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Spin coating and Langmuir film based deposition techniques

CHEM-L2000

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Learning objectives

After this lecture the student is able:

- To explain the basic theoretical aspects of spin coating, Langmuir-Blodgett and Langmuir-Schaefer deposition
- To reject a certain film deposition technique based on the knowledge of these coating tecniques
- To list which parameters affect specific properties in certain deposition techniques

Outline

(1) Spin coating: overview and theory

(2) Spin coating: pragmatic aspects

(3) Spin coating: application examples

(4) Langmuir films: overview and theory

(5) Langmuir-Blodgett deposition

(6) Langmuir-Schaefer deposition

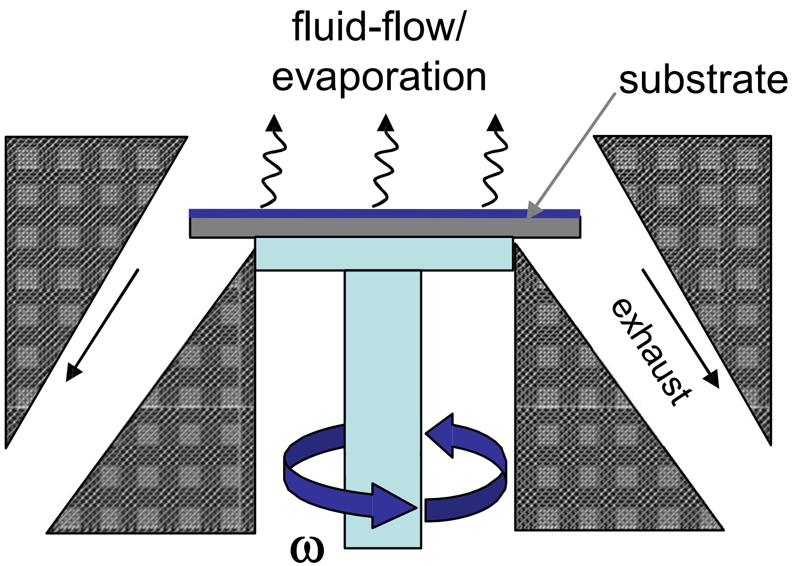
(7) Case studies in Langmuir-Schaefer deposition

Spin coating – general issues

(also known as spin casting)

Short description:
A method to prepare films from a dissolved/dispersed substance by removing the solvent with high speed spinning.

Films are usually in the ultrathin regime (< 100 nm).



Spin coating – general issues

- Used for preparation of ultrathin films with high degree of smoothness
- Widely used
- Totally reproducible
- Also capable of preparing submonolayer “open” films
- Thick films also possible, although with a larger roughness

Rule of thumb:
If you can dissolve or disperse a substance, it is possible to prepare a film from it by spin coating.

Phases of spin coating

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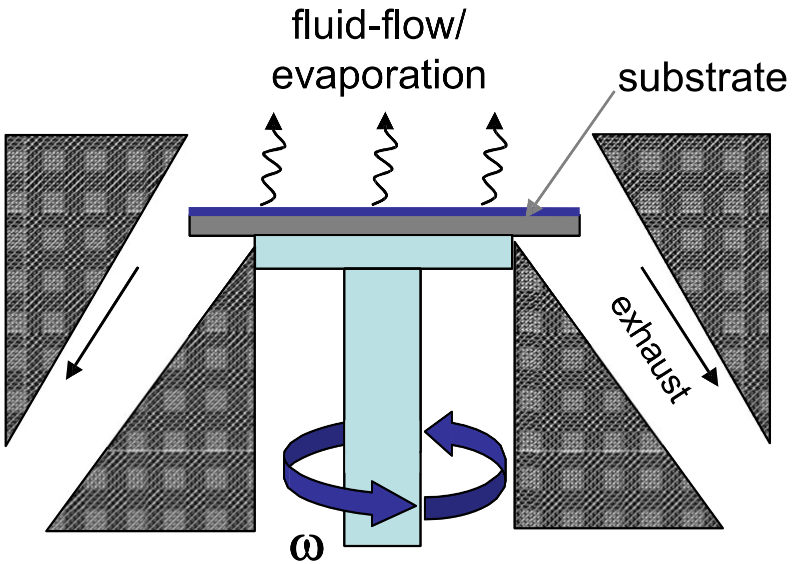
Phases of spin coating

(1) Spin-up
(2) Spin-off (fluid flow from the edges of the substrate)
(3) Evaporation

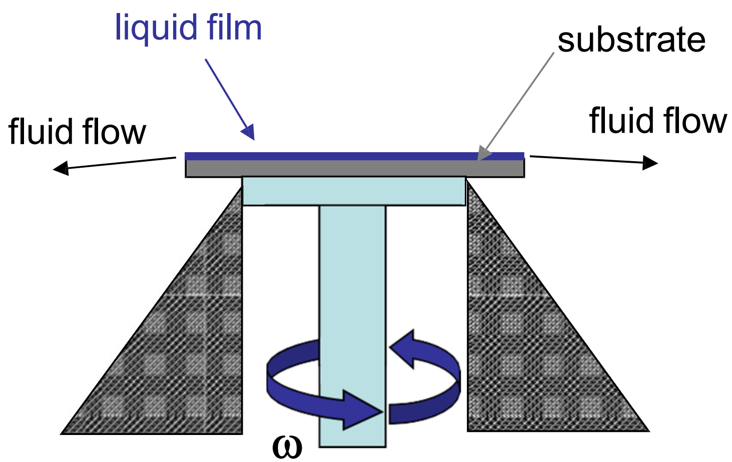


Phases of spin coating: (I) Spin-up

- The substrate is accelerated to the final rotation speed in 0.5-2 seconds
- Final rotation speeds range from 500-10000 rpm (usual 2000-5000 rpm)
- Spin-up removes most of the solution which has been initially deposited on the substrate (full initial coverage of the solution required)
- Spin-up is the reason why the solution has to wet the substrate (otherwise spin-up would remove all of the solution)

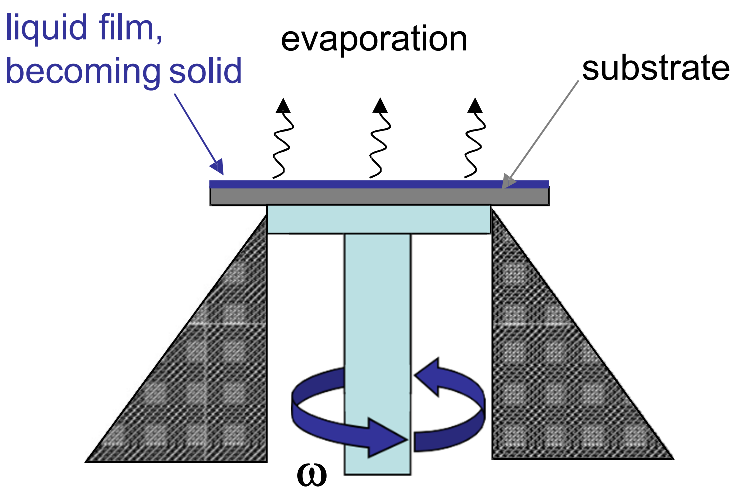
Phases of spin coating: (II) Spin-off

- Spin-up phase has left a liquid film of ~100 μm
- High-speed spinning casts solution off from the edge of the substrate
- Centrifugal rotation forces are balanced by viscous dissipation effect of the solution

