Neue nanostrukturierte Membranen für die Wasseraufbereitung

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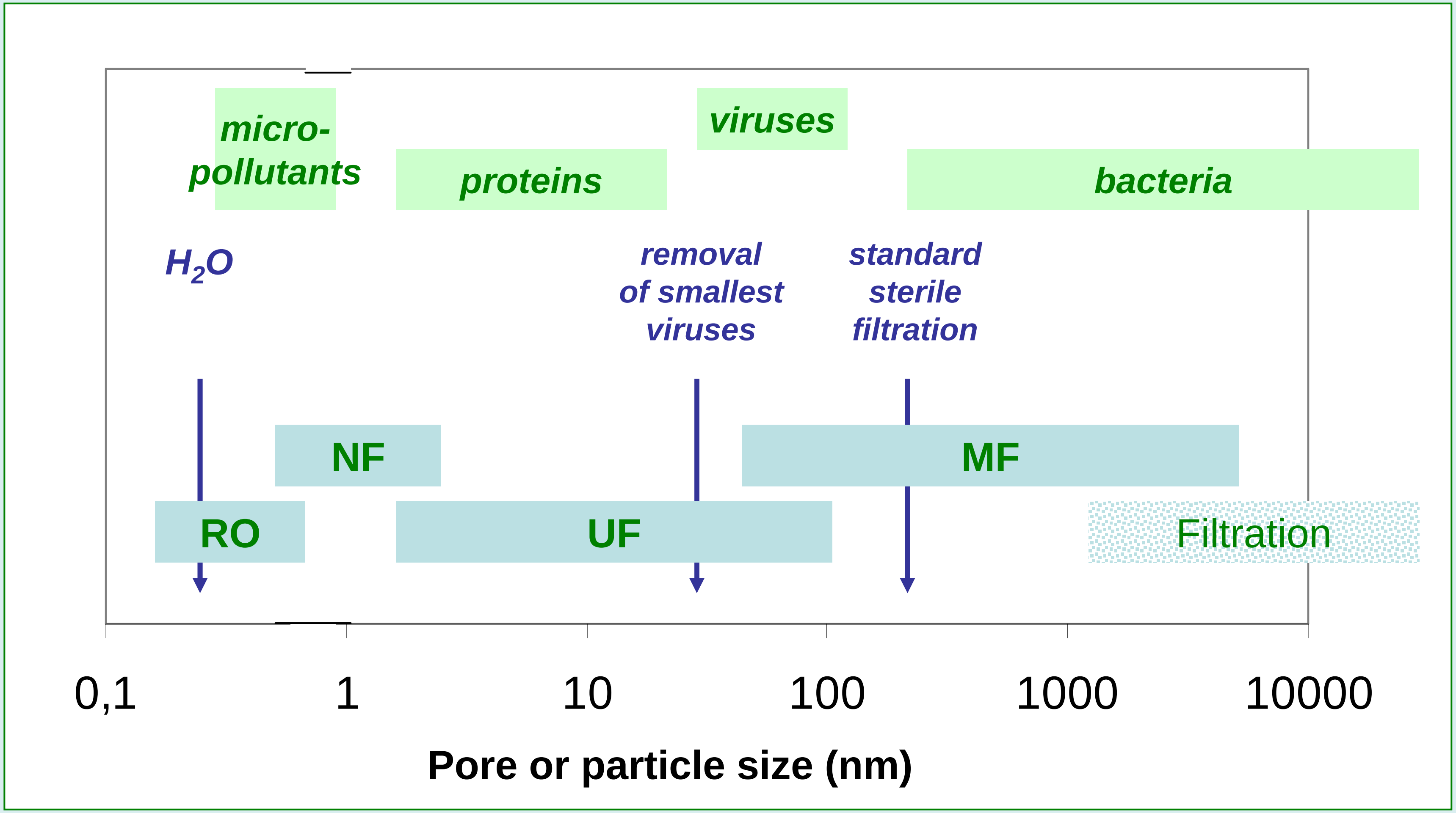
nANO MEETS WATER, Oberhausen; Nov. 10, 2011

Membrane processes

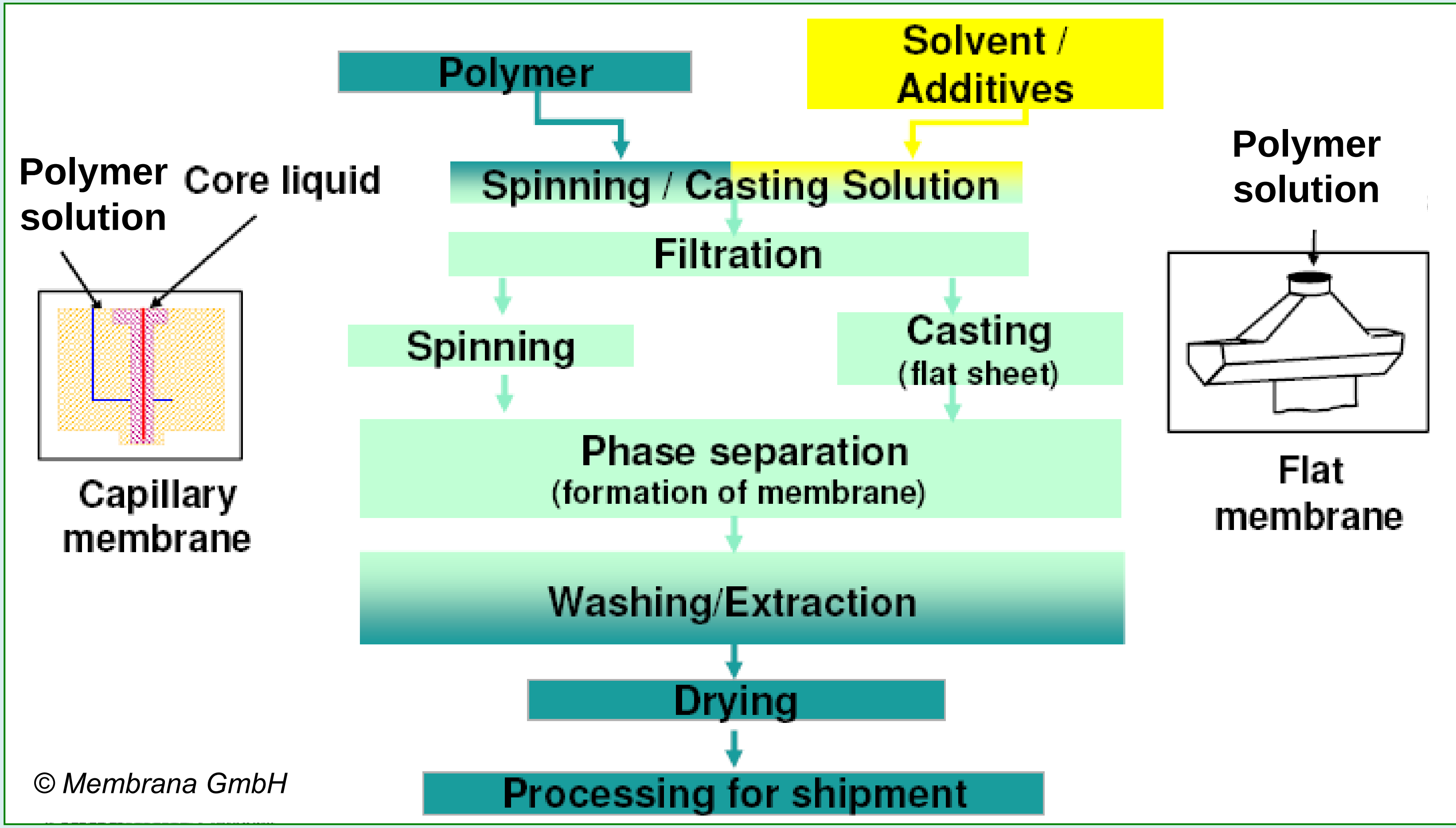
… pressure driven

… for water purification → „absolute barrier“ for various solutes / particles



Polymer membranes

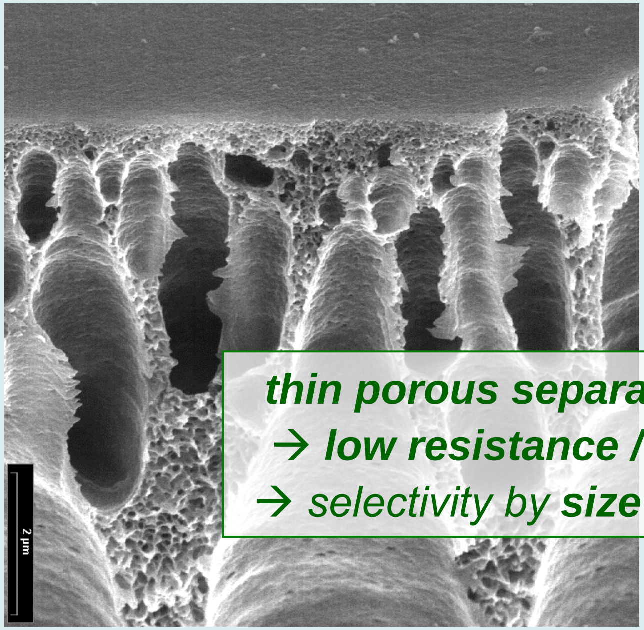
… via nonsolvent-induced phase separation (NIPS)
… established large-scale industrial processes



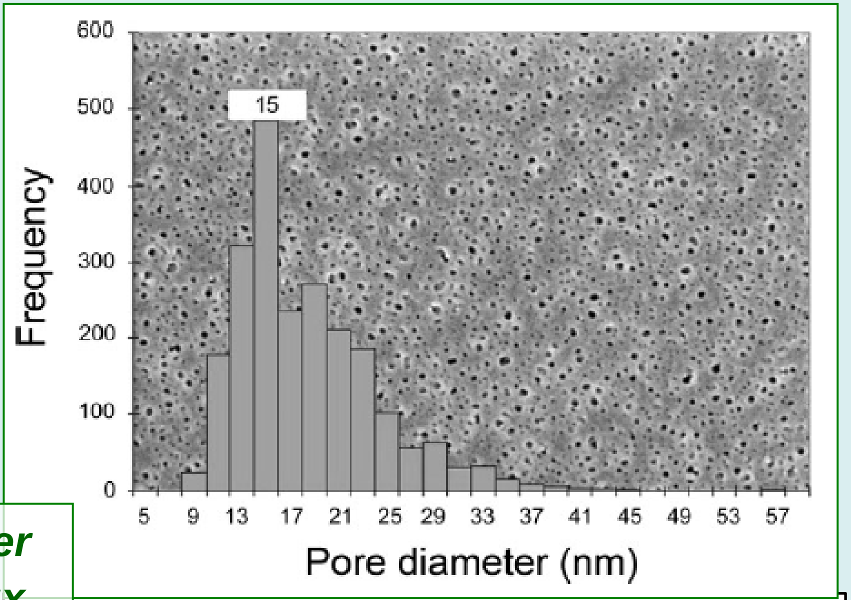
Polymer membranes

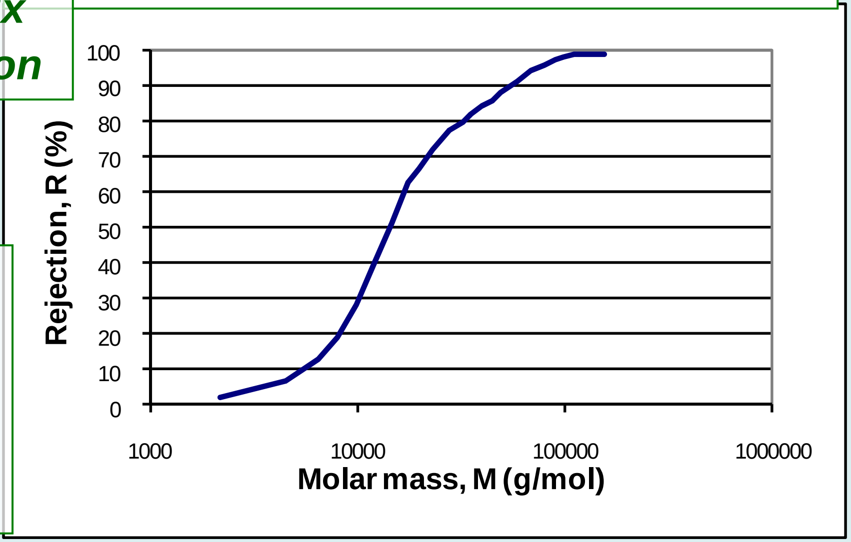
Ultrafiltration membranes

here PAN; prepared by **NIPS**



thin porous separation layer
*→ **low resistance / high flux***
*→ selectivity by **size exclusion***



