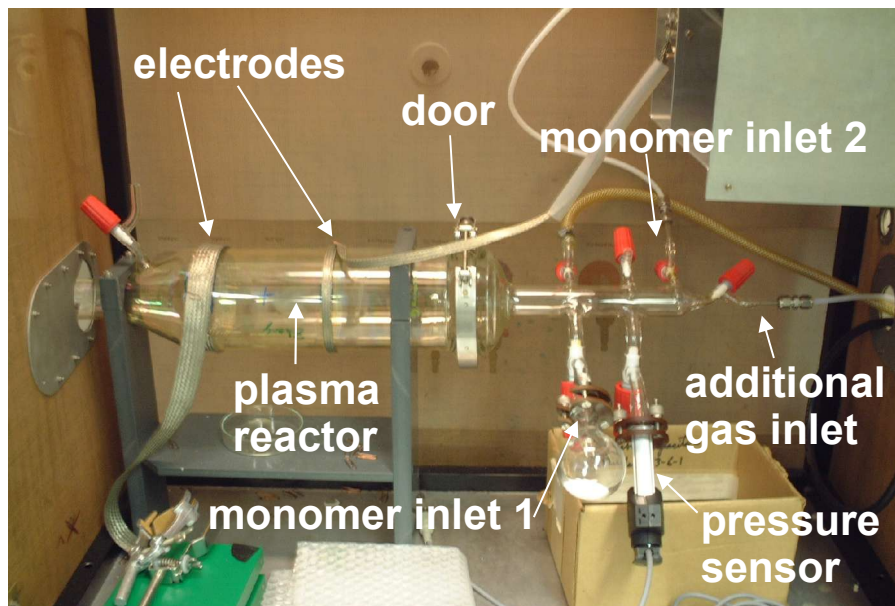


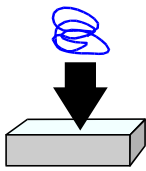
generation of **hydrophobic** coating from CF_4



monomer types:

- type I: $-\text{C}-\text{C}-$, aromatic
- type II: $>\text{C}=\text{C}<$, cyclic
- type III: aliphatics (excluded by I & II)
- type IV: O-containing (alcohols, ethers, esters)





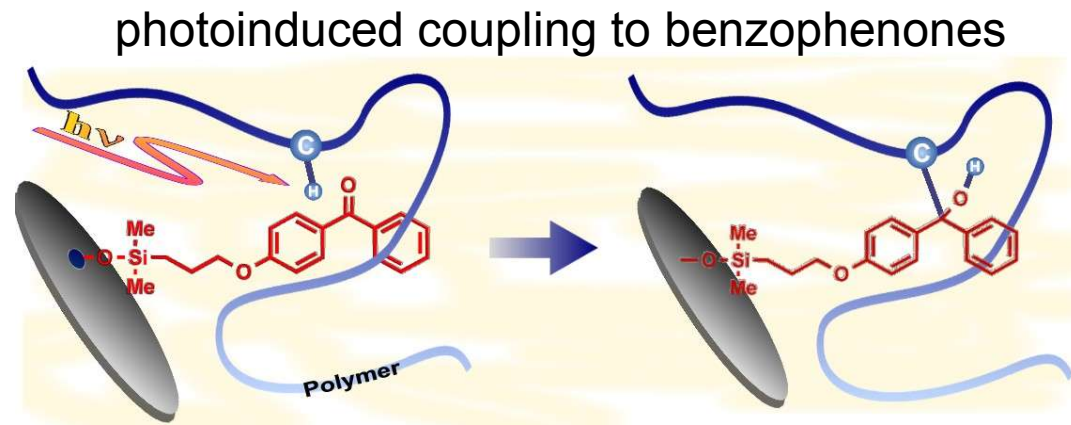
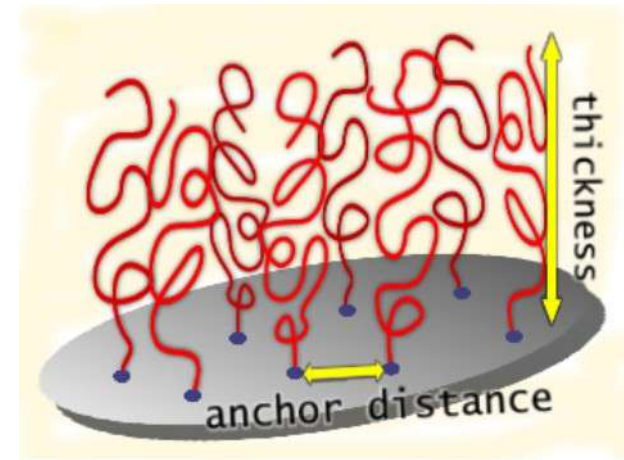
D3) Polymer "Grafting to" Surface