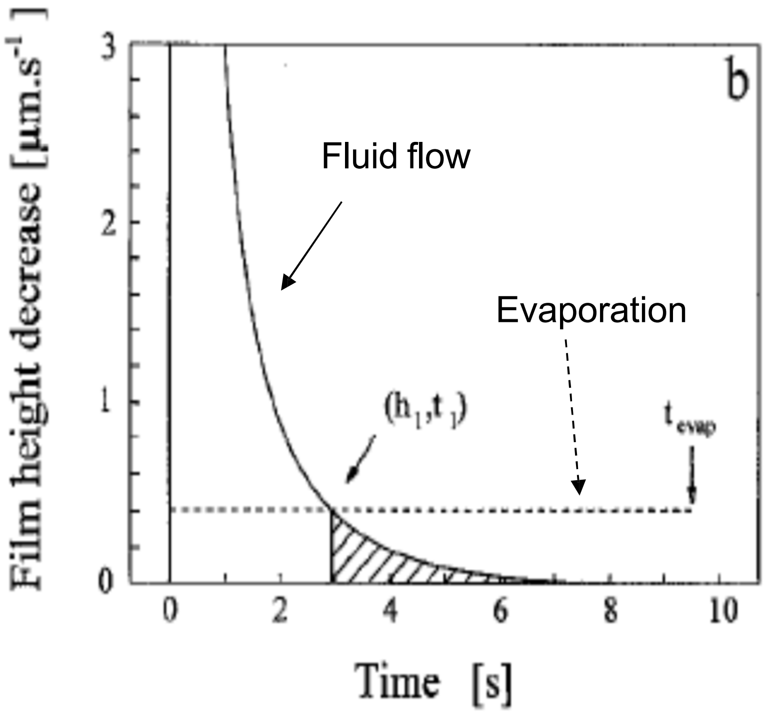


Phases of spin coating: (III) Evaporation

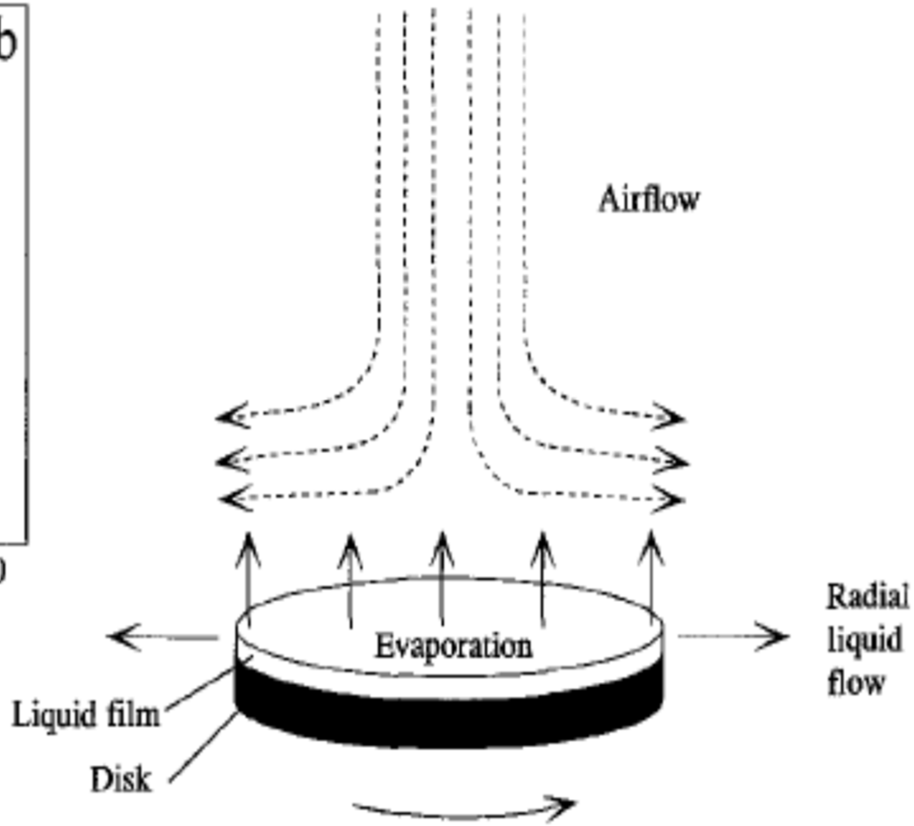
- After the solvent has been removed to a certain extent in the spin-off stage, the viscosity of the film increases
  $\rightarrow$ evaporation starts to remove only the solvent
- Transition between spin-off and evaporation is abrupt
- Evaporation phase does not determine the thickness of the final film because only solvent is removed
- Roughness/smoothness of the final film is largely dictated by evaporation



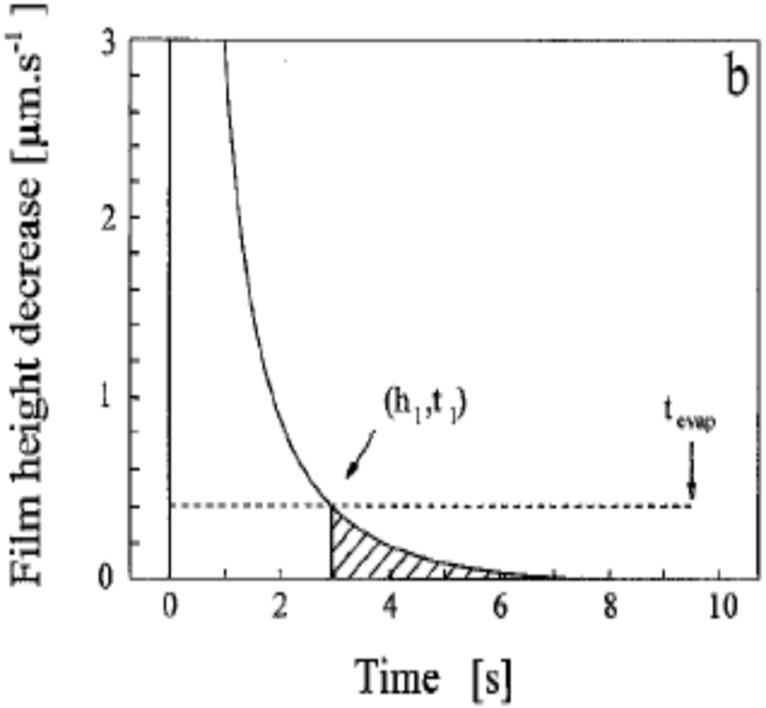
Fluid flow (spin-off) *vs.* evaporation



Individual contributions of
fluid flow and evaporation on
film thickness during spin coating.



Fluid flow (spin-off) *vs.* evaporation



Individual contributions of fluid flow and evaporation on film thickness during spin coating.

$$h_\infty \propto \omega^{-1/2}\eta^{1/3}c_0$$

h_∞ - film thickness
η - viscosity
ω - spinning speed
c_0 - solution concentration

J. Appl. Phys. **1958**, *29*, 858.
J. Appl. Phys. **1978**, *49*, 3393.
Appl. Surf. Sci. **1995**, *84*, 339.

Parameters for spin coating

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Spin coating parameters

(1) Initial concentration of the solution

(2) Molar mass (with polymers only)

(3) Choice of solvent

(4) Choice of substrate

(5) Spinning speed

Initial solution concentration

$$h_{\infty} \propto \omega^{-1/2} \eta^{1/3} c_0$$

- concentration **largely** determines the film thickness
$\rightarrow$ the larger the concentration, the thicker the film

- concentration also affects the roughness of the film
$\rightarrow$ the larger the concentration, the larger the roughness

Molar mass and concentration

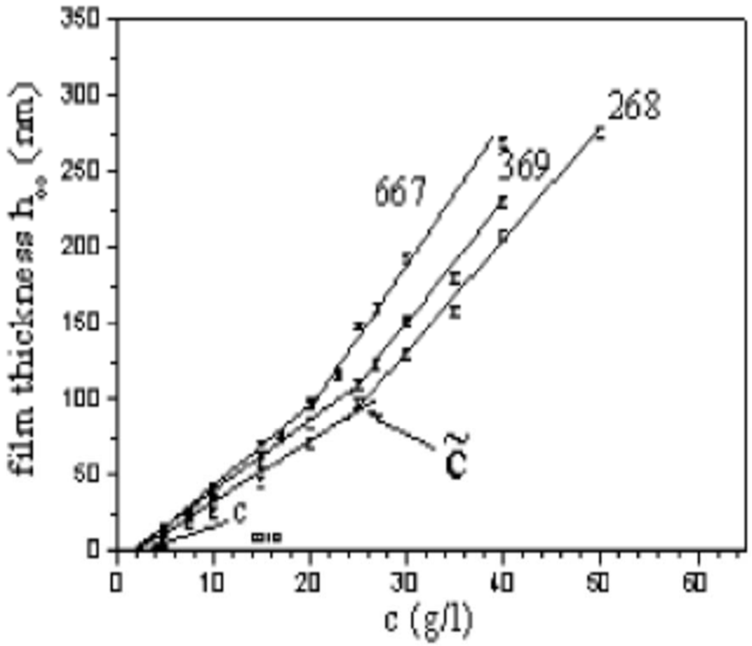


Fig. 7 Film thickness as a function of concentration and molar mass. The numbers at the curves indicate the corresponding molar mass in units of kg/mol of the respective polystyrene sample dissolved in toluene.

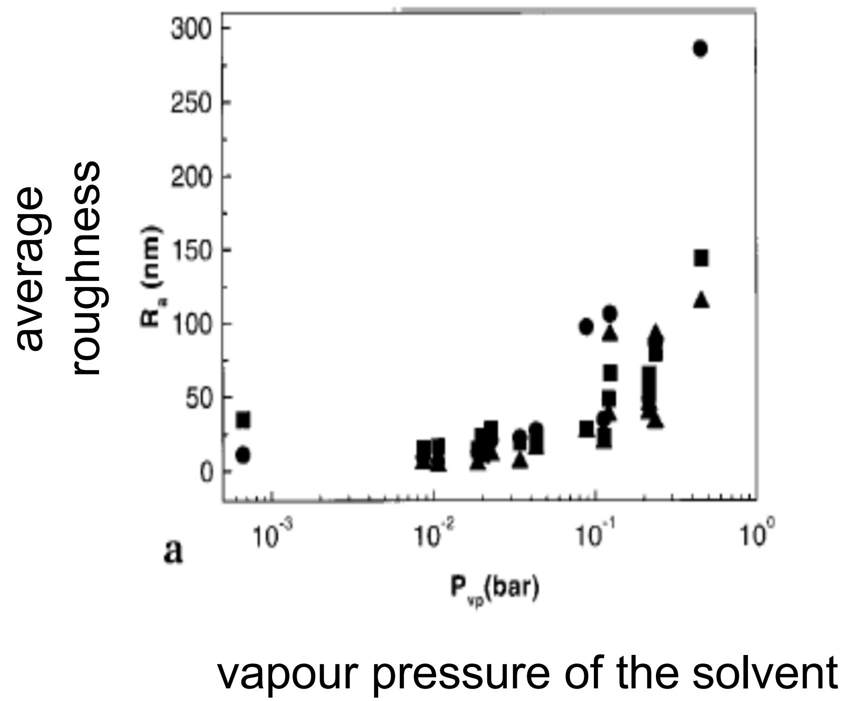
$$h_\infty \propto \omega^{-1/2} \eta^{1/3} c_0$$

The larger the molar mass, the thicker the film (chain overlap with longer chains amounts to higher thickness)

Mater. Res. Innovat. **2003**, *7*, 314.