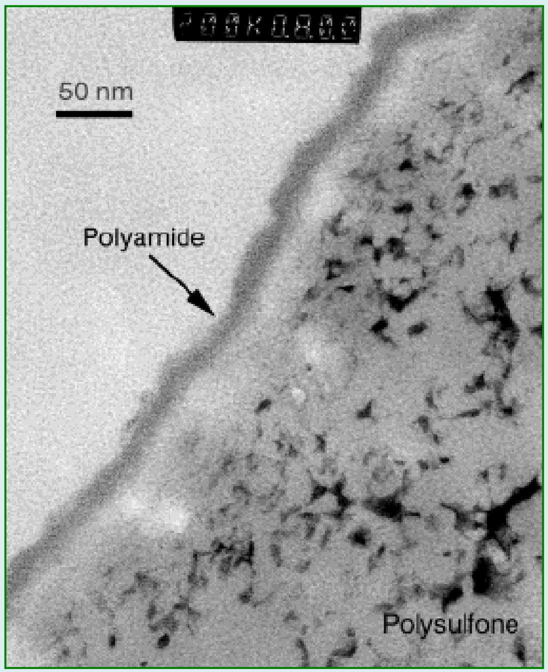


***however**:*
● relatively broad pore size distribution
→ moderate size selectivity
● relatively low porosity
→ limited flux

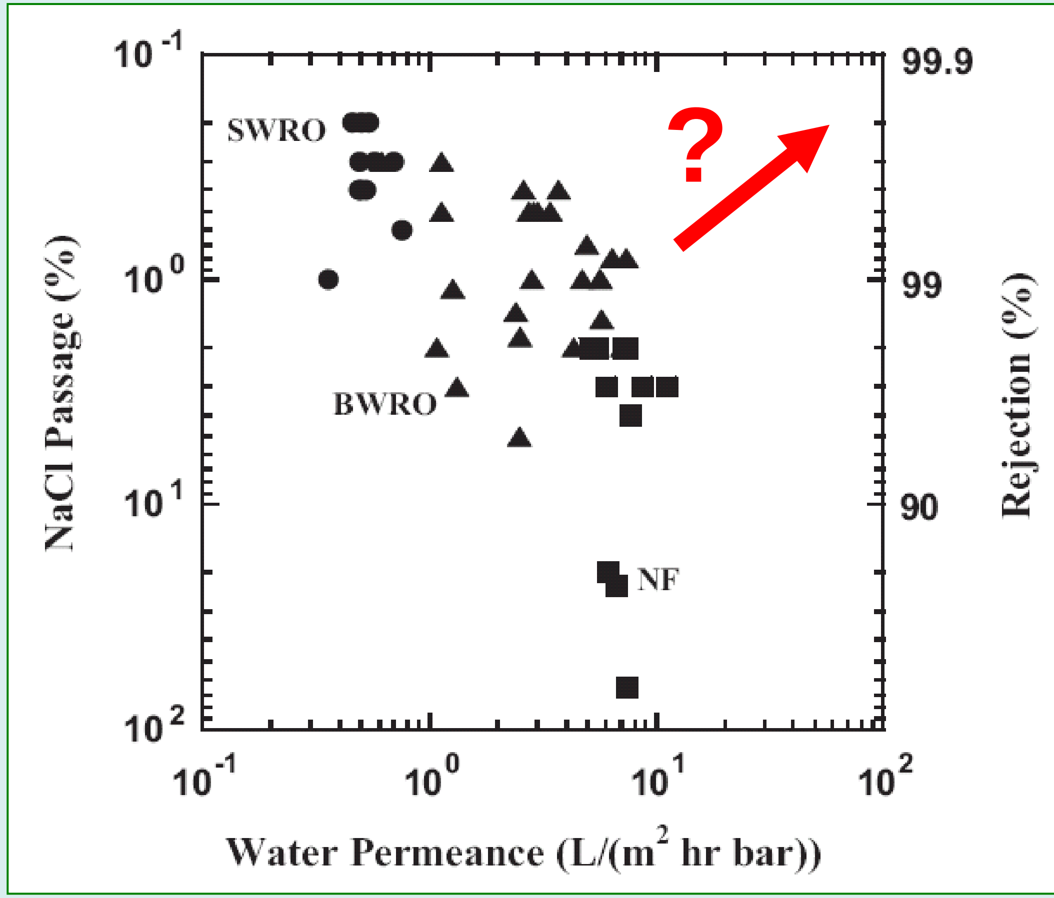
Membrane performance

Reverse osmosis membranes

polyamide, prepared by interfacial polymerization on UF-type support membrane



Thin barrier layer of RO composite membrane.



Trade-off between permeability and selectivity for state-of-the-art polyamide composite RO membranes.

V. Freger, *Langmuir* **2003**, *19*, 4791. // G. M. Giese et al., *J. Membr. Sci.* **2011**, *369*, 130.

Reverse osmosis for desalination:

well-defined objective for separation = **pure H_2O**
easy standardization (compared to other water purifications!)

Aims

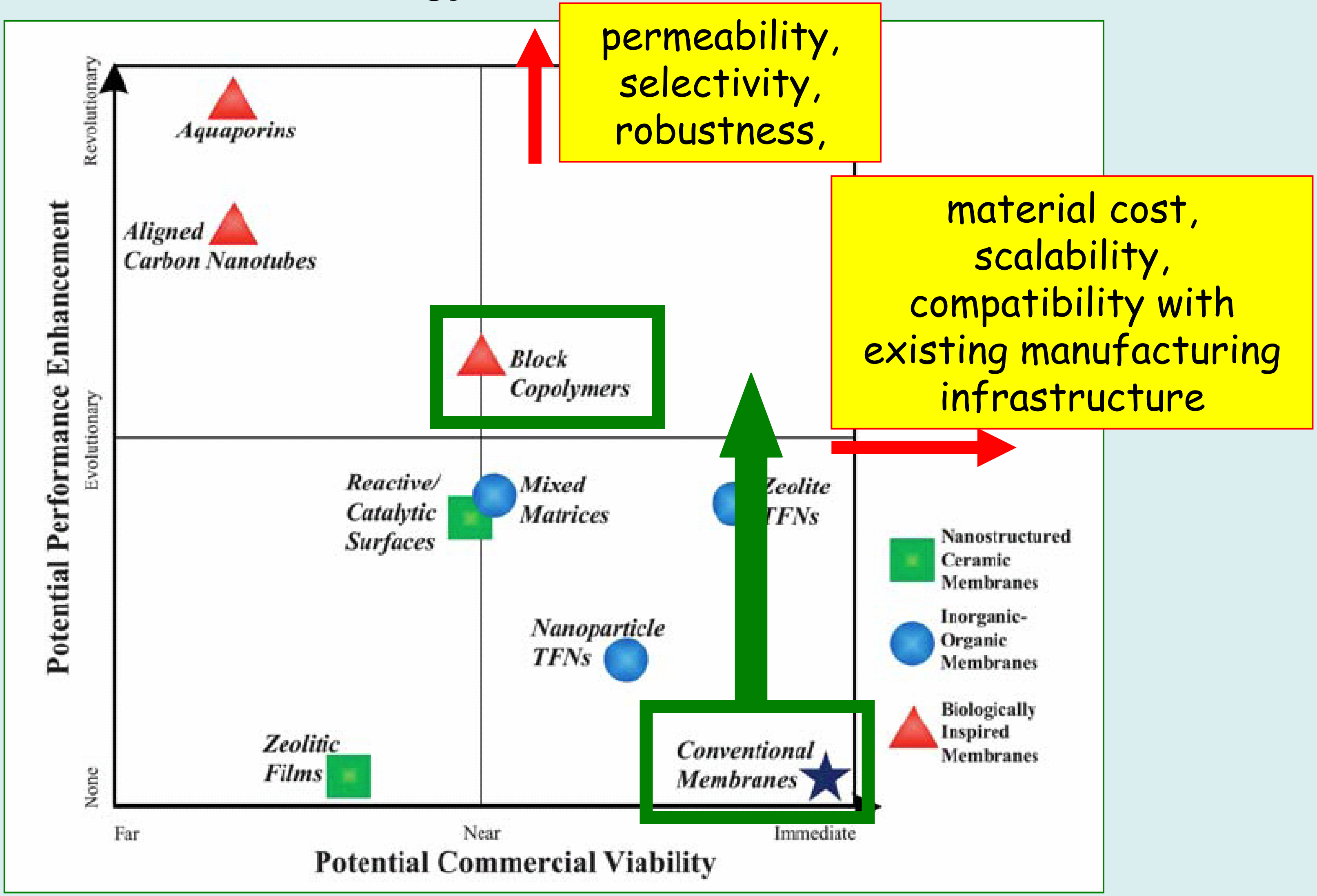
- **higher permeability**
- **higher selectivity (especially for uncharged solutes!)**
- **higher stability**

- **minimize concentration polarization (*i.e., accumulation of rejected solute*)**
- **no fouling (*i.e., reversible or irreversible deposition on the membrane*)**
- **minimize cleaning**

→ smaller foot-print **→ lower investment cost**
→ less material
→ less energy **→ lower operating cost**
→ less/no cleaning chemicals

Advanced membranes

… via nanotechnology



M. M. Pendergast, E. M.V. Hoek, *Energy Environ. Sci.*, **2011**, *4*, 1946.

Aims for improvement
(for all membrane processes!)