"grafting (on)to": attachment of polymer chains to surfaces by chemical surface reaction leads to a polymer brush "monolayer"

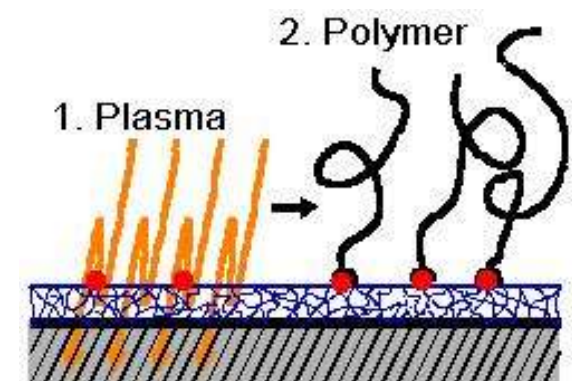
→ important factors determining layer structure (grafting density and thickness) are:
a) anchor distance and
b) polymer weight (globular conformation)

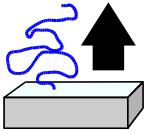
surface attachment can be achieved by
- **activation** (e.g. light) of **reactive surface groups** (e.g. benzophenones) in the presence of the polymer chains, or
- **introduction of functional groups** at the **surface** (e.g. plasma treatment) and reaction with **reactive polymer** chain ends

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)



coupling to plasma activated surface



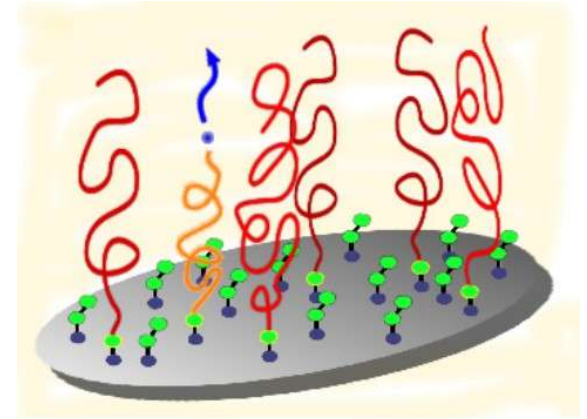


D4) Polymer "Grafting from" Surface

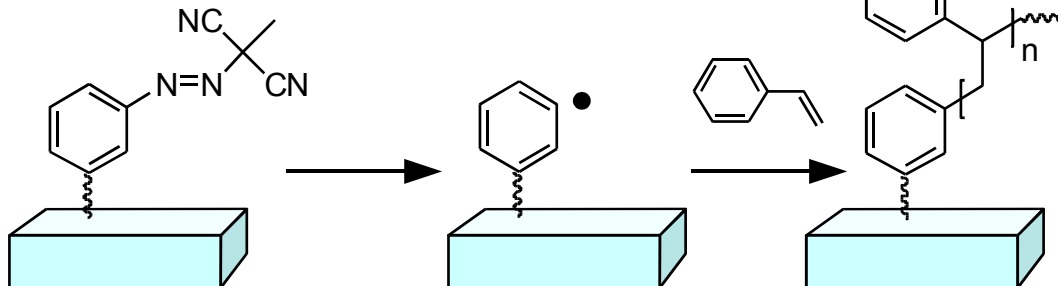
"grafting from" (also "surface graft polymerization"):
growth of the polymer chain from an initiator decorated surface

polymerization methods:

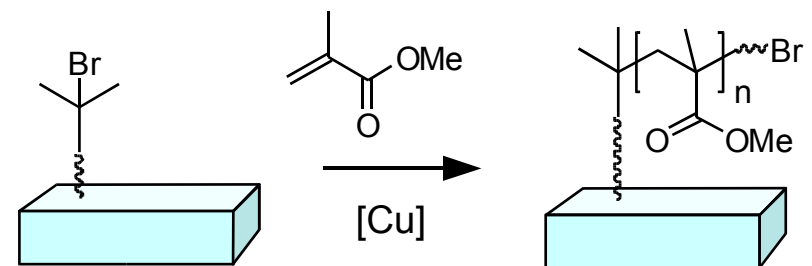
- thermally induced free radical polymerization (e.g. azo initiators, acrylic acid chains on polyethylene)
- radiation / photochemically induced free radical polymerization (e.g. benzophenone initiators, acrylamide on polypropylene)
- (pseudo)-living polymerization (like atom transfer radical polymerization - ATRP) allows also for block copolymer formation



radical surface graft polymerization



controlled radical polymerization ATRP



D5) Block Copolymer Adsorption

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

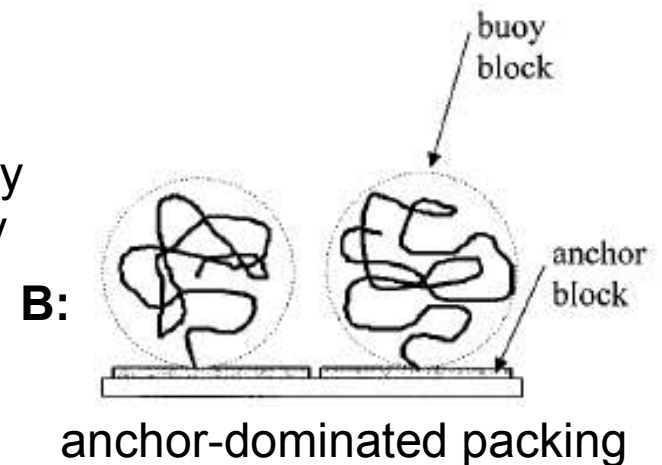
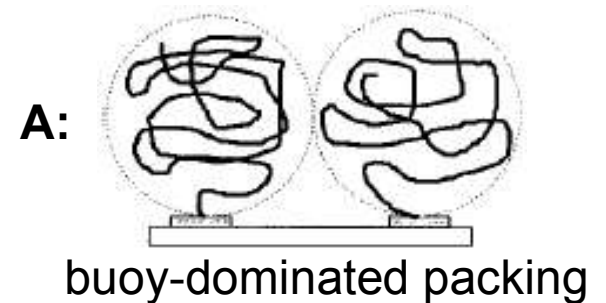
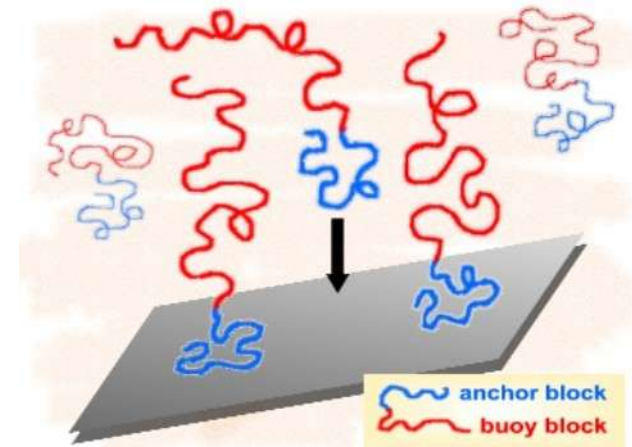
- **anchor block**: high affinity to substrate, adsorbs to surface
- **buoy block**: high affinity to solvent, expands into medium