Choice of solvent

- The more volatile the solvent, the rougher the film
- Volatile solvents induce so-called Marangoni instability



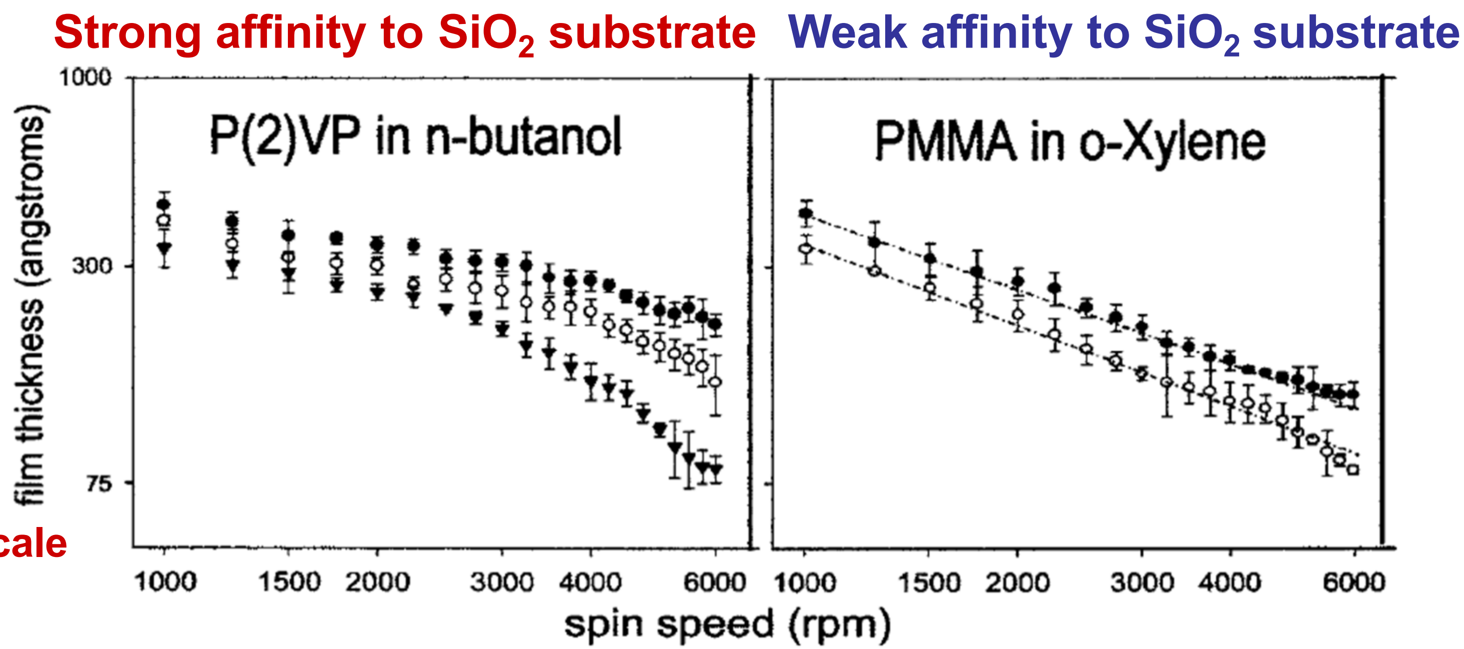
Macromolecules **2001**, *34*, 4669.

Choice of substrate

Prerequisite: solvent and substrate have to match, i.e. solvent has to wet the substrate (reasonably low contact angle).

- The affinity of the to-be-coated material towards the substrate has an effect on the film thickness
- An “anchoring polymer” is used sometimes to improve the affinity between the substrate and the coating
- Anchoring polymer does not (usually) affect the film formation as such – it anchors the coating to the surface which prevents the film’s detaching in, e.g., aqueous conditions in the post-treatment stage

Choice of substrate



Note: log-scale

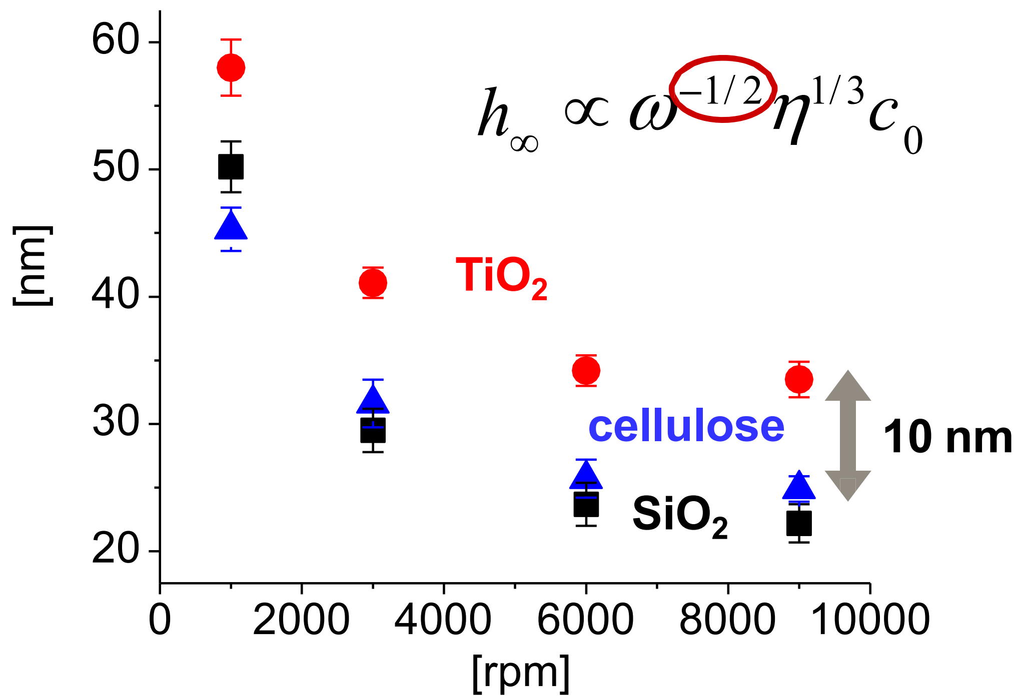
Higher affinity towards the substrate results in a flatter conformation of the polymer.

➡ **Slightly thinner film results.**

Appl. Phys. Lett. **2005**, *87*, 214103.

Choice of substrate

Film of cellulose nanocrystals (anionic) with ~7-8 nm width on different substrates.



SUBSTRATES:

TiO_2 – cationic

SiO_2 – anionic

cellulose – neutral

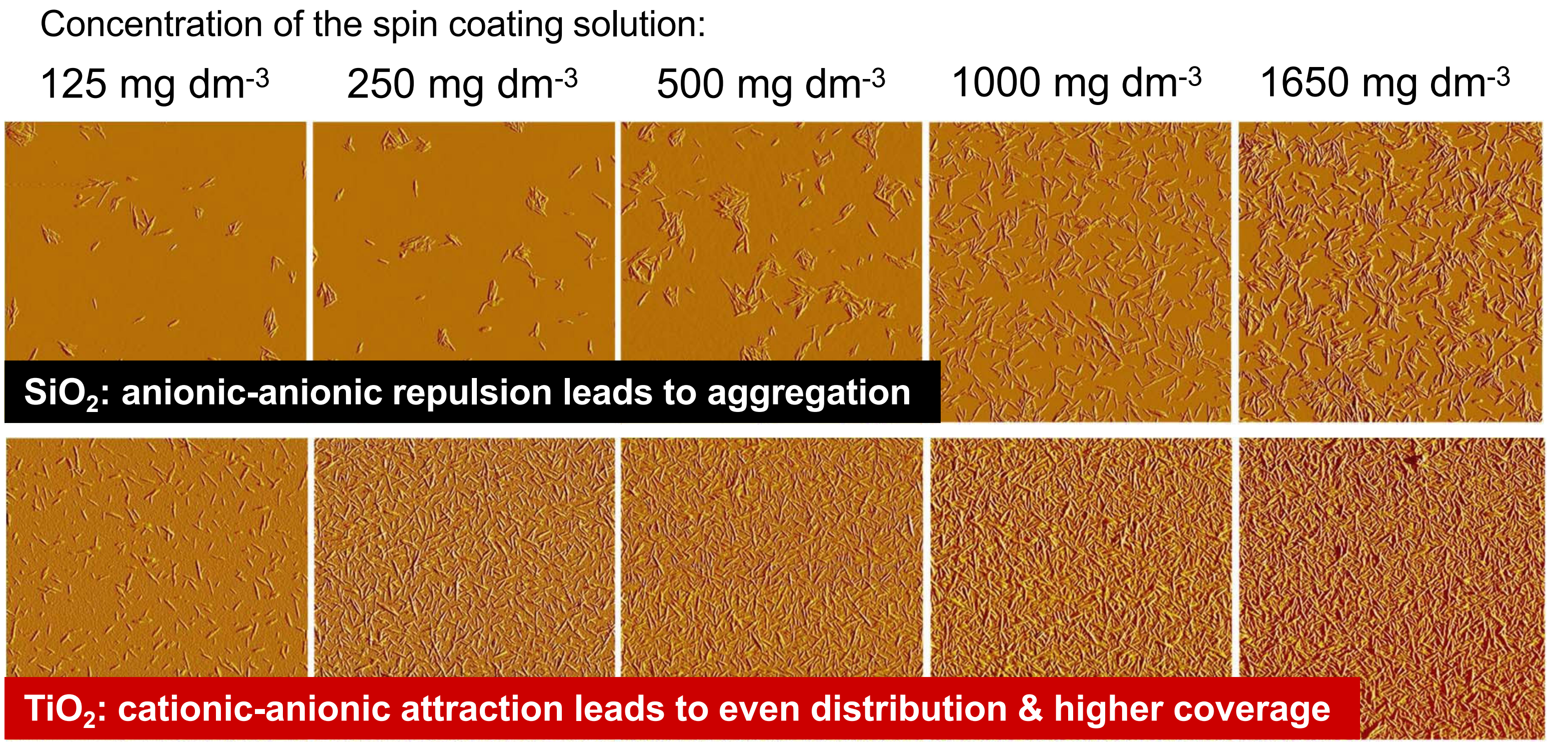
Films are apparently monolayer thicker for TiO_2 substrates.