- higher permeability
- higher selectivity (especially for uncharged solutes!)
- higher stability

- minimize concentration polarization
- no fouling
- minimize cleaning

} → ***these problems are also, typically even more relevant for membranes with high permeability!***

One (also our) **strategy**
add or integrate additional functions to/in membrane barrier structure
by functional nanolayers or nanoparticles

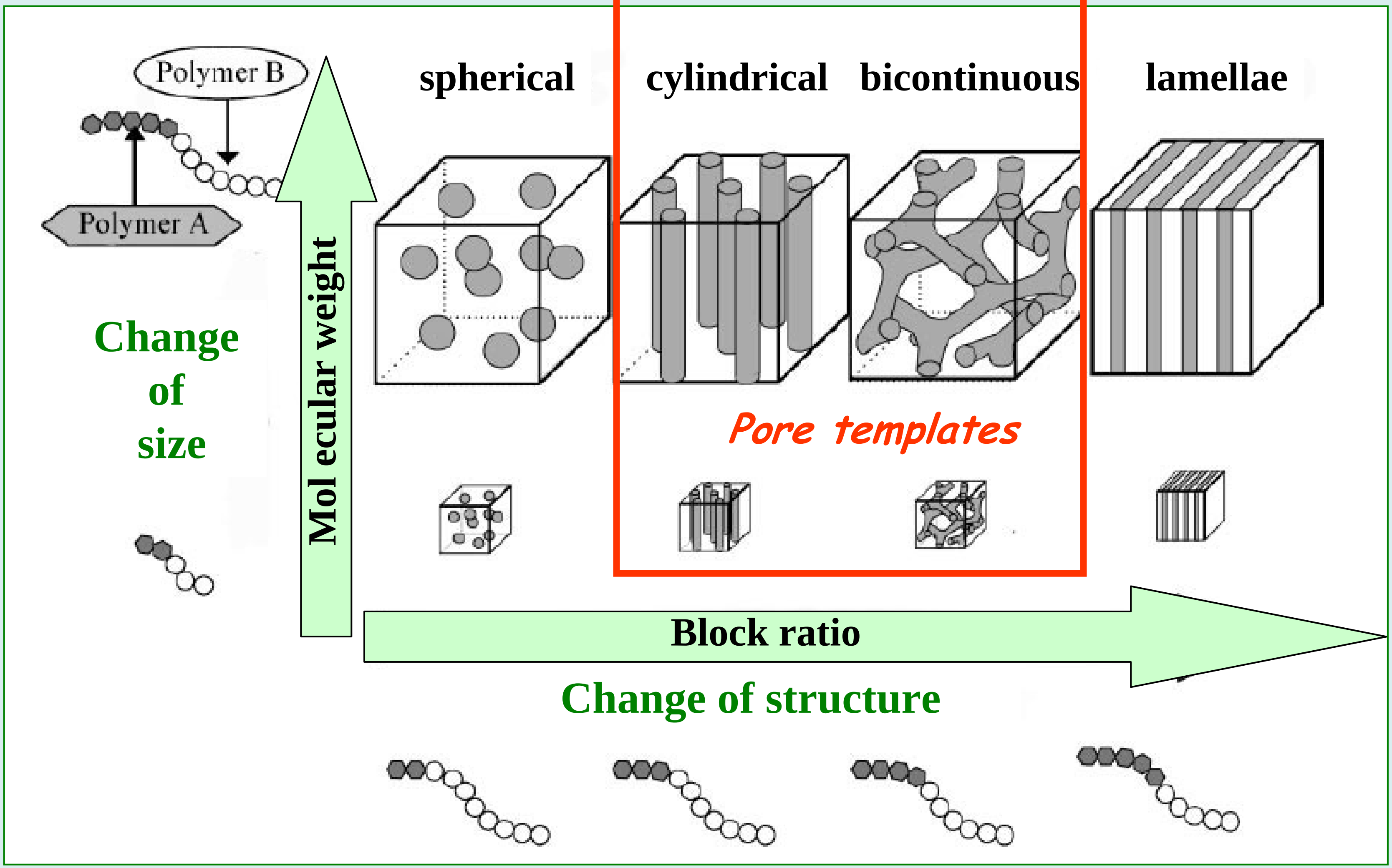
→ protection*
→ adsorber
→ catalyst*
→ stimuli-responsivity*

} → additional elimination pathways, e.g., for micropollutants (adsorber, catalyst)

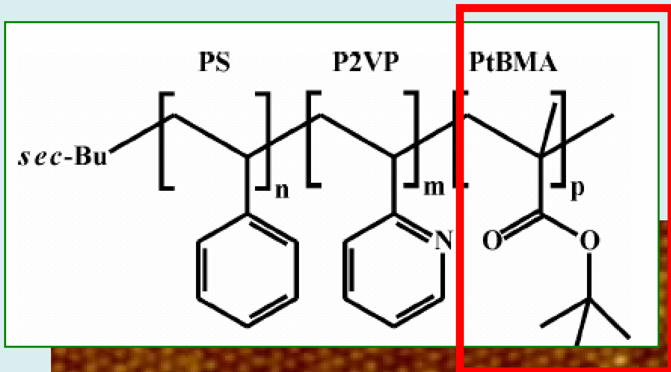
* → anti-fouling / fouling-release

Block copolymers

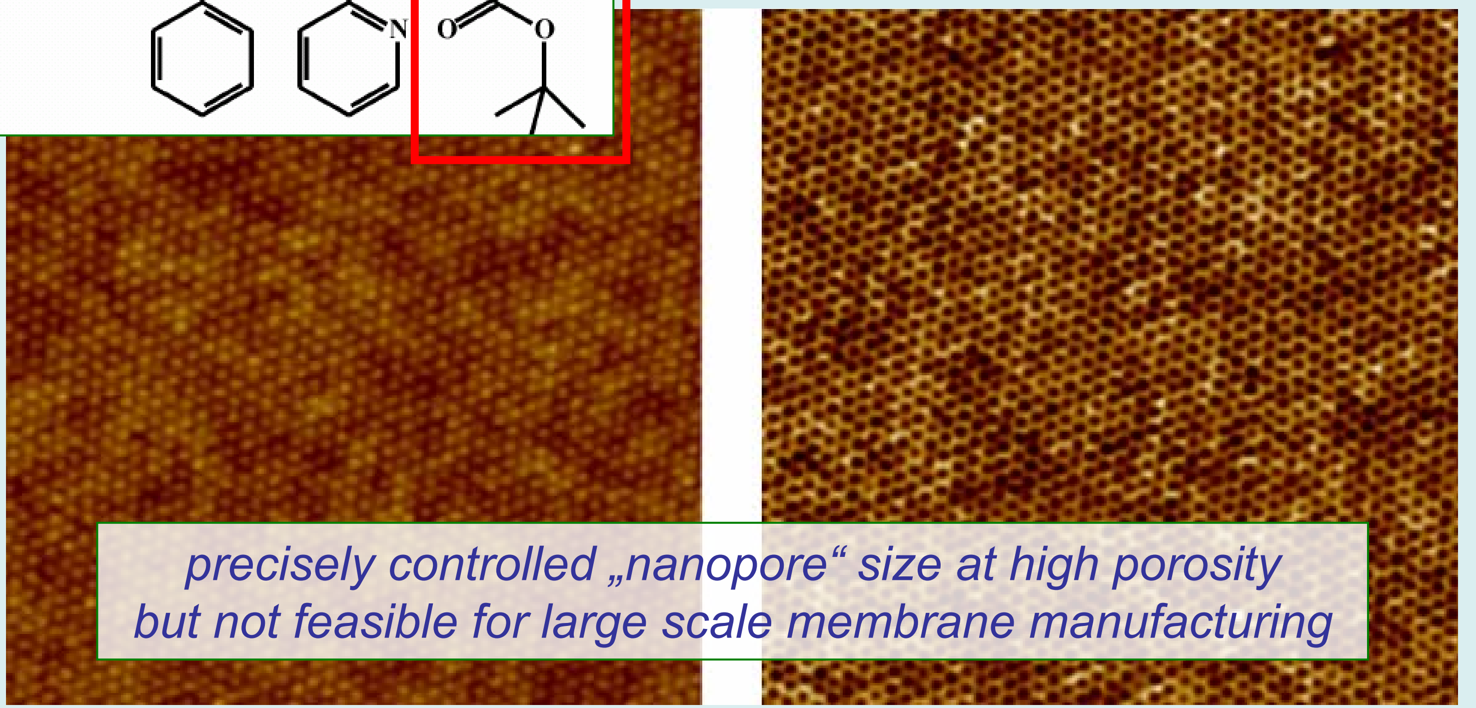
… tailoring pore and surface structure on the nanoscale



Phase separated block copolymers as pore template



block (microdomain)
can be removed by UV irradiation

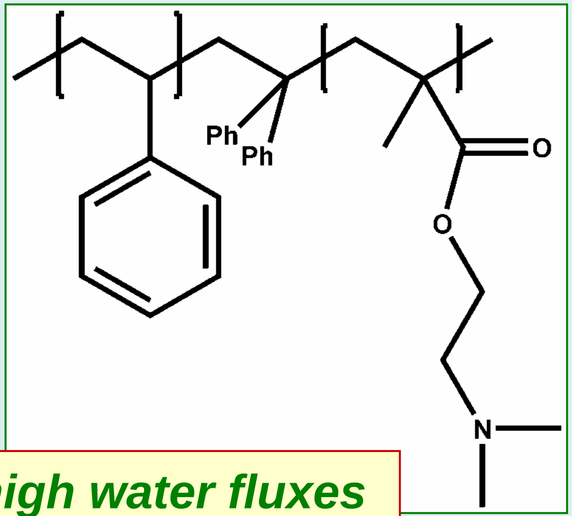


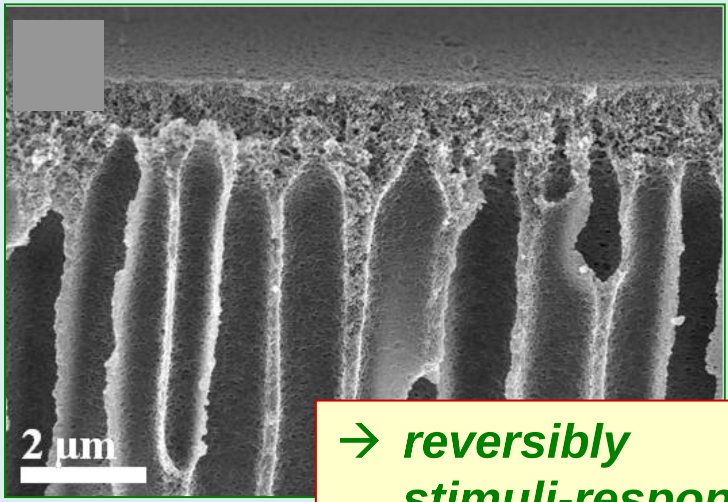
precisely controlled „nanopore“ size at high porosity
but not feasible for large scale membrane manufacturing

tapping mode AFM topography of triblock copolymer film:
before ... after **UV irradiation**

