Nanotubes by Wetting of Porous Templates

VW-Project: “Functional polymer nanotubes by wetting of ordered templates”

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Aim:

• Control of nanotube formation

Investigations:

• Wall morphology
  - Comparison melt / solvent wetting
  - Influence of solvent quality

• Chain conformation
  - SANS measurements to determine the radius of gyration

• Interactions of nanotubes
  - Introduction of repulsive forces through Layer-by-Layer self-assembly
Wetting Process

a → b → c → d

Polymers       Oligomers       Small Molecules
Choice of Highly Ordered Templates

Al, Si

regular arrangement

high aspect ratio: 10 000
Available Templates

![Graph showing pore diameter vs. lattice constant for porous alumina and macroporous silicon.](image)

- Pore diameter $d$ (nm)
- Lattice constant $a$ (nm)

Key:
- Porous alumina
- Macroporous silicon
Resulting Polymer Nanotubes

Polystyrene

Polyetheretherketone
Investigation

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Melt / Solvent Wetting

Planar substrates

- Number of adsorbed molecules per unit area large
- Number of contact points molecules/substrate small
- Number of adsorbed molecules per unit area small
- Number of contact points large
- Spatial overlap of molecules weak

Comparison

**melt-wetting**

2h, 250°C, argon atmosphere  
\(d_{\text{wall}} > 150\text{nm}\)

**solvent-wetting**

10-wt% in toluene  
\(d_{\text{wall}} < 100\text{nm}\)  
\(d = 3.2\ \mu\text{m}\)  
\(M_w = 96.000 \text{ g/mol}\)

M. Milbrandt, P. Miclea, R. Wehrspohn, Universität Paderborn
Surface Structure – Melt Wetting

- intact surface structure
- roughness determined by smoothness of template

$M_w = 96.000 \text{ g/mol}$

M. Milbrandt, P. Miclea, R. Wehrspohn, Universität Paderborn
Surface Structure – Solvent Wetting

- formation of „holes“ ($d_{\text{hole}} \sim 250\text{nm}$)
- size distribution depends on PS concentration
- formation of particles ($d_{\text{particle}} \sim 250\text{nm}$)

$M_w = 96.000 \text{ g/mol}$

M. Milbrandt, P. Miclea, R. Wehrspohn, Universität Paderborn
Quality of Solvent

Assumption:
Structure of wall material depends on quality of solvent

Investigation:
Wetting with polystyrene in good, poor and theta solvents
## Solvents for Polystyrene

<table>
<thead>
<tr>
<th>Good solvent</th>
<th>Theta solvent</th>
<th>Bad solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane &gt;35 °C</td>
<td>Cyclohexane 34,5 °C</td>
<td>Cyclohexane &lt;29 °C</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Cyclopentane 20 °C</td>
<td>Methanol</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
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</tbody>
</table>

10 % PS in Cyclohexane

28 °C

35 °C

42 °C

d = 400 nm; M_w = 75.000 g/mol
10 % PS in Cyclohexane

28 °C

35 °C

42 °C

\[ M_w = 75.000 \text{ g/mol} \]
Results Solvent Wetting:

- Influence on wall stability/thickness through solvent quality:
  - Good solvent conditions: only small holes
  - Theta solvent conditions: partly instable tube walls
  - Bad solvent conditions: instable tube walls
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Melt Wetting - Planar Substrate

Wetting process

precursor film

G. de Gennes; *Rev. Mod. Phys* 57, 827 (1985)

Final configuration

Melt Wetting

Verification of theory:

• radius of gyration is accessible via neutron scattering

Investigation:

• Wetting of ordered templates (35 nm, 180 nm, 400 nm) with PS-standards of different molecular weights and SANS measurements
Chain Conformation in Nanotubes

Neutron scattering on nanotubes

$M_w = 90.000 \text{ g/mol}$

$\phi = 180 \text{ nm}$

Measured at PAXY spectrometer with L. Noirez, LLB-CNRS, Saclay
Chain Conformation in Nanotubes

Neutron scattering on nanotubes

$M_w = 90,000 \text{ g/mol}$

$\varnothing = 180 \text{ nm}$

in Alumina

Measured at PAXY spectrometer with L. Noirez, LLB-CNRS, Saclay
Preliminary Results Neutron Scattering on Nanotubes:

- **Nanotubes without template**
  - Strong reflection caused by PS/air interface

- **Nanotubes within alumina template**
  - Alumina does not disturb SANS-measurements
Investigation

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Langmuir–Blodgett Assembly of Polymer Nanotubes

Aggregation after Template Removal

→ Introduction of repulsive forces

$M_w = 75,000$ g/mol
Layer-by-Layer Self-Assembly

PAA (Poly(acrylic acid)) in 0.5 M NaCl

PAH-FITC (Poly(allylamine hydrochloride) labelled with fluorescein isothiocyanate) in Milliq water
LbL Self-Assembly on Template

2 bilayers
4 bilayers
8 bilayers

PAA in 0.5 M NaCl; PAH-FITC in MilliQ water
Fluorescence Measurements

2 bilayers
4 bilayers
8 bilayers
PAA in 0.5 M NaCl; PAH-FITC in Milliq water
Conclusions

• LbL assembly with PAA and PAH on empty templates results in charged nanotubes

• Intensity increases linear with the number of bilayers

→ More layers to increase stability

→ Langmuir-Blodgett assembly of the resulting tubes
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