Electrostatic effect.

Langmuir **2007**, *23*, 9674.

Choice of substrate

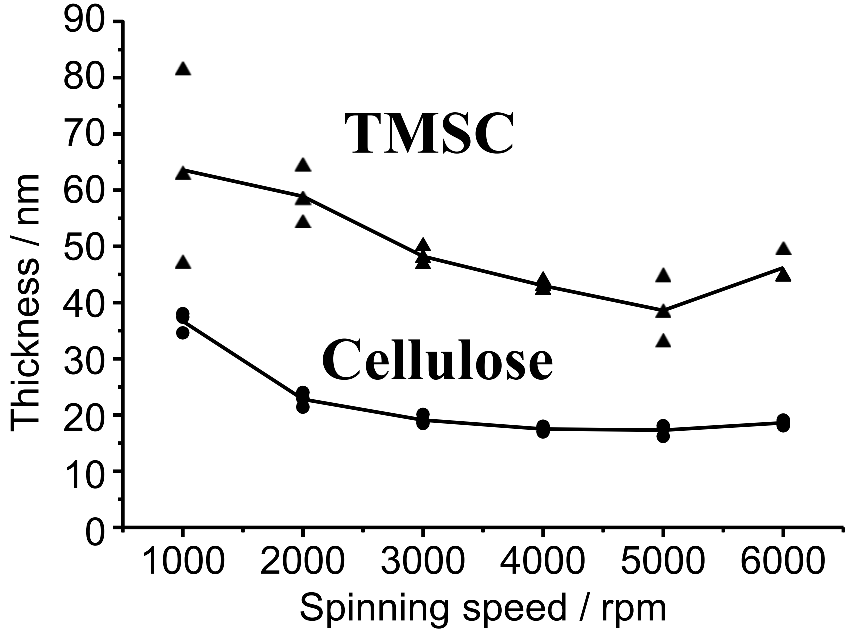
Submonolayer arrangement of cellulose nanocrystals (anionic in charge)



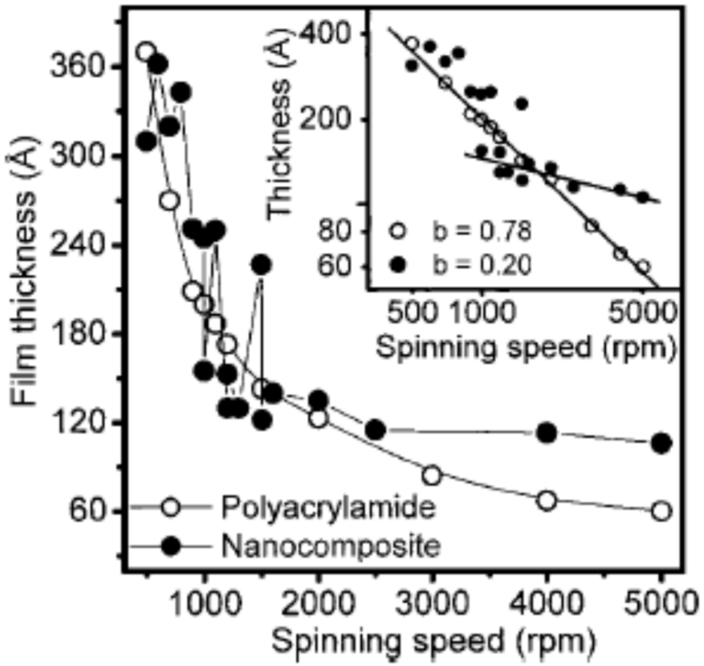
Langmuir **2007**, *23*, 9674.

Spinning speed

- The higher the rotational speed, the thinner the film
- Effect in the “usual” speed regime (2000-5000 rpm) is not remarkable
- Smoothness of the films is also affected by the spinning speed



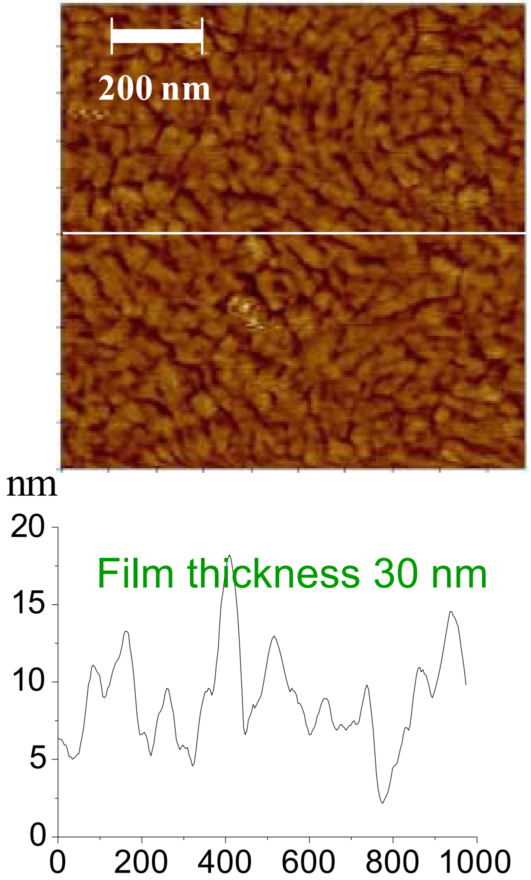
Langmuir **2003**, *19*, 5735.



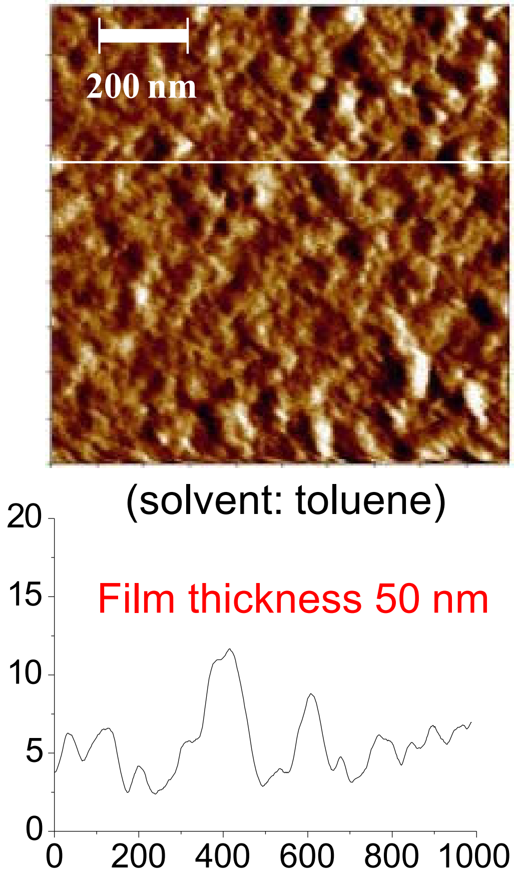
Phys. Rev. E **2004**, *70*, 051608.