A. Sperschneider, et al., *Small* **2007**, *3*, 1056.

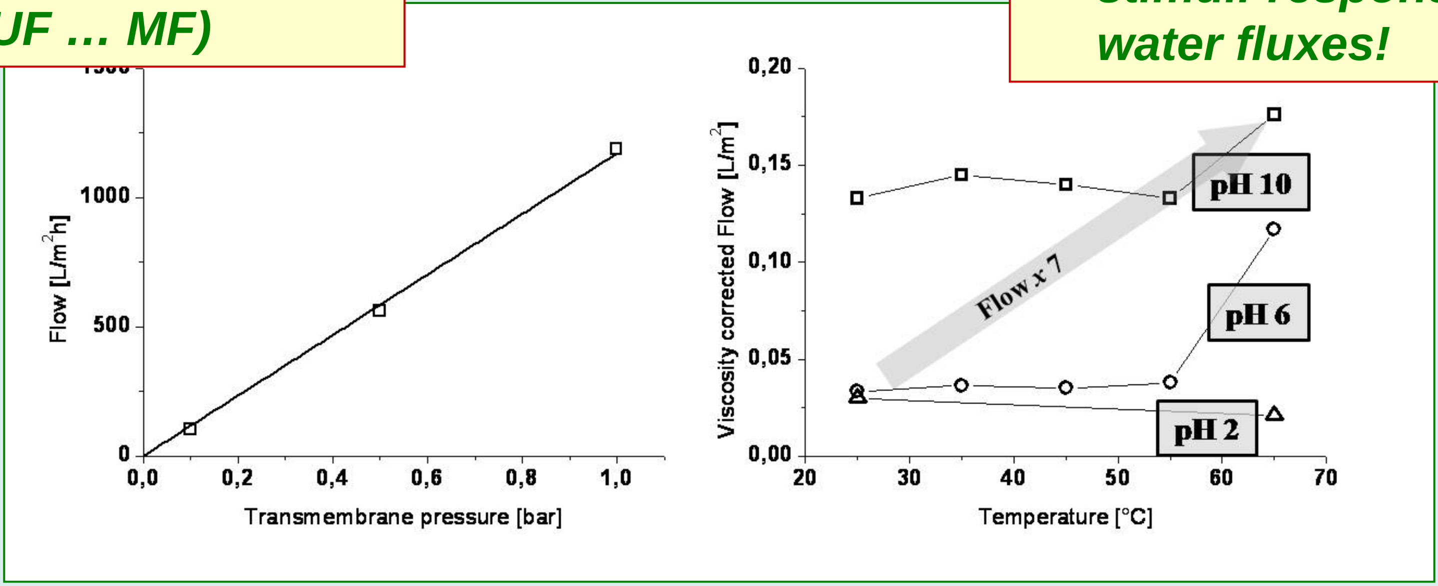
... via scalable NIPS process





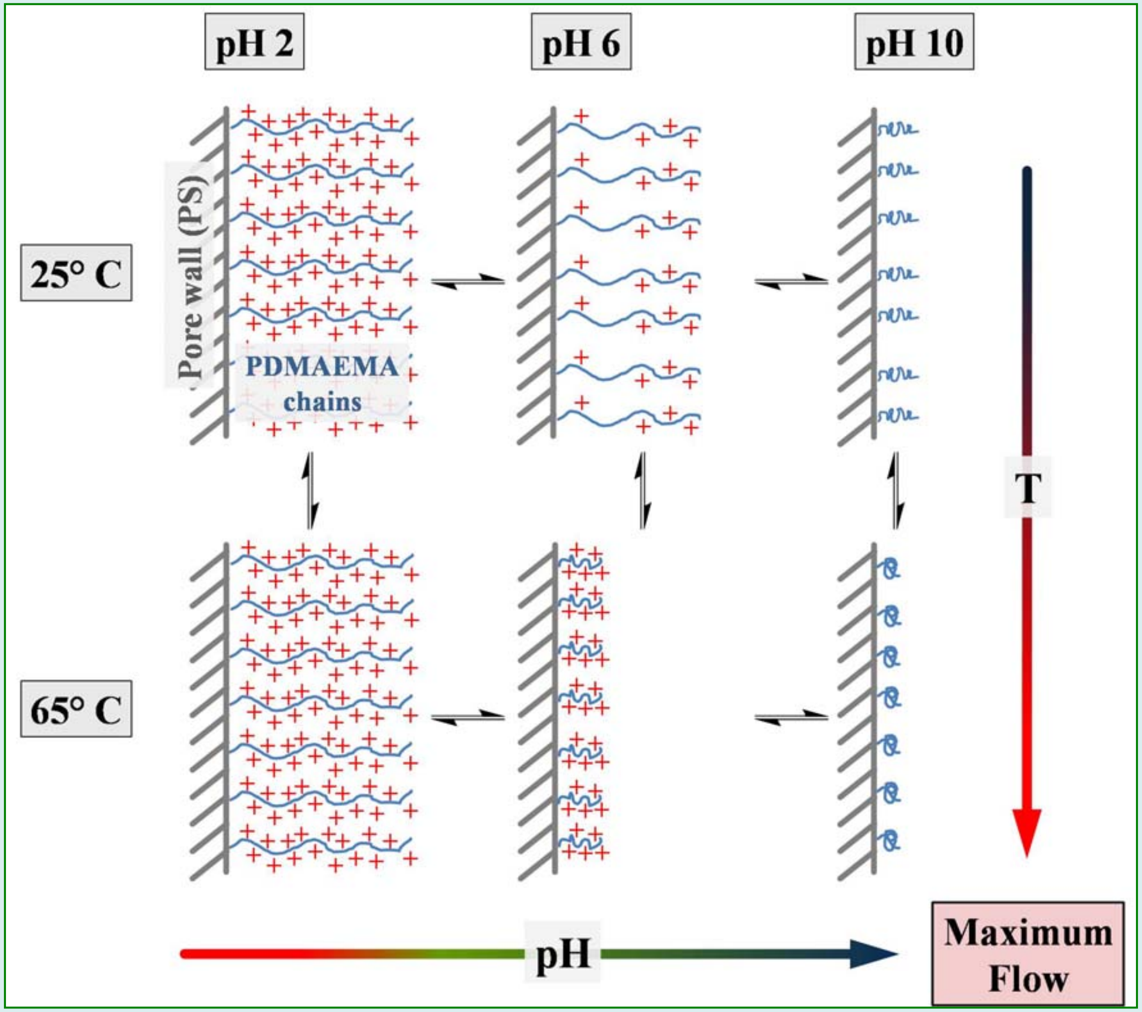
→ *high water fluxes (UF … MF)*

→ *reversibly stimuli-responsive water fluxes!*



F. Schacher, et al., *Adv. Funct. Mater.* **2009**, *19*, 1040.

Phase separated, double stimuli-responsive pore structure



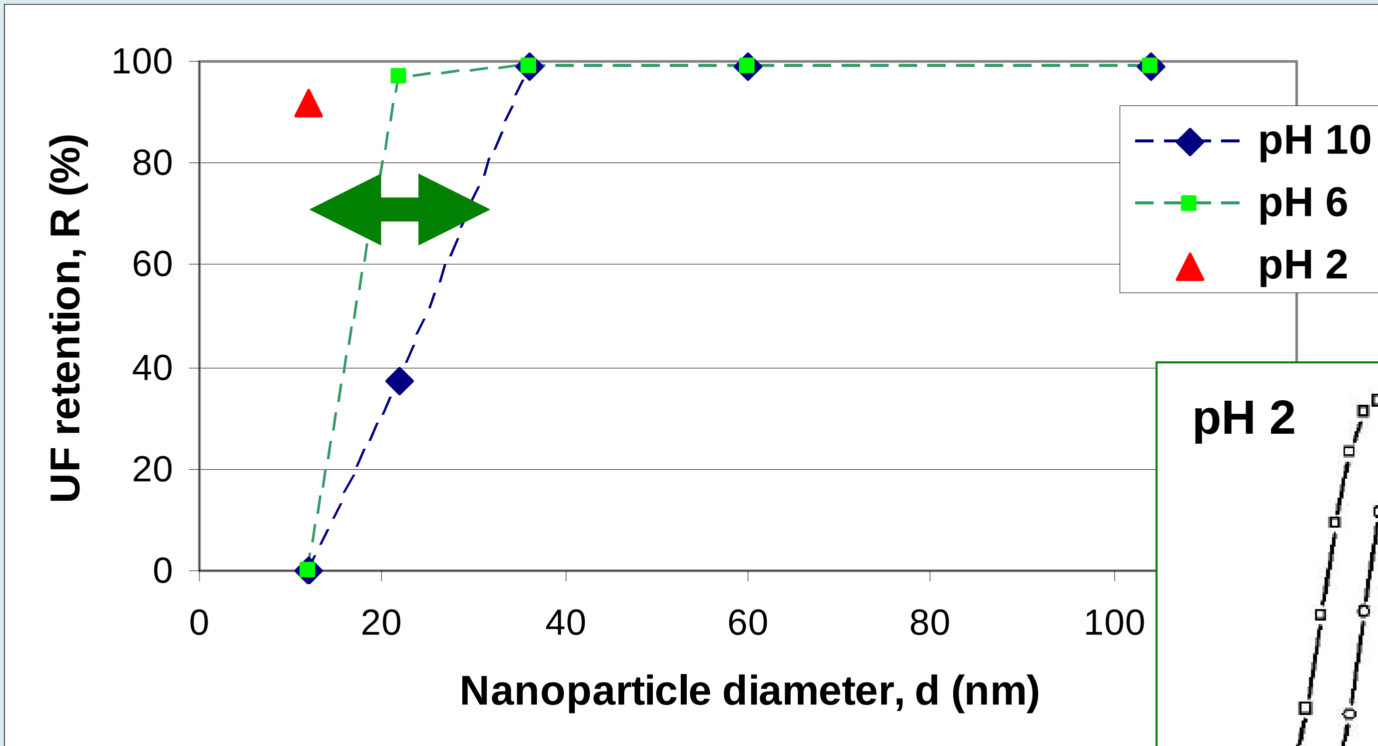
Surface and pore structure from micro- <u>and</u> macrophase separation

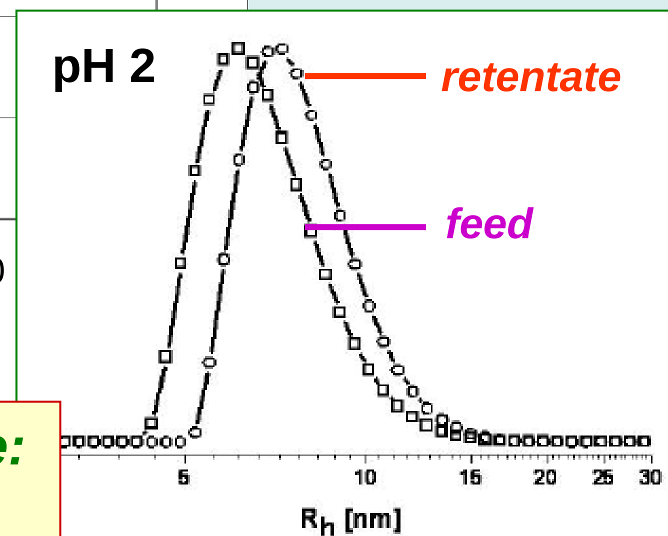
F. Schacher, et al., *Adv. Funct. Mater.* **2009**, *19*, 1040.