example: poly(styrene-block-ethylenoxid) PS-*b*-PEO
or poly(styrene-block-methylmethacrylate) PS-*b*-PMMA (to suppress dewetting of PS homopolymer films at SiO₂ surfaces)

important structural parameter:

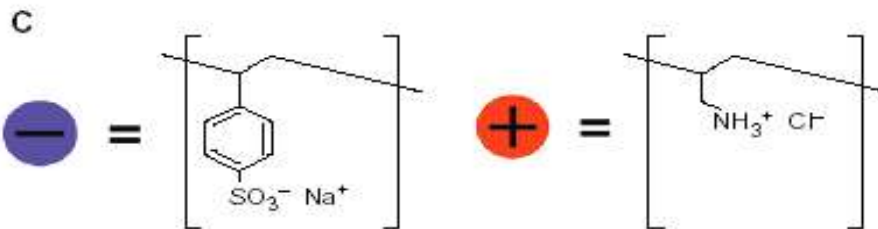
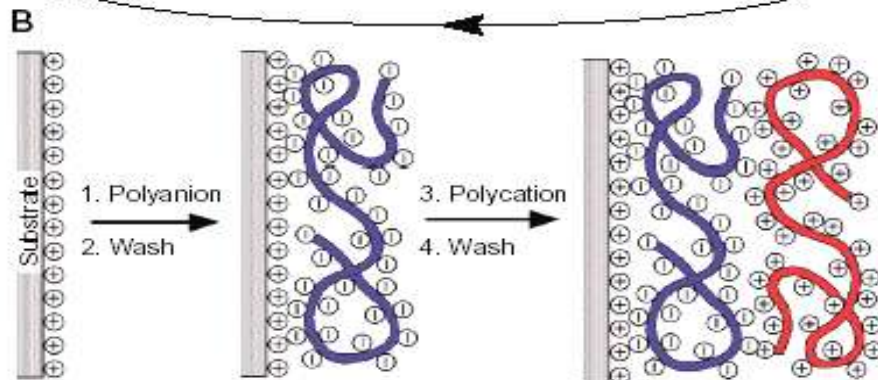
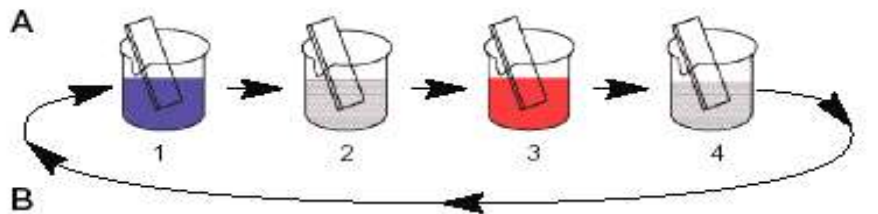
- **chemical nature** of the monomers / functional groups
(determines solubility and surface affinity)
- **relative** block lengths (ratio of buoy to anchor block)
- **overall** molecular weight (polymer conformation)