Examples on the parameter effect

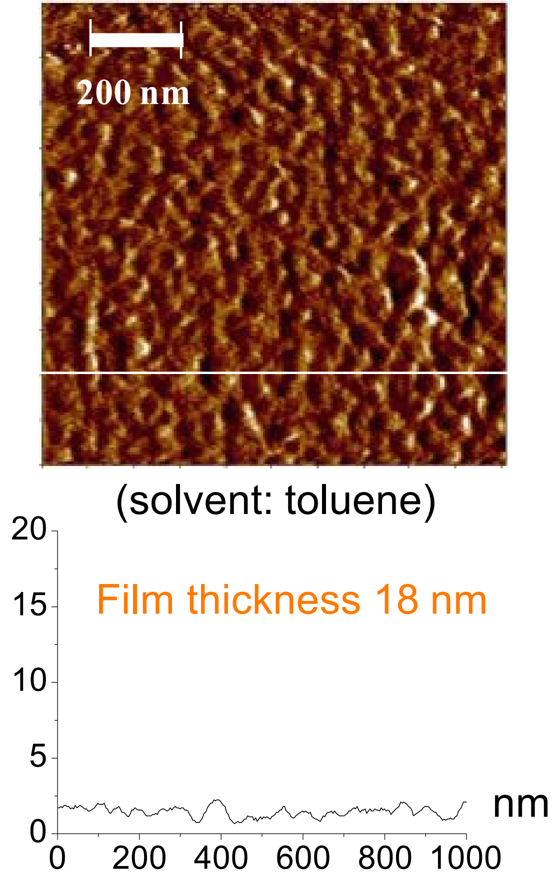
SOLVENT: CHLOROFORM



DOUBLE CONCENTRATION



REFERENCE

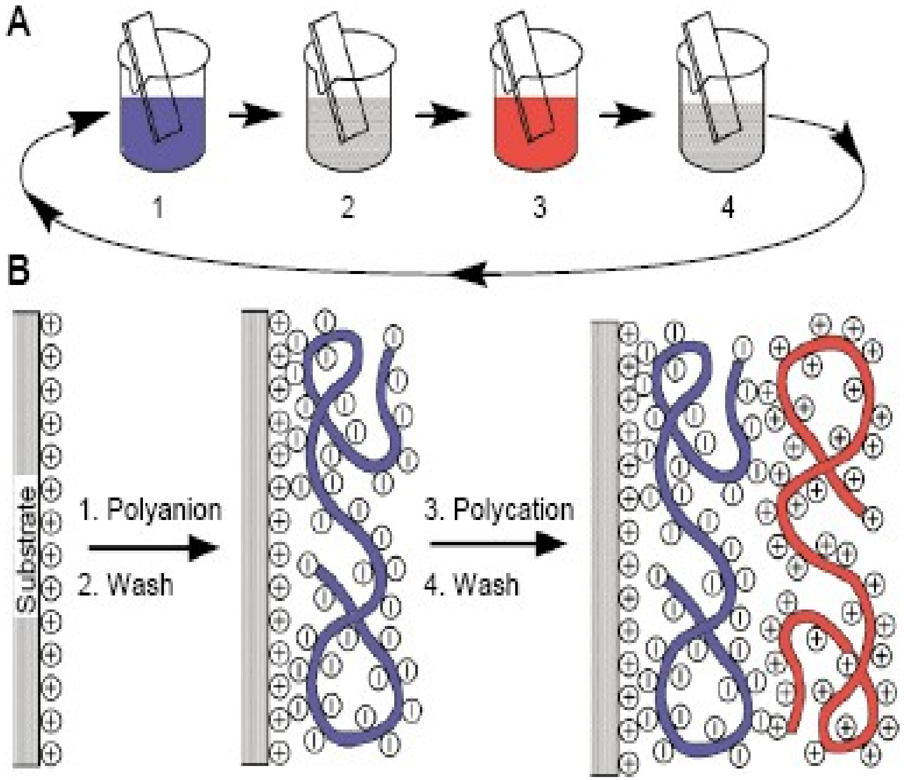


Langmuir **2003**, *19*, 5735.

Applications of spin coating – some examples

(1) Layer-by-layer deposition
(2) Patterned structures

Layer-by-layer deposition

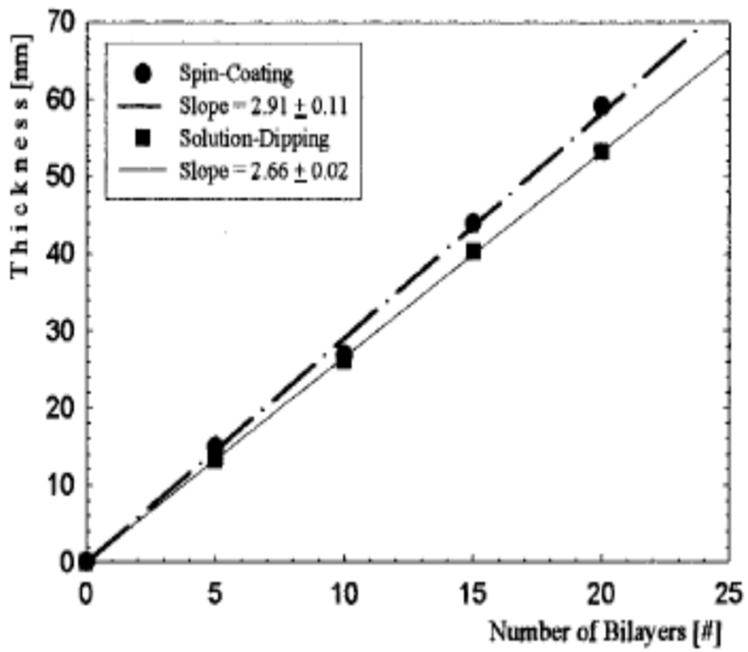


TRADITIONAL WAY BY ADSORPTION

- Polyelectrolytes of opposite charges can be deposited one after another
- Experimentally a very easy technique: requires only polyelectrolyte solutions and washing in between

Science **1997**, *227*, 1232.

Layer-by-layer deposition by spin coating



SPIN COATING OFFERS A FASTER WAY

- spin coating can be applied to LbL-deposition, making the process easier and faster
- deposition of one layer takes < 1 min

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Macromolecules **2001**, *34*, 5358.
Langmuir **2003**, *19*, 7592.

Patterned structures – why?

Use of ultrathin films:

(1) Modelling aspect
- **defined chemistry**
- **defined morphology**

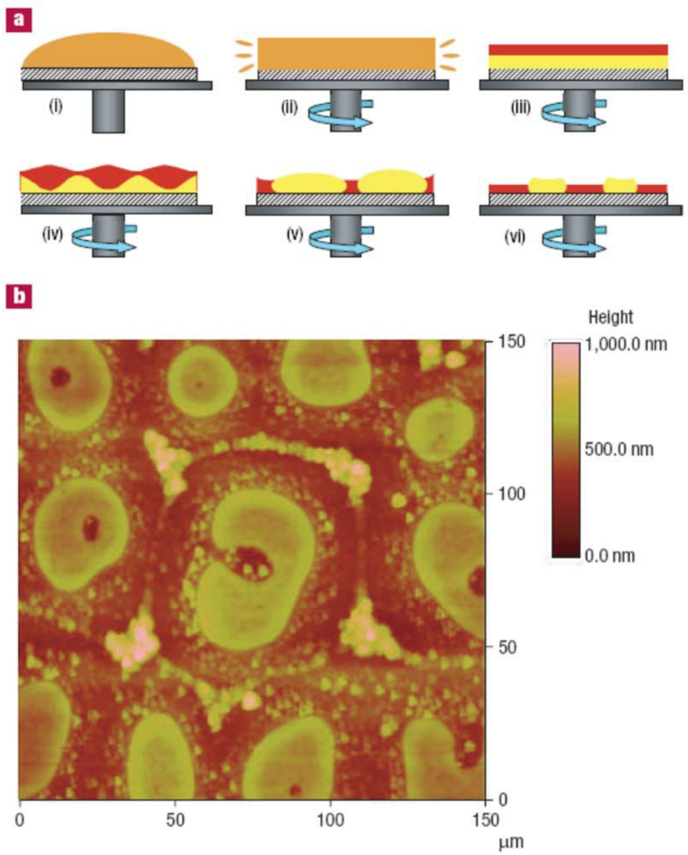
(2) Functional materials
- **sensors**
- **transistors**
- **photonic devices**
- **receptors**
- **templates for nanomaterials**

etc.

Often requires patterned structures which can be rather demanding to prepare (microcontact printing etc.).

Spin coating sometimes offers a quick-and-easy way to patterned structures on ultrathin films.

Patterning with polymer blends



Immiscible polymers phase separate during spin coating.

- vertical phase separation leads to lateral phase separation

- strong solvent and substrate dependence

Heriot and Jones
Nature Mater. **2005**, *4*, 782.

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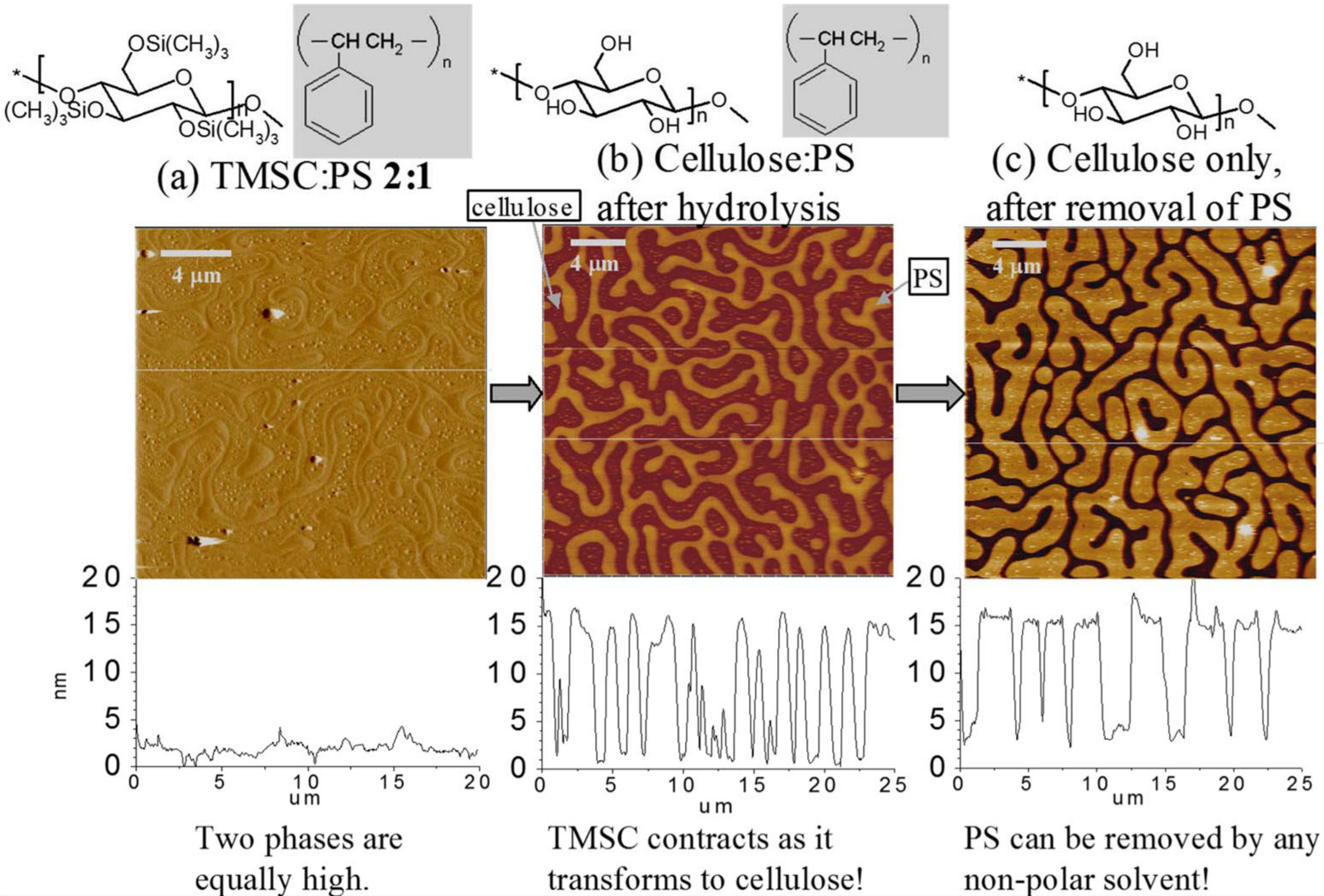
Patterning with polymer blends