Stimuli-responsive ultrafiltration of nanoparticles

as function of pH (@ 25°C)

silica (22 to 104 nm), LUDOX AM-30 (12 nm), 0.1 wt% in water, 0.2 bar.





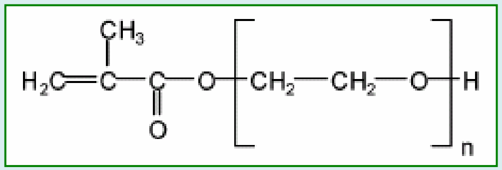
→ *Significant change of cut-off pore size: from < 15 nm to > 25 nm*

F. Schacher, et al., *Adv. Funct. Mater.* **2009**, *19*, 1040.

Graft copolymerization of anti-fouling layers on UF membranes

UV wavelength: > 300 nm

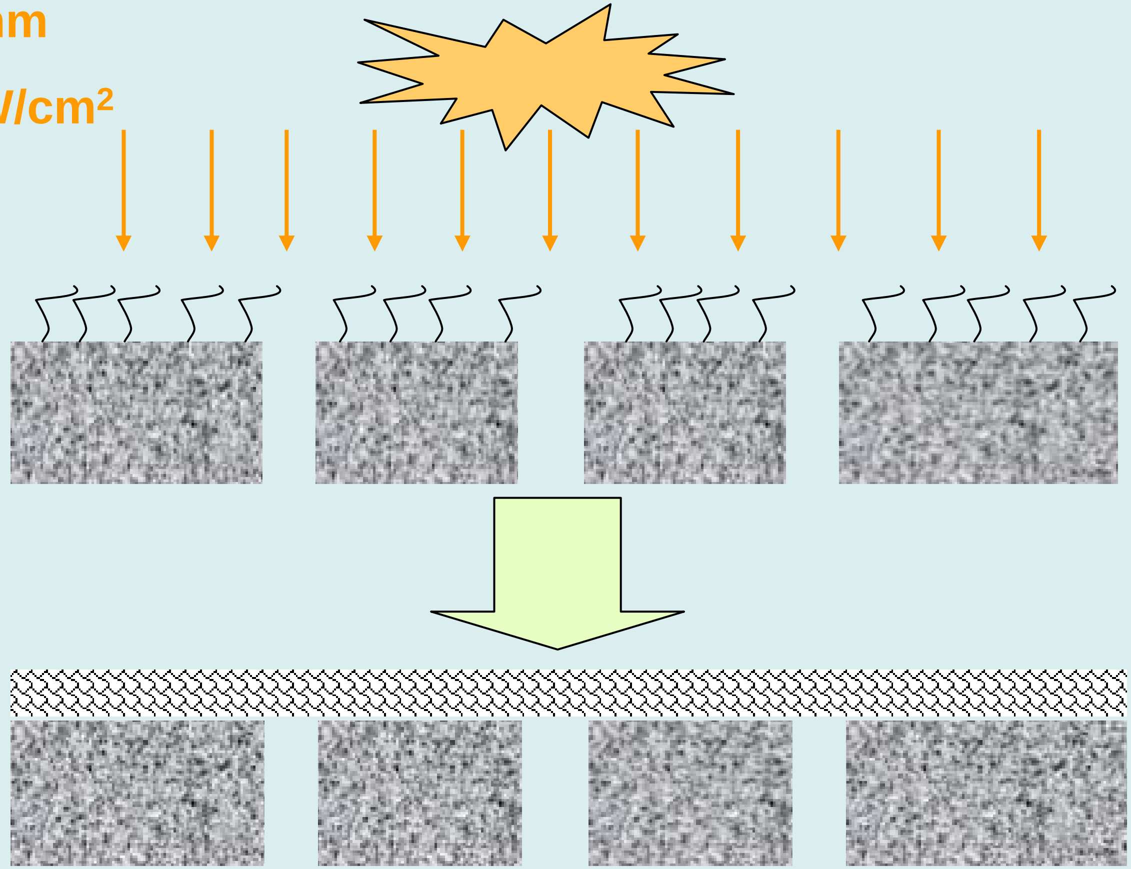
UV intensity: 35 $\pm$ 5 mW/cm²



monomer (PEGMA)

PES UFM (100 kDa)

grafted ultrathin hydrophilic, flexible polymer layer

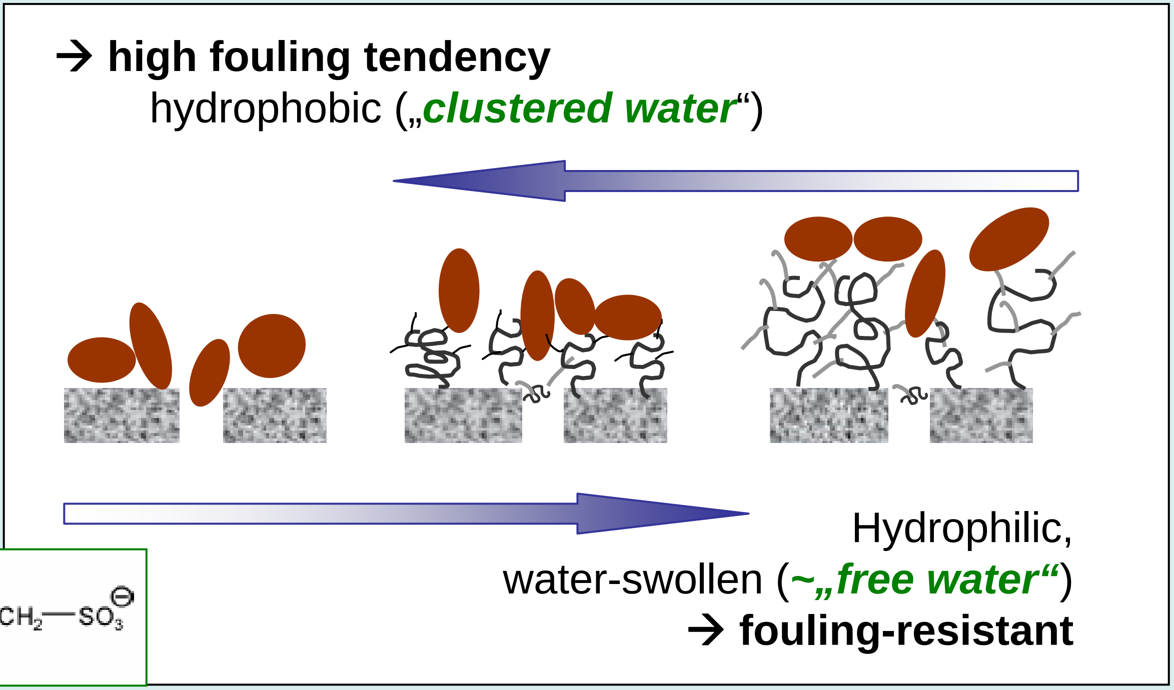


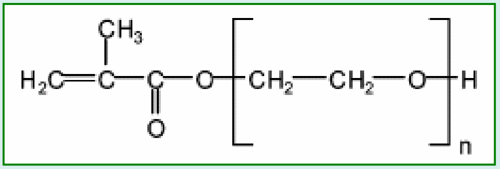
PES-based thin-layer hydrogel composite membrane

H. Susanto, M. Ulbricht, *Langmuir* **2007**, *23*, 7818-7830 / cf. G. Belfort et al., 1995ff.

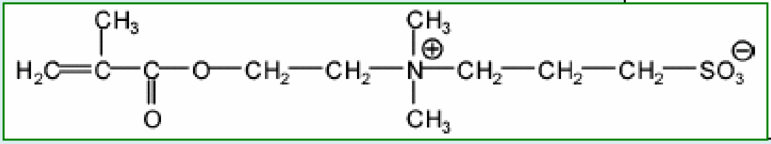
Anti-fouling

… via grafted polymer hydrogel layers





PEGMA



SPE

Grafted polyPEGMA vs. **polySPE** (zwitterionic)

at same DG: flux PEGMA > SPE
rejection PEGMA < SPE

fouling resistance PEGMA > SPE

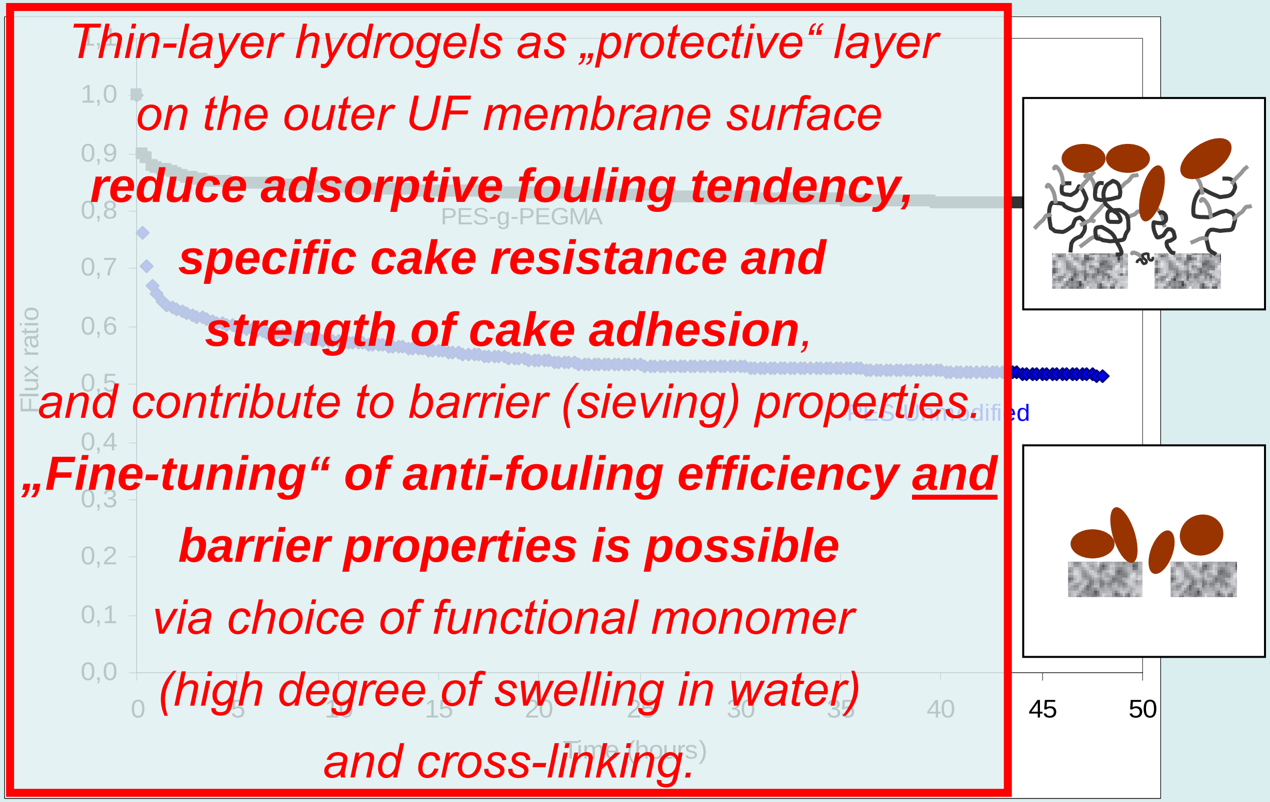
Equilibrium swelling ratio

polySPE	7.7
polyPEGMA	12.2

H. Susanto, M. Ulbricht, *Langmuir* **2007**, *23*, 7818.

Anti-fouling

PES-based thin-layer hydrogel composite membrane (MWCO 10 kDa)



Thin-layer hydrogels as „protective“ layer on the outer UF membrane surface

reduce adsorptive fouling tendency, specific cake resistance and strength of cake adhesion,

and contribute to barrier (sieving) properties.