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



D6) "Layer-by-Layer" (LbL) Deposition

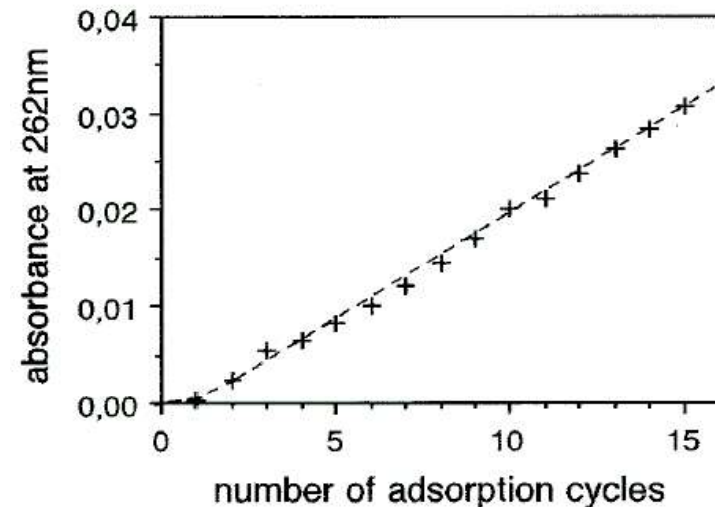
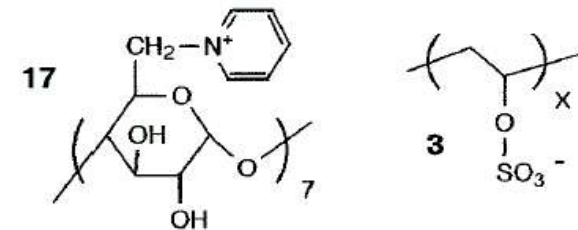
simple dipping process of (e.g. negatively) **charged substrate** / surface layers into **oppositely charged polyelectrolyte** solution (e.g. polycation) can lead to polyelectrolyte adsorption and **surface charge inversion** (now positive), by subsequent dipping into **polyelectrolyte** solution of **opposite charge** (e.g. polyanion) and repetition of process polymer multilayer films can be produced → thickness is proportional to overall dipping number



Polystyrenesulfonate sodium salt (PSS)

Polyallylamine (PAH)

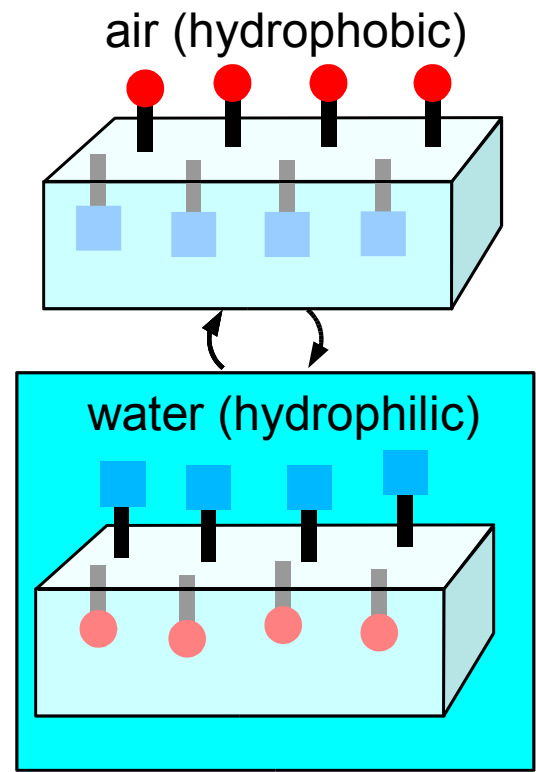
linear increase of absorbance (~ layer thickness) with number of adsorption cycles