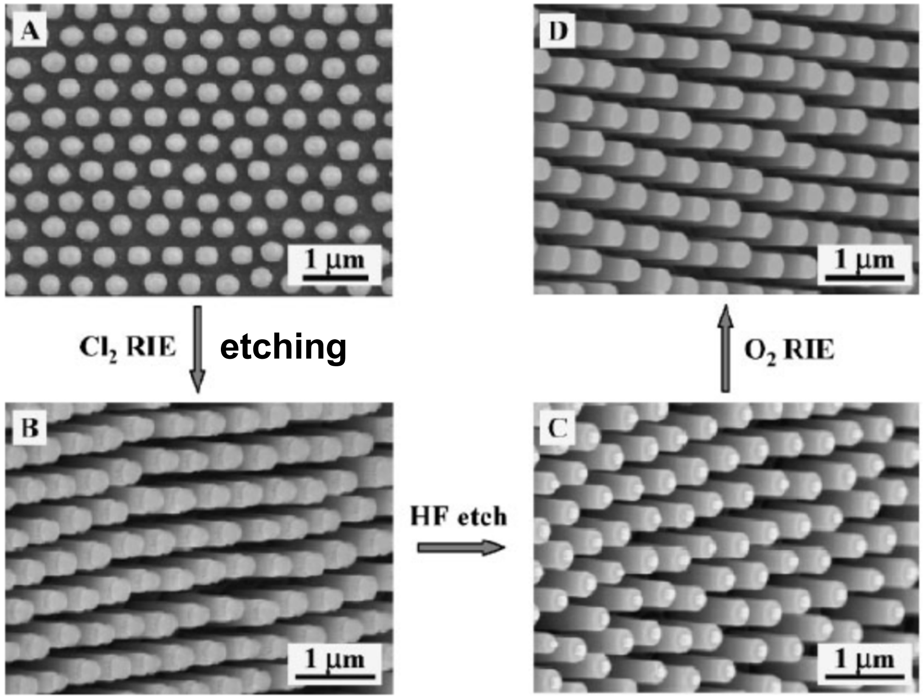


Macromolecules **2005**, *38*, 10712.

Ordered silicon pillars as antireflective, self-cleaning coatings

Deposition of hexagonally ordered silica nanoparticles on a silicon wafer by spin coating.

Silica nanoparticles protect silicon underneath them during etching.
→ Silicon pillars form.



Impurities are removed.

Silica nanoparticles are removed by HF treatment from top of the pillars.

Based on crystallization of colloidal objects during correctly chosen spin coating conditions.

Adv. Mater. **2008**, *20*, 3914.

Spin coating - summary

- spin coating is a fast method for preparing smooth ultrathin films
- consists of three phases: (i) spin-up, (ii) spin-off (fluid flow), and (iii) evaporation
- coating solution has to wet the substrate; otherwise no film occurs
- concentration of the coating solution largely determines the film thickness
- use of volatile solvents result in rougher films

Langmuir-Blodgett deposition
Langmuir-Schaefer deposition

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Basic idea

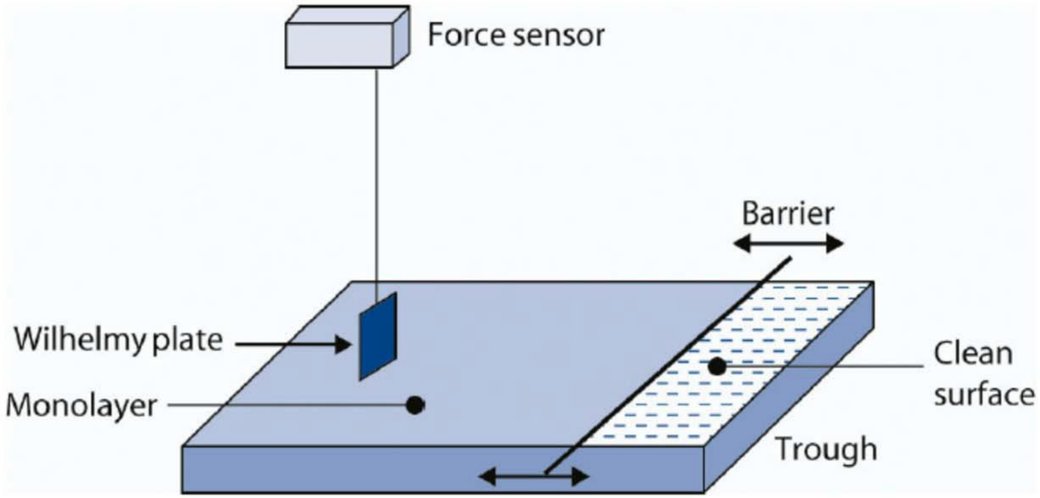
- Immiscible substance or solution is spread on the liquid surface
- The substance forms a film on the liquid surface
- The surface pressure is adjusted mechanically with barriers

- surface pressure

$$\Pi = \gamma_w - \gamma_f$$

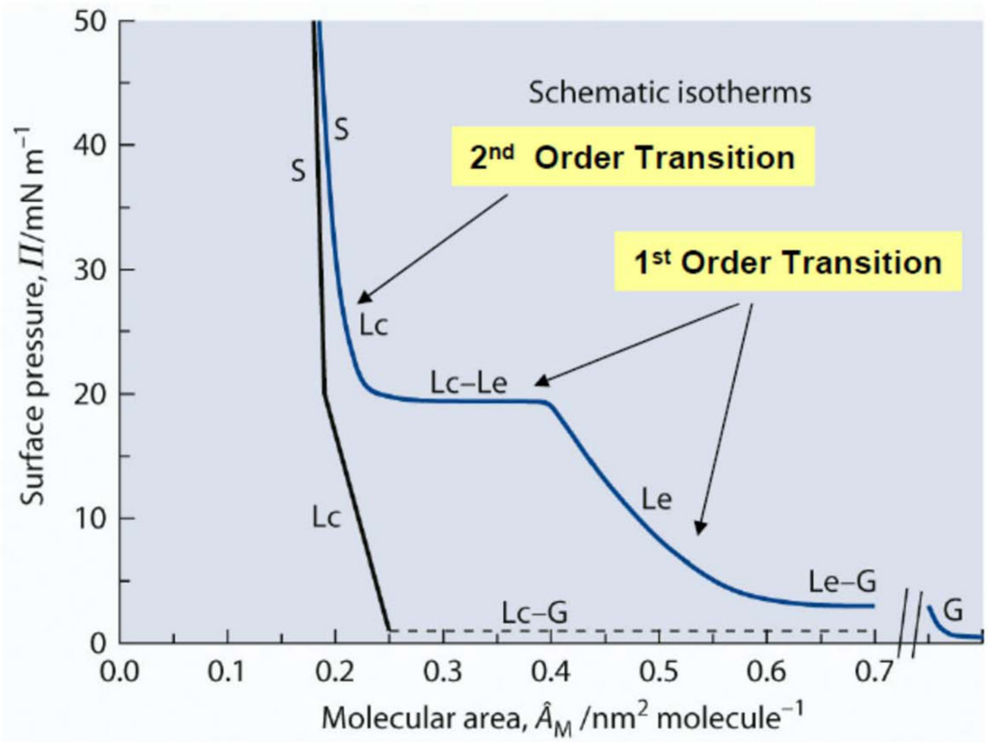
- area per molecule

$$A_M = A / N_M$$



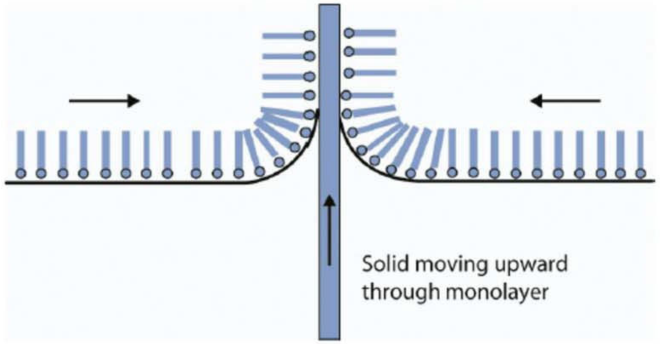
Surface film balance (Langmuir trough)