„Fine-tuning“ of anti-fouling efficiency and barrier properties is possible

via choice of functional monomer (high degree of swelling in water) and cross-linking.

PES-g-PEGMA

PES unmodified

- similar results with proteins, polysaccharides and mixtures thereof.

H. Susanto, M. Ulbricht, *Langmuir* **2007**, *23*, 7818-7830.

H. Susanto, M. Ulbricht, *Water Research* **2008**, *42*, 2827-2835.

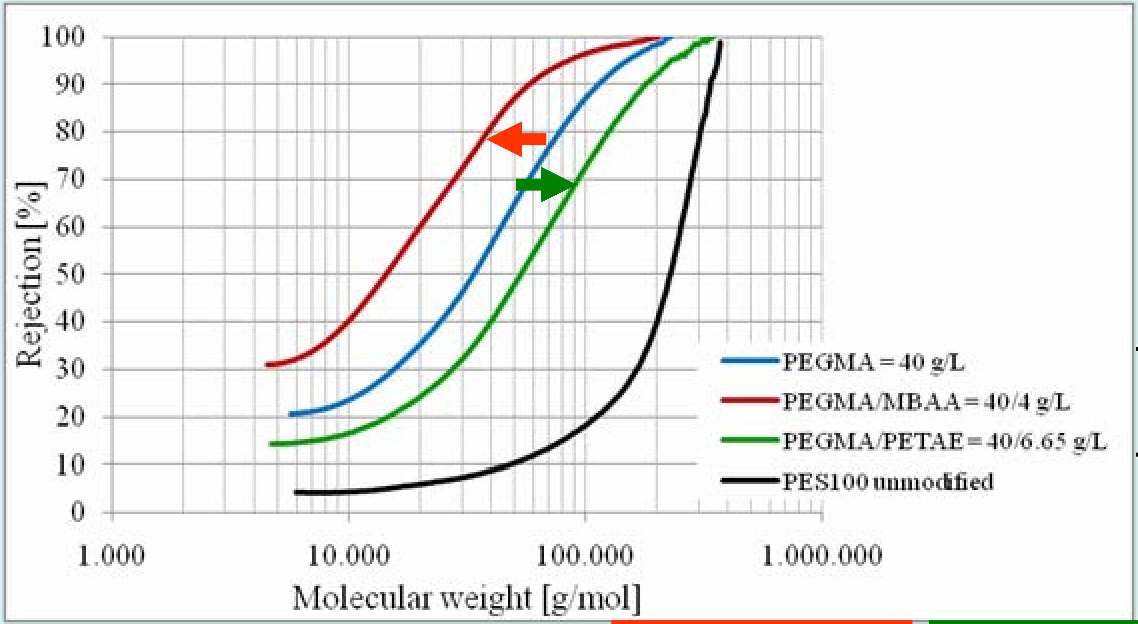
H. Susanto, H. Arafat, E. Janssen, MU, *Separ. Purif. Tech.* **2008**, *63*, 558.

PES-based thin-layer hydrogel composite membrane

PES UF membrane (<u>100 kDa</u>, Sartorius) photo-grafted with polyPEGMA

→ influence of cross-linker structure and ratio

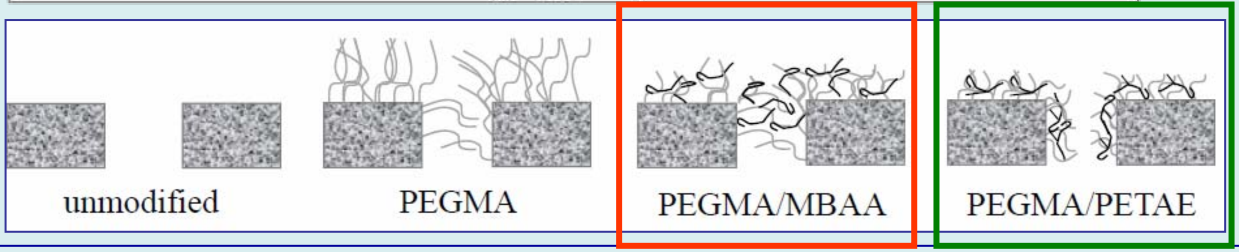
sieving curves (dextran)



additional sieving through hydrogel

pore covering hydrogel

PES 100 kDa
high cross-linker content
UV dose 11 mJ/cm^2



P. D. Peeva, T. Pieper, M. Ulbricht, *J. Membr. Sci.* **2010**, *362*, 560.

Hydrogels for antifouling

… from surface grafting to thin-layer composite membranes

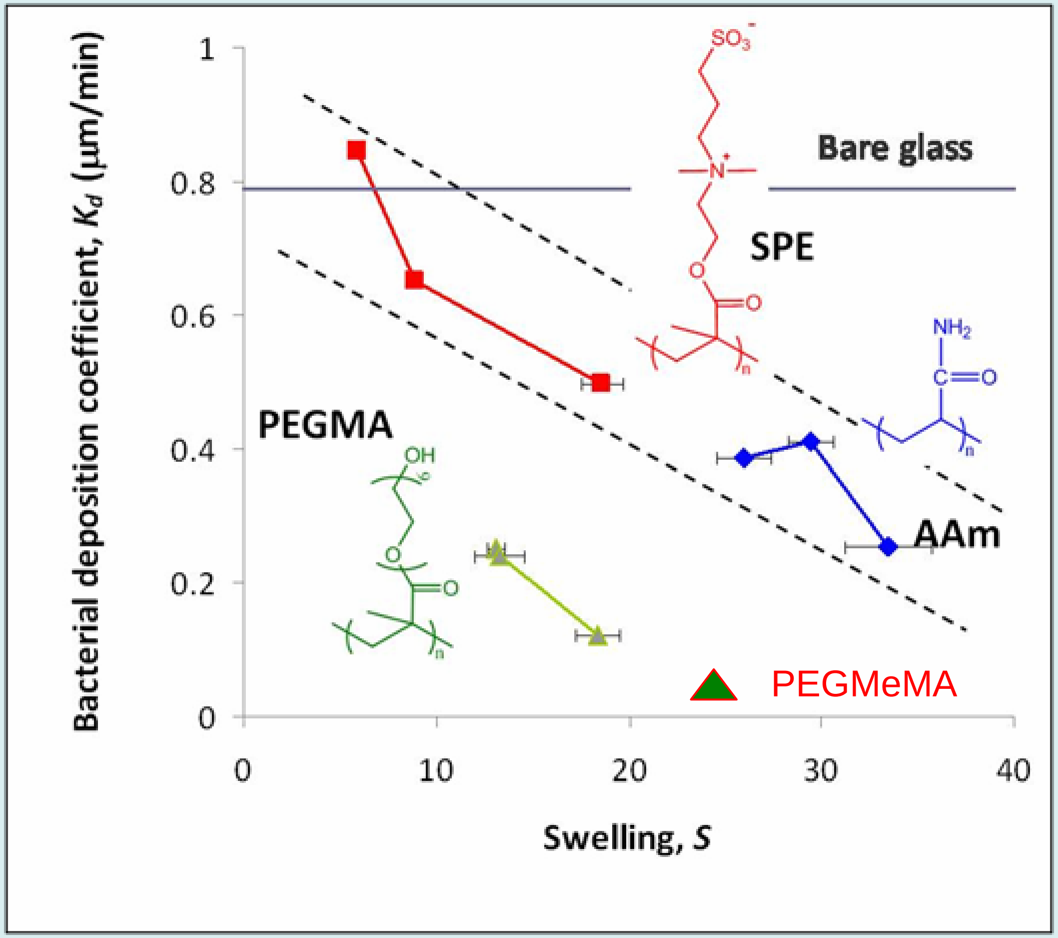
common sense: kosmotropic surfaces (PEG, zwitterionic, ...) are best suited, but there are also specific requirements:

with respect to foulants:

biofouling
→ maximize swelling degree

organic fouling
→ exclude biomacromolecules

+ mechanical strength



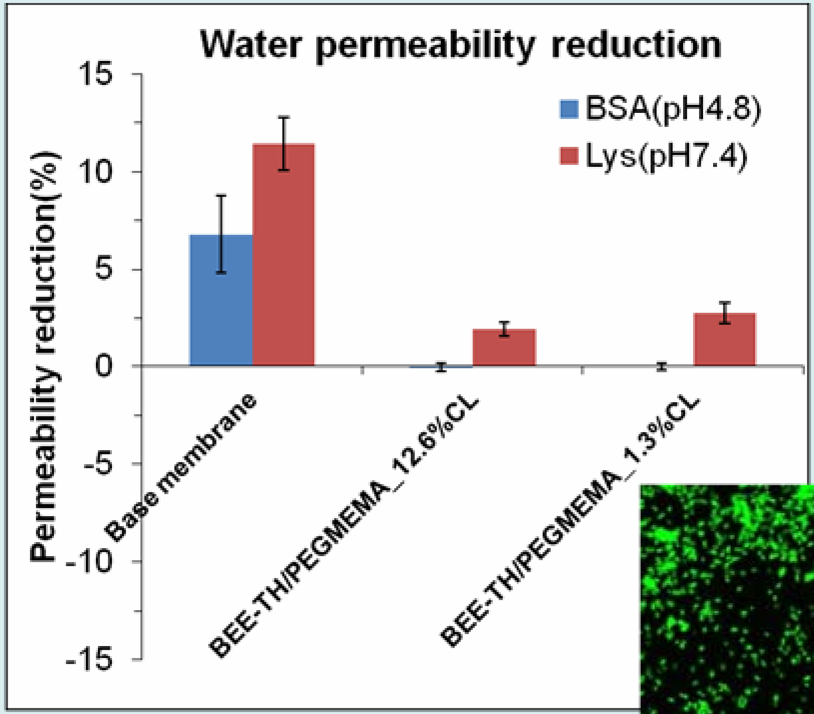
Initial deposition of *P. fluorescens* F113 on different hydrogels at varied cross-linking