Surface Segregation

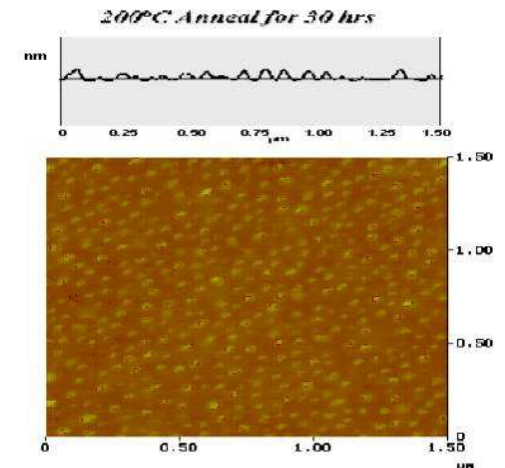
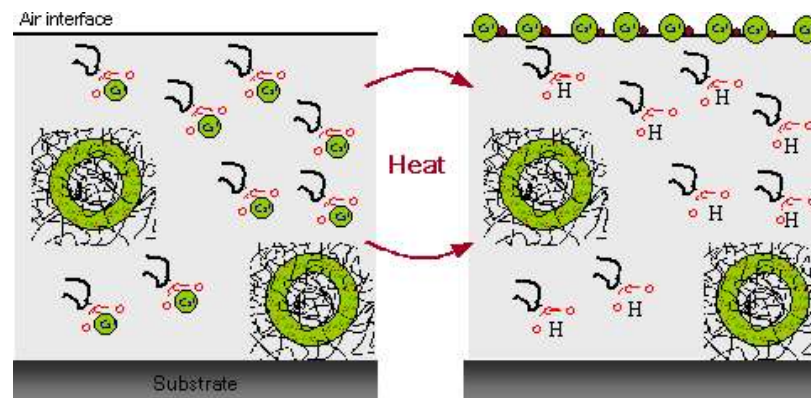
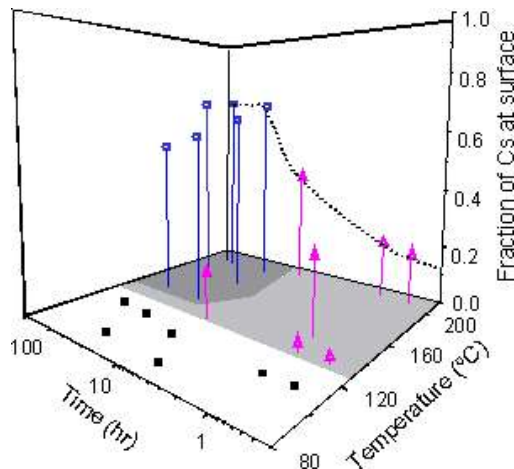
surface segregation (also "reconstruction"): at sufficient dynamics / mobility of polymer chains close to an interface

- 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. $-\text{CH}_3$) ■ hydrophilic (e.g. $-\text{OH}$)

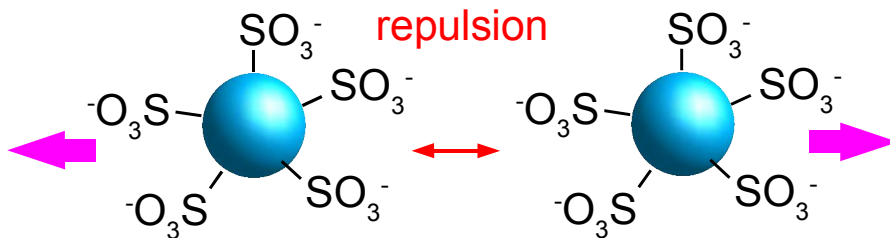
example: Cs ion segregation in poly(styrene-co-methacrylic acid) films at high temperature:



Interactions between Polymer Particles

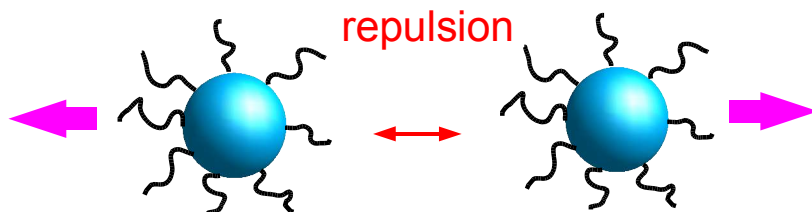
- charge stabilization:

ionic groups on particle surface repel equally charged particles → colloid stabilization by coulomb repulsion