Surface pressure isotherms

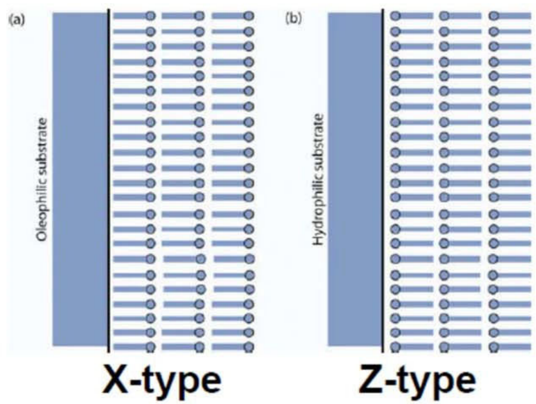


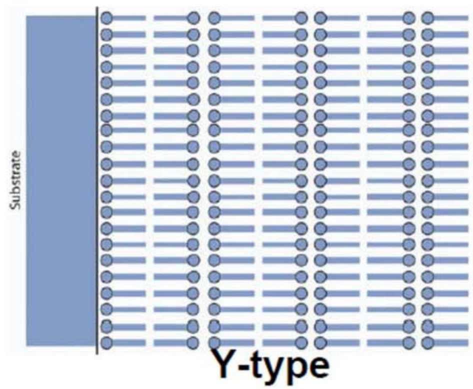
- gaseous phase (G)
- liquid expanded (L_e or L_1)
- liquid condensed (L_c or L_2)
- Solid phase (S)

Langmuir-Blodgett deposition



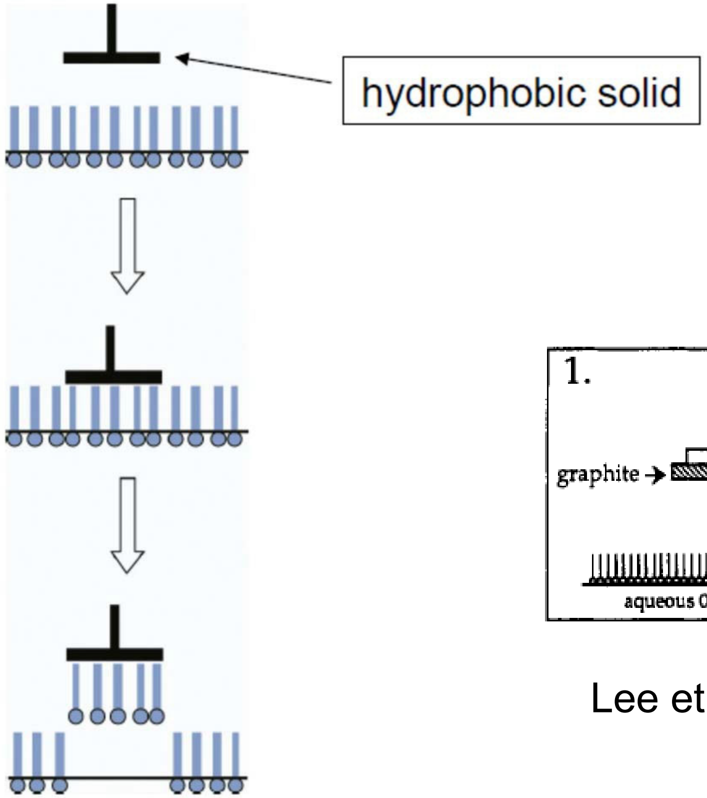
- efficiency of deposition - transfer ratio – ratio of area transferred to the solid to area decrease in the monolayer
- usual substrates (depends on application): mica, silicon, quartz etc.
- film quality depends on pH, ionic strength in subphase



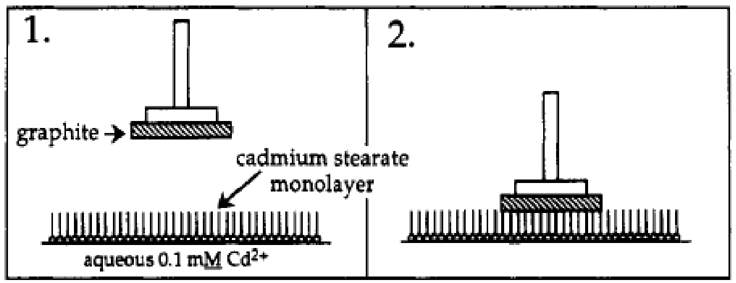


Film thickness is determined by the number of dipping steps.

Langmuir-Schaefer deposition

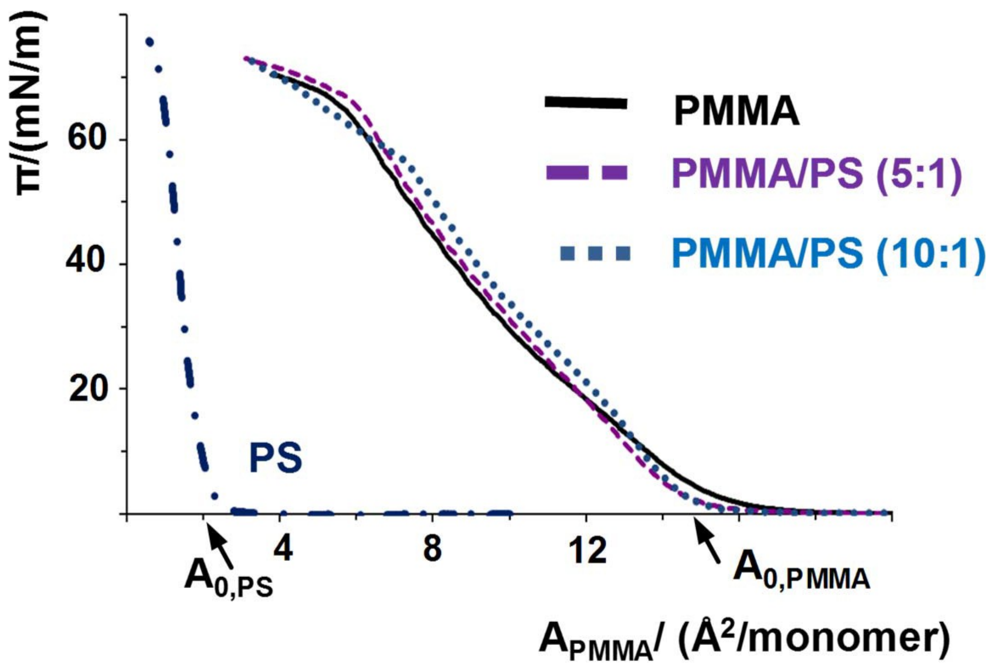


- Horizontal deposition
- Works particularly well for hydrophobic substrates

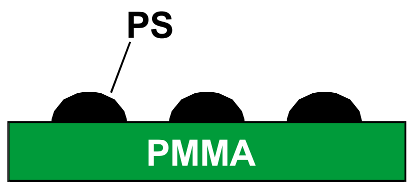


Lee et al. *Langmuir* **1992**, *8*, 1243.

Langmuir-Schaefer deposition: blends



NOTE. The surface pressure isotherms have been plotted as a function of a mean molecular area taken by a PMMA monomer.

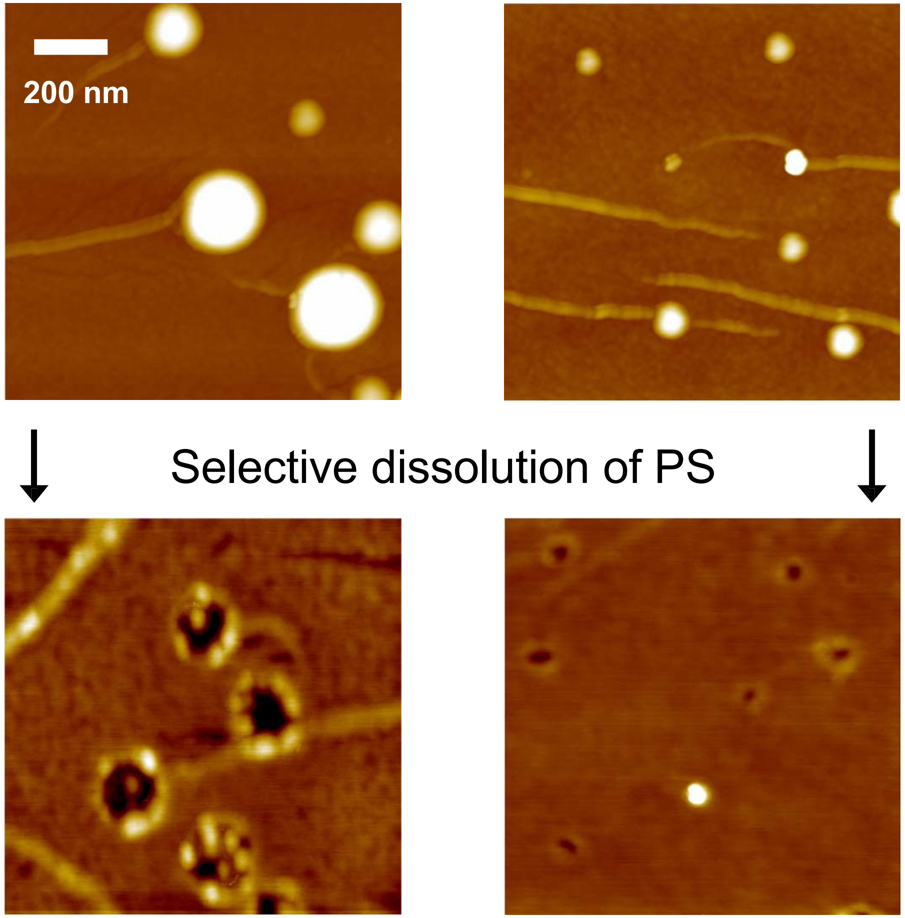


⇒ **On a Langmuir film (on water), PMMA appears to form a continuous film with polystyrene on top of it.**