I. Eshet, V. Freger, R. Kasher, M. Herzberg, J. Lei, M. Ulbricht, *Biomacromolecules* **2011**, *12*, 2681.

Hydrogels for antifouling

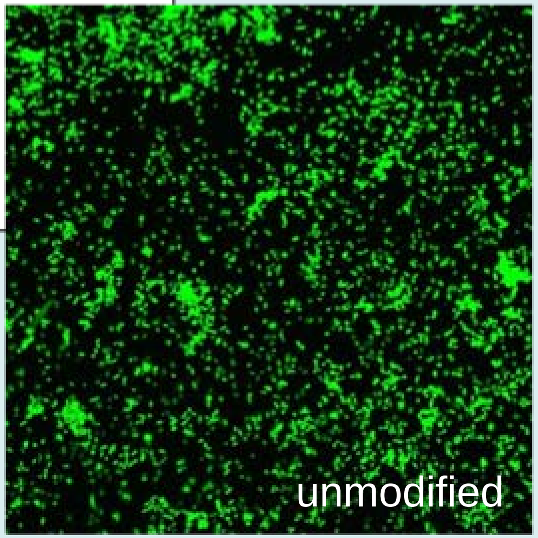
… on polyamide composite NF membranes (NF 270)

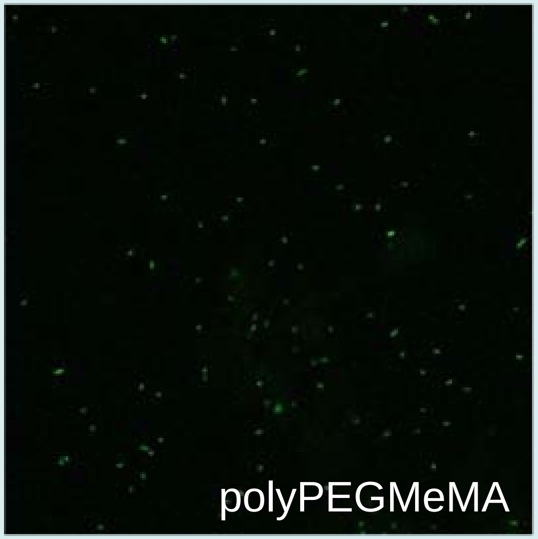
after protein filtration (1 hour)



→ ***largely reduced organic fouling (but function of solute size!)***

after biofilm growth
(*P. fluorescens* F113; 2 days)