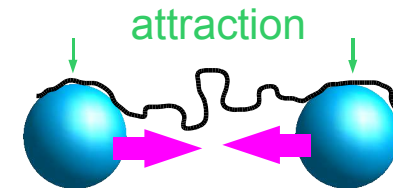
- steric stabilization:

soluble side arms, which are attached to the particle surface, repel each other by steric interaction → entropic (conformation) and osmotic stabilization



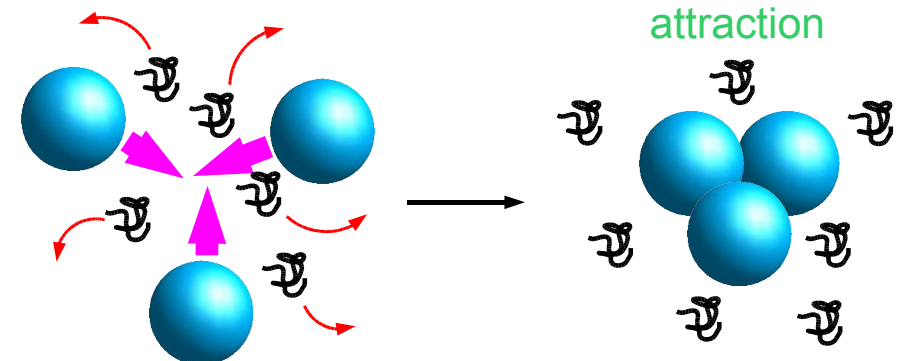
- flocculation / bridging interaction:

water-soluble polymer molecules adhere with both ends to two particles, leading to particle-particle attraction and precipitation

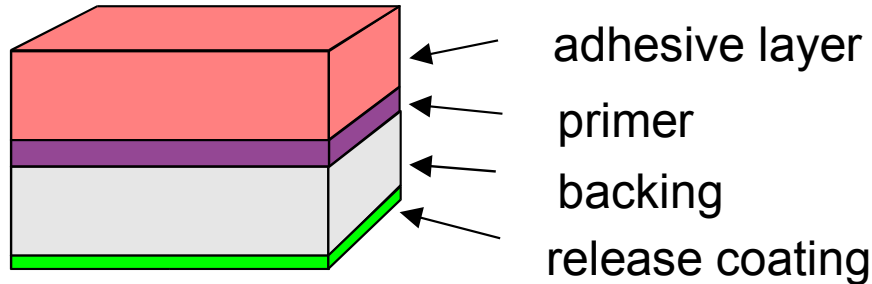


- depletion interaction:

entropy-driven attraction (or osmotic pressure, respectively) between large particles and walls *via* displacement of small particles and soluble polymer chains



Practical Example: Adhesive Tape



tack: in adhesives tack describes the property to bond at moderate applied pressure (tack involves both, 1. bonding and 2. debonding step)

adhesion layer: - base elastomer (rubber, polyacrylates, block copolymers), high M_w , low T_g (below RT)
- tackifiers (rosin, terpenes, hydrocarbon resins), low M_w (300-3000 g/mol), high T_g (> RT)

primer: increases adhesion (\rightarrow covalent bonding) of adhesive layer to backing (phenolic elastomer resins, corona-treatment, chlorinated polyolefins)

backing: supports adhesive layer, mechanical strength (paper, polypropylene)

release coating: reduces adhesion of adhesive layer and allows release of rolled up tapes etc. (silicones, alkyds, stearyl derivatives of vinyl polymers)

physical parameters determining adhesion properties:

- **tack:** immediate "bond" formation upon contact with surface
- **adhesion:** force required to remove adhesive tape / "break bond" \rightarrow depends on debonding process
- **cohesion:** internal mechanical strength that holds adhesive layer (and whole tape structure) together