Langmuir-Schaefer deposition: blends

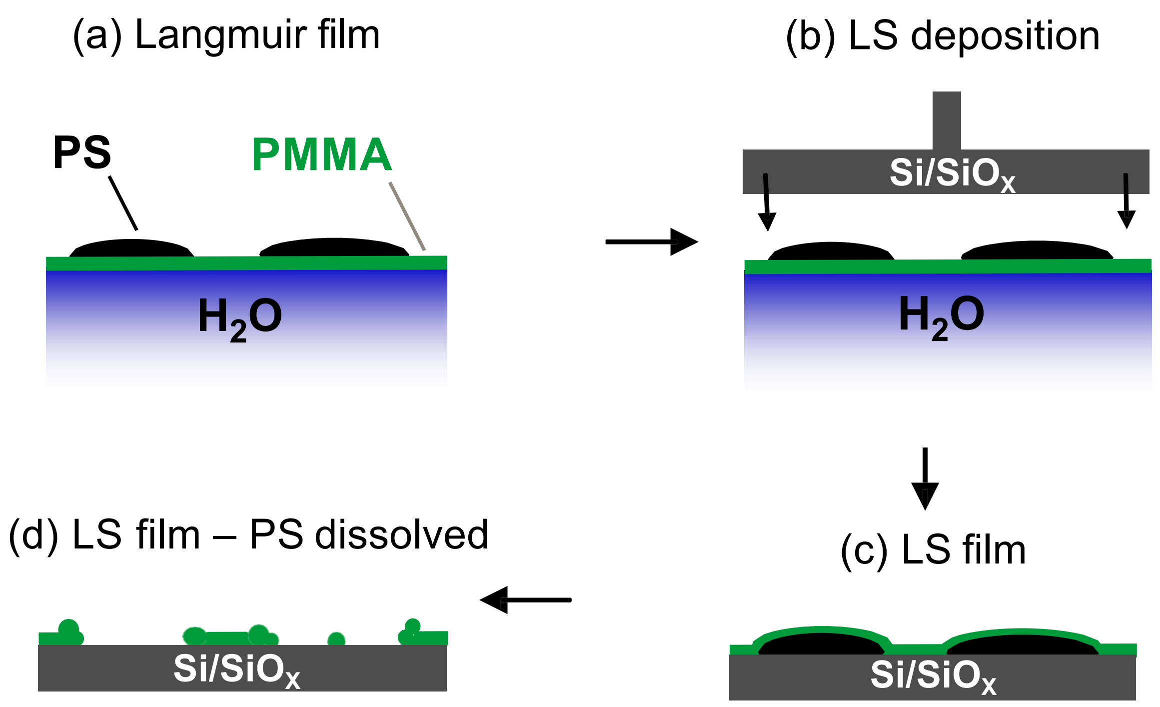
PMMA/PS 5:1 PMMA/PS 10:1

One LS deposition step



PS can be selectively dissolved with cyclohexane which leaves PMMA intact.

Langmuir-Schaefer deposition: blends



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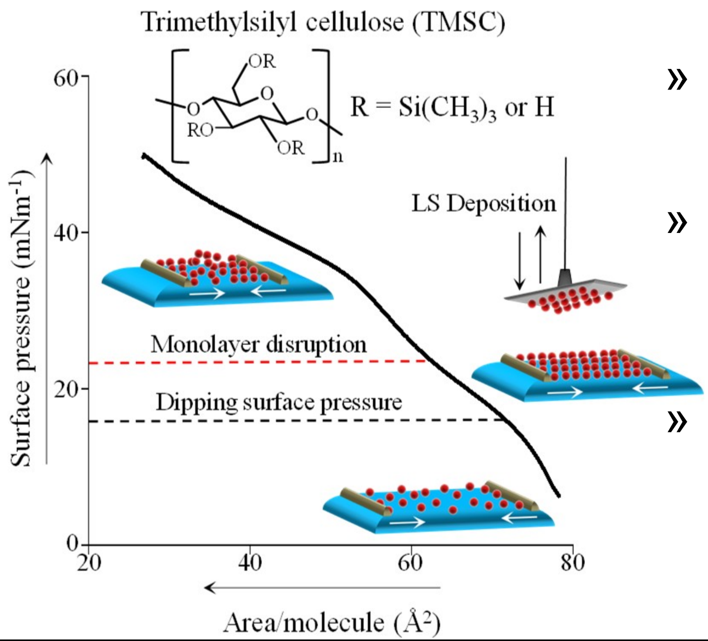
Soft Matter **2011**, *7*, 743.

Langmuir-Schaefer deposition: substrate effect

Background



- 2D patterns becoming more frequent in, e.g., electronic applications or smart materials
- Cellulose can be used to form 2D morphological patterns
- Langmuir-Schaefer deposition used to demonstrate 2D fractal patterns using amphiphilic polysaccharide (trimethylsilyl cellulose)
- Role of supramolecular interplay highlighted using various substrates

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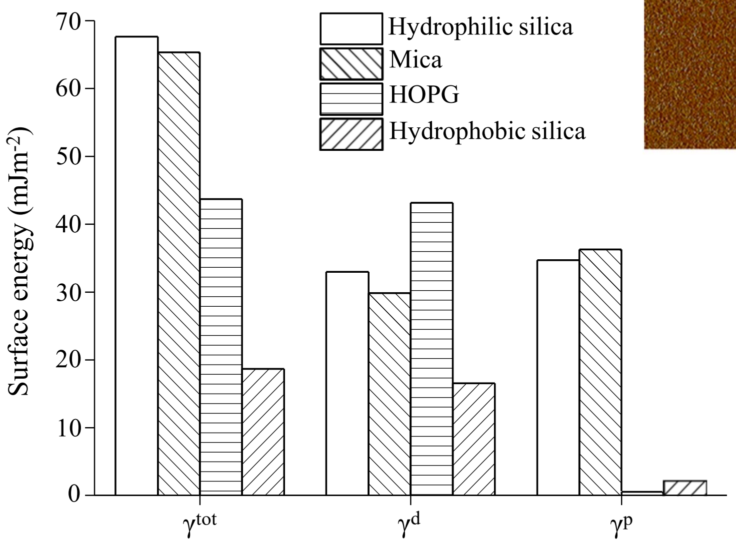
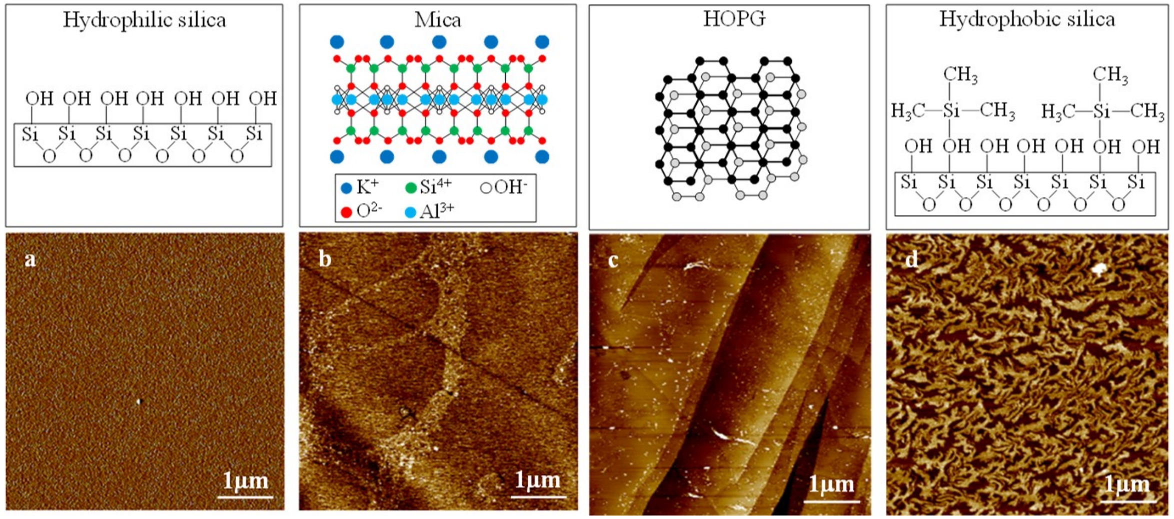
Langmuir-Schaefer deposition: substrate effect

» Morphology of TMSC film can be controlled through supramolecular interactions between polymer and substrate





» Decrease in total surface free energy shows a shift in film morphology

» Surface free energy provides indication of supramolecular properties of the substrate surface

Soft Matter **2014**, *10*, 1801.

Langmuir film based deposition

- Pure liquid or a solution is spread on a liquid (usually water) surface in a Langmuir trough
- In case of solution, the solvent is allowed to evaporate → Langmuir film
- Surface pressure (film packing) is adjusted with mechanical barriers
- Deposition on a solid substrate by dipping:
    - Vertically in Langmuir-Blodgett deposition
    - Horizontally in Langmuir-Schaefer deposition

Summary LB and LS deposition

- LB and LS depositions allow highly controlled film growth

- Surface area / pressure isotherms yield additional information on the system

General requirements:

- Coated substance must be soluble/dispersible
- Solvent used for dissolving the coated substance must not be miscible with the lower phase solvent in the Langmuir trough (usually water)
- Coated substance should not be miscible with the lower phase