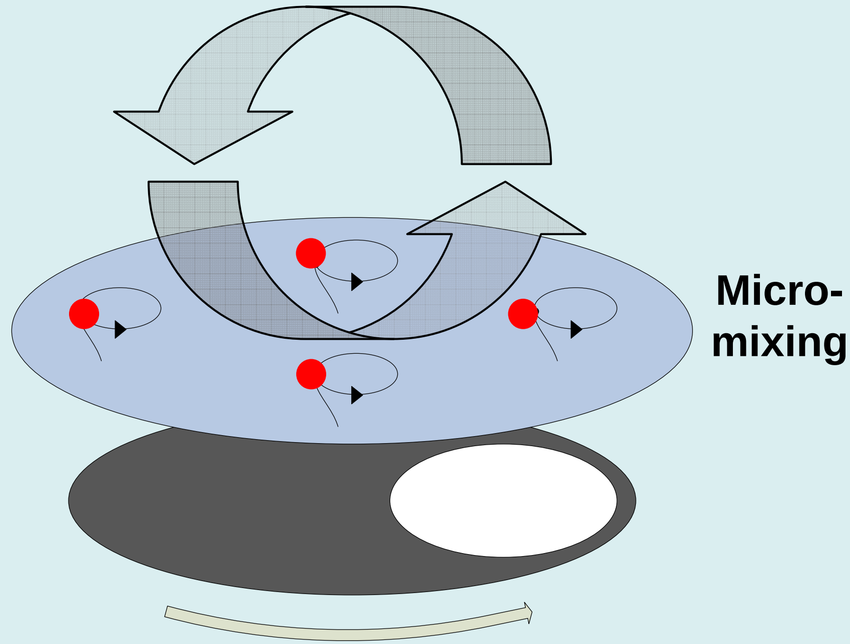


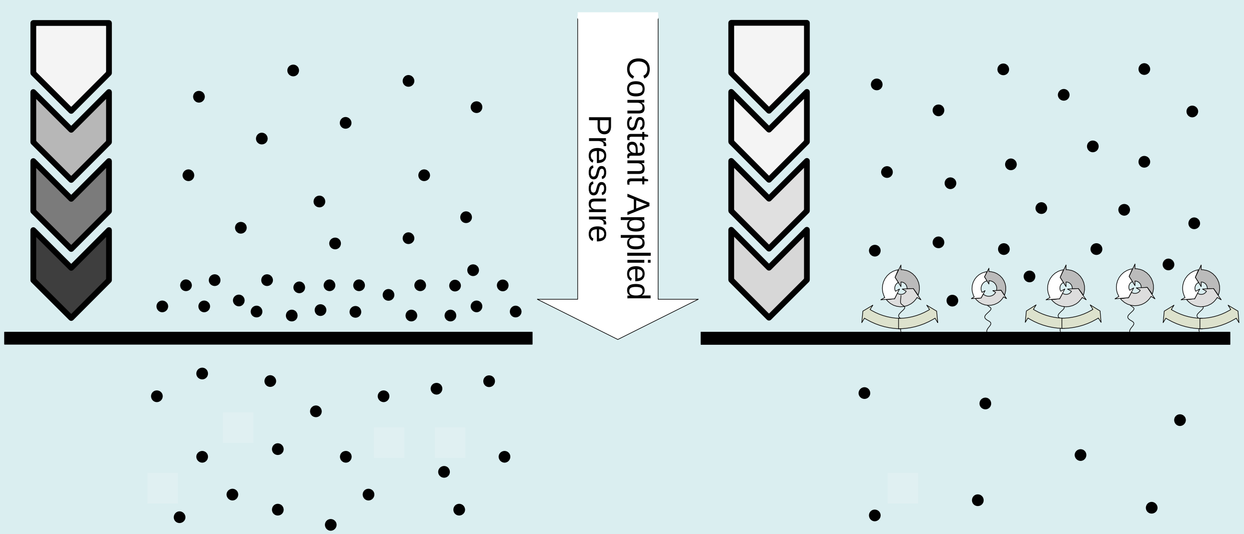
→ ***almost eliminated biofouling***

J. Lei, *Ph.D. project - UDE*, **2011**.

Functional hybrids

Magnetically activated micromixers for separation membranes

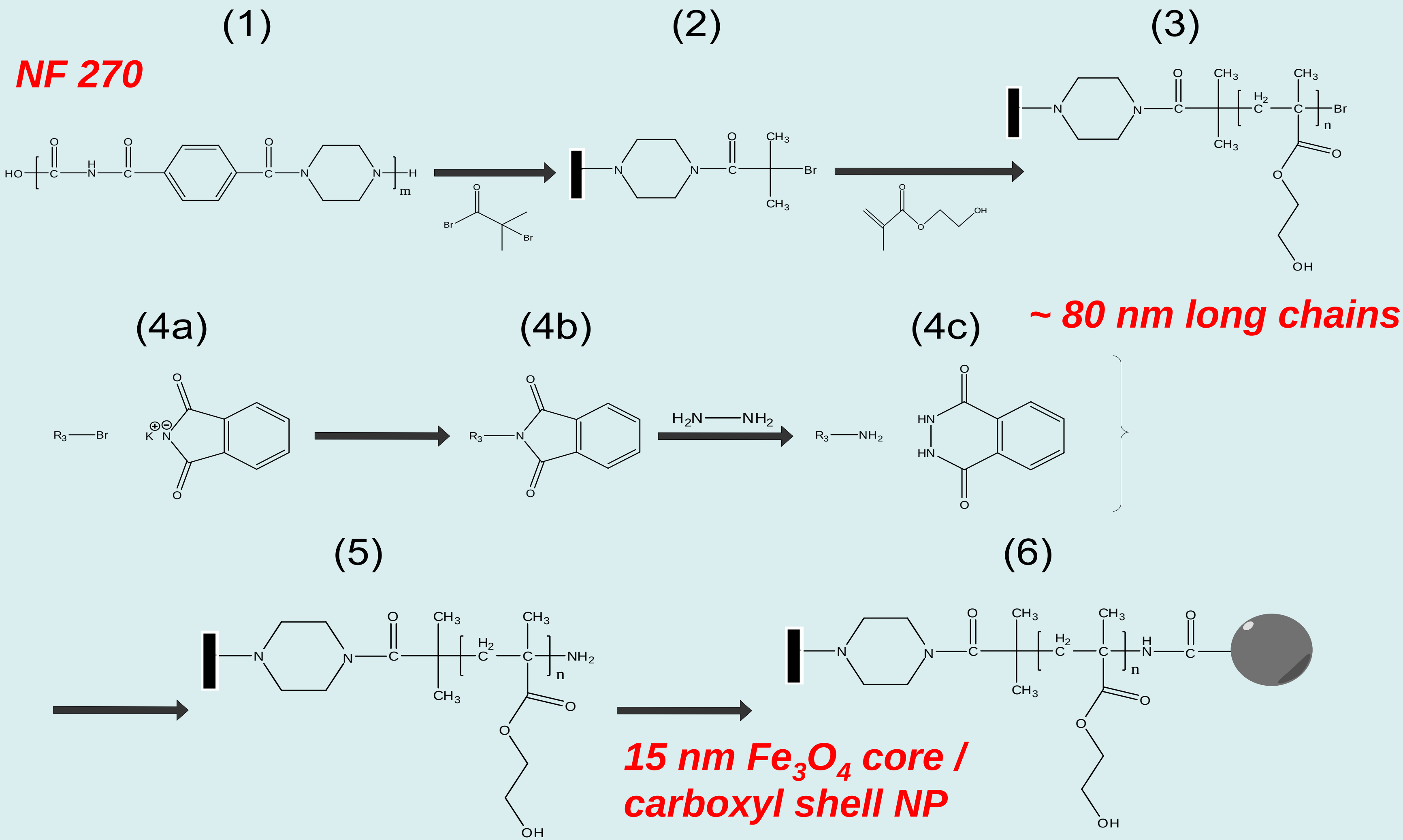




H. H. Himstedt, Q. Yang, L. P. Dasi, X. Qian, S. R. Wickramasinghe, MU, *Langmuir* **2011**, *27*, 5574.

Functional hybrids

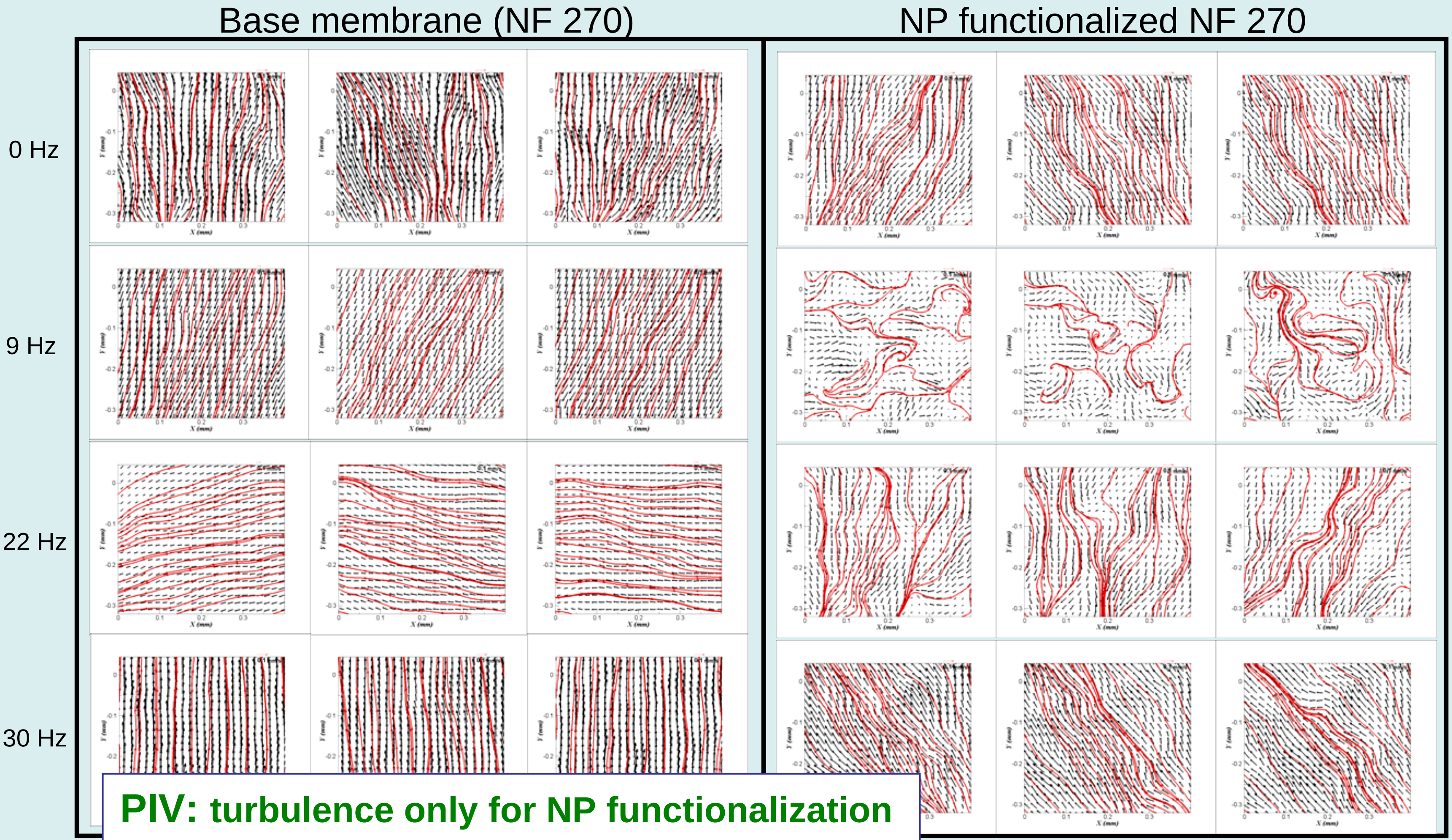
Synthesis by controlled surface initiated graft copolymerization and nanoparticle coupling



H. H. Himstedt, Q. Yang, L. P. Dasi, X. Qian, S. R. Wickramasinghe, MU, *Langmuir* **2011**, *27*, 5574.

Functional hybrids

Visualization of macromixing



PIV: turbulence only for NP functionalization and medium rotation frequency!

H. H. Himstedt, Q. Yang, L. P. Dasi, X. Qian, S. R. Wickramasinghe, MU, *Langmuir* **2011**, *27*, 5574.

Functional hybrids

Stimuli-responsive nanofiltration membrane

micromixing at the surface reduces concentration polarization

Table 1. Average Fluxes and Salt Rejections for Control and Modified Membranes at 45 psig (3.1 bar)

	500 ppm $CaCl_2$		2000 ppm $MgSO_4$	
	control	modified	control	modified
Salt Rejection (%)				
with field	34.4 ± 0.2	40.4 ± 0.2	66.5 ± 0.2	74.4 ± 0.2
without field	32.5 ± 0.2	34.2 ± 0.2	66.0 ± 0.2	67.7 ± 0.2
Filtrate Flux ($L/m^2 \cdot h$)				
with field	13.4 ± 0.6	9.6 ± 0.7	5.4 ± 0.3	6.0 ± 0.4
without field	12.8 ± 0.6	7.8 ± 0.7	5.6 ± 0.4	4.0 ± 0.2

NF: significant improvement of flux and salt rejection only for NP functionalization and rotating magnetic field (~ 10 Hz)

H. H. Himstedt, Q. Yang, L. P. Dasi, X. Qian, S. R. Wickramasinghe, MU, *Langmuir* **2011**, *27*, 5574.

Conclusions

Polymeric membranes for RO, NF or UF are well established materials; function and performance depend critically on their nanoscale structure (the same is true for inorganic membranes)**.**

Current performance limitations can be overcome by advanced nanotechnologies.

Surface functionalization with „protective“ (anti-fouling, fouling-release) nanolayers is most relevant (and already done at industrial scale); careful adaptation to the respective application and membrane barrier structure are necessary.

Integration of adsorber or catalytic properties via functional nanoparticles into separation membranes is a parallel approach.

Next generation membranes will comprise:
- **stimuli-responsive surfaces or pores**
- **functional nanochannels (e.g., carbon nanotubes)**

Acknowledgements

… to the group

… to collaborators & their group:

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Prof. Dr. V. Freger
Ben-Gurion University, Israel

Essen, June 2011.

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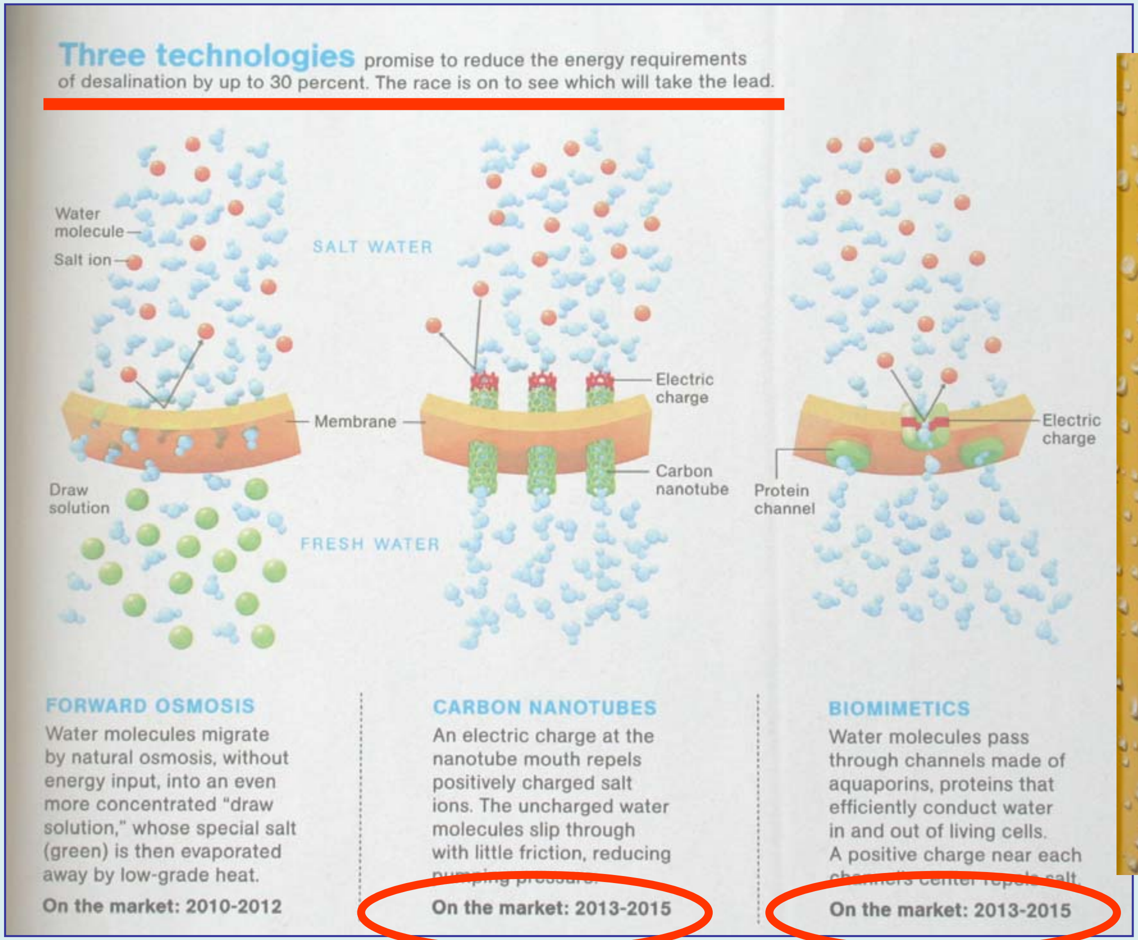
Bio-inspired nanotechnology:

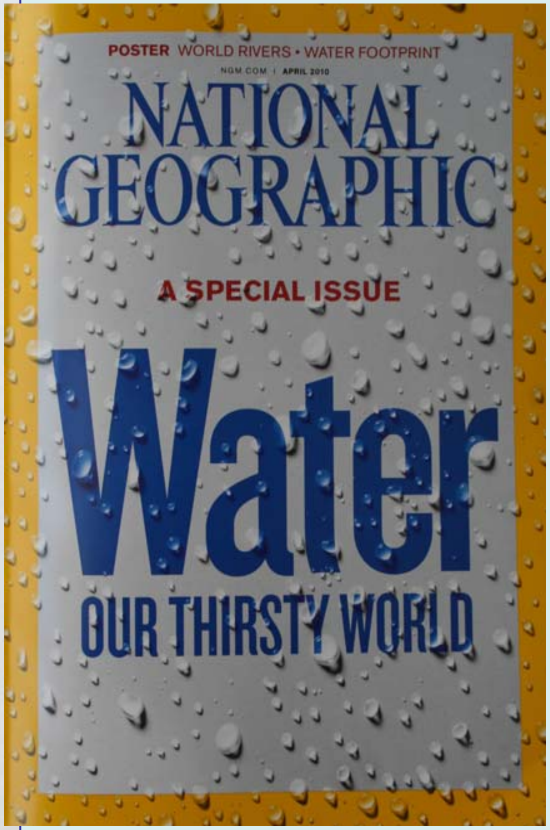
maximize selectivity at high permeability


Three technologies promise to reduce the energy requirements of desalination by up to 30 percent. The race is on to see which will take the lead.

FORWARD OSMOSIS
Water molecules migrate by natural osmosis, without energy input, into an even more concentrated "draw solution," whose special salt (green) is then evaporated away by low-grade heat.
On the market: 2010-2012

CARBON NANOTUBES
An electric charge at the nanotube mouth repels positively charged salt ions. The uncharged water molecules slip through with little friction, reducing pumping pressure.
On the market: 2013-2015

BIOMIMETICS
Water molecules pass through channels made of aquaporins, proteins that efficiently conduct water in and out of living cells. A positive charge near each channel's center repels salt.
On the market: 2013-2015



April 2010