Research Topic:
Toward nanoporous composite membranes with tailored block copolymers as selective layer
By
Marcel Gawenda
Outline of the presentation:

1. Motivation of the project
2. Concept of the project and basics
3. Characterization of the membrane
4. Preparation and Characterization of thin polymer films
5. Preparation of the composite membrane
6. Outlook
7. Acknowledgements
1. Motivation

- synthetic membranes featuring transport selectivity for molecules different from water
- nature: highly specific transport through biological membranes, based on molecular recognition processes within macromolecular assemblies

**AIM:** Development and characterization of novel synthetic membranes with pore diameters of 2 to 20 nm
exploiting the self-assembly properties of binary or ternary block copolymers to adjust the morphology of the phase-segregated microdomains

Special Aim

permeability can be reversibly switched by external stimuli such as change of temperature (PNIPAM) or pH (P2VP)
2. Concept

Campus Essen

Characterization of support membranes (Gawenda/Ulbricht)

Preparation and characterisation of composite membranes

Campus - Bayreuth

Synthesis of a suitable AB diblock and ABC triblock copos (Schacher/Müller)

Thin block copo films phase diagrams orientation in thin films (Sperschneider/Krausch)

special characterisation by single molecule spectroscopy (to be announced/Köhler)
Sara, M. and Sleytr, U.B. in 1987:
Proteins of cell walls from bacteria - S-layer ultrafiltration membranes (Bacillus stearothermophilus)

Channels of 3 to 6 nm diameter
deposition on commercially available microfiltration membranes

Sara, M. and Sleytr, U.B. in 1987
Rejection Curve of S-Layer Ultrafiltration Membranes made of S-Layer Material from Bacillus Stearothermophilus

Very steep rejection curve

Sara, M.
and Sleytr, U.B.
in 1987
The characteristics of the thin film:

- Cylindrical microdomains perpendicular with respect to the plane of the film
- Selective removal of the minority component yields a nanoporous membrane
- Switching the size of the residual minority component selectively allows to control the diameter of the pores
- Using ABC triblock-copolymers allows the preparation of core/shell cylinder structures
Procedure to create a composite membrane

1. Preparation of oriented block copolymer film on a wafer by spin-coating methods
2. Separation of the film from the wafer (e.g.: salt wafer – separation with water)
3. Deposition of the film on the support membrane
4. Fixing the film on the support
5. Analysing the composite structure via gas permeation

Porous composite membrane

removal of the „pore template“ component / phase
Procedure to create a composite membrane

1. Preparation of oriented block copolymer film directly on the support membrane

2. Analysing the composite structure via gas permeation

3. Removal of the "pore template" component/phase
Campus Essen:

1. Characterisation of support membranes
SEM of oxyphen PET track-etched membrane with 30 nm nominal pore diameter
The diffusion measurement
Lable dye fluorescein isothiocyanat for dextran diffusion (FITC)
\[ J = -D \cdot \frac{\Delta c}{d} \quad \text{(1. fick law)} \]

\[ D = -J \cdot \frac{\Delta t}{d} \]

\[ J = \frac{\Delta n}{\Delta t \cdot A_{\text{eff}}} \]

\[ A_{\text{eff}} = A \cdot \varepsilon \]

\[ D_{\text{eff}} = -\frac{\Delta n \cdot d}{\Delta t \cdot \Delta c \cdot A \cdot \varepsilon} \]

\[ D_{\text{eff}} = \text{effective diffusion coefficient} \left[ \frac{m^2}{s} \right] \]

\[ \Delta n = n_{\text{in (feed)}} - n_{\text{in (feed)}} = n_{\text{in (perm)}} - n_{\text{in (perm)}} [\text{mol}] \]

\[ d = \text{thickness of the membrane} [\text{m}] \]

\[ \Delta t = t_{\text{n+1}} - t_{\text{n}} [\text{s}] \]

\[ \Delta c = c_{\text{feed, in}} - c_{\text{perm, in}} \left[ \frac{\text{mol}}{L} \right] \]

\[ A = \text{membrane area} [m^2] \]

\[ \varepsilon = \text{porosity index} [:] \]
results of the diffusion measurement (FITC labeled dextrane 4 kDa)

Test solution: FITC labeled dextran mixture (5 kDa),
Concentration: 25 μmol/L

Used Membrane: RoTrac ® capillary pore membranes,
PET, Porediameter 0.03 μm by Oxiphen GmbH
results of the diffusion measurement (FITC labeled dextrane 4 kDa)
results of the diffusion measurement (FITC labeled dextrane 4 kDa)
Diffusion measurement with dextran mixture
Results of the Diffusion coefficient measurement via dextran mixture

Feedside Cell 2

Permeate Cell 2

Signal Intensity [V]

Elution Volume [mL]

- Feed
- after 624 h
- after 360 h
- after 264 h
- after 192 h
- after 144 h
- after 96 h
- after 72 h
- after 48 h
- after 30 h
- after 24 h
- after 14 h
- after 2 h
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Universität Duisburg-Essen, Lehrstuhl für Technische Chemie II, 45117 Essen, Germany

concentration [mol/L]

0,00E+00
0,00E+00
1,00E-05
2,00E-05
3,00E-05
4,00E-05

time [h]

0 200 400 600 800

decrease of molar concentration with time feedside

0,00E+00
0,00E+00
1,50E-05
1,00E-05
5,00E-06
0,00E+00

time [h]

increase of molar concentration with time permeatside
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diffusion measurements with FITC labeled dextran

![Graph showing diffusion coefficient vs. measurement No. with error bars.](image)
Permporometry measurements
Oxyphen PET track-etched membrane - nominal pore diameter 30 nm
Permporometry measurements

Oxyphen PET track-etched membrane - nominal pore diameter 30 nm

![Graph showing the distribution of pore diameters for Oxyphen PET membrane with a nominal pore diameter of 30 nm. The graph displays a histogram with the x-axis representing pore diameter in micrometers and the y-axis representing relative occurrence percentage.]
2. Establishing and Characterizing of thin block-terpolymer films

Actually used terpolymer:

\[ B_x V_y T_z \]

(polybutadiene-\(b\)-poly(2-vinyl pyridine)-\(b\)-poly(tert-butyl methacrylate))
The wafer and the Film

24 mm
rotation speeds vs. film thickness

film thickness [nm]

rotation speed [rpm]

2000

4000

0

10

20

30

40

50

60

[Image of a bar chart showing the relationship between rotation speed (rpm) and film thickness (nm).]
Further work 1 – characterization of the membrane

- Improvement of existing methods diffusion, permporometry…

- Diffusion measurements with different dextrans and their mixtures

- Evaluation of base membranes:
  track-etched PET - 20 to 100 nm pore diameter
  Anopore membrane – 20 nm UF membranes
Further work – 2  - thinfilm and composite membrane
- Creation of thin films of block copolymers
- Atomic Force Microscopy (AFM) of block copo films
- Preparation of block copolymer – composite – membranes
- Analyzing the new composite – membrane
Acknowledgements

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