2.500 Desalination and Water Purification

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Amphiphilic Graft Copolymers for Nanofiltration Membranes with Tunable Pore Size

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The waterCAMPWS
The Center of Advanced Materials for the Purification of Water with Systems

ONR Office of Naval Research

NF membranes

- Size cut-off 0.5-10 nm
  - Size scale of molecules
- Uses
  - Water treatment
  - Food industry
  - Pharmaceutical industry
  - Chemical industry
  - Textile industry
- Limitations
  - Low flux
  - Fouling
  - Wide pore size distribution

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Molecular sieves and size-selective NF membranes

- Commercial NF
  - negatively charged → selectivity not based on size
- Different approaches

Images removed due to copyright restrictions. Please see: Fig. 1a in Jirage, Kshama B., John C. Hulteen, and Charles R. Martin. "Nanotubule-Based Molecular-Filtration Membranes." *Science* 278 (October 1997): 655-658.

Scheme 1 in Czaplewski, Kenneth F., Joseph T. Hupp, and Randall Q. Snurr. "Molecular Squares as Molecular Sieves: Size-Selective Transport Through Porous-Membrane-Supported Thin-Film Materials." *Advanced Materials* 13 (December 2001): 1895-1897.

Fig. 1 in Zhou, Meijuan, et al. "Supported Lyotropic Liquid-Crystal Polymer Membranes: Promising Materials for Molecular-Size-Selective Aqueous Nanofiltration." *Advanced Materials* 17 (2005): 1850-1853.

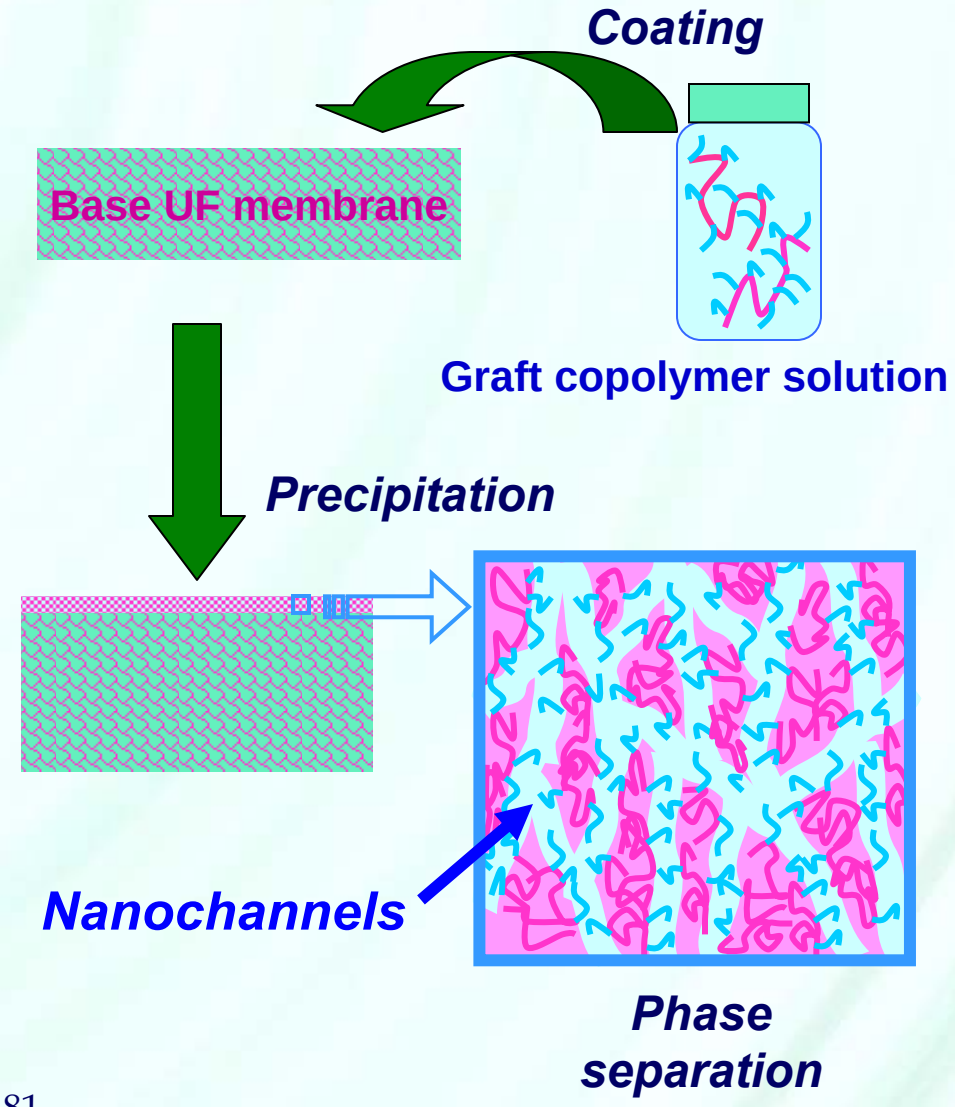
Jirage *et al.*, 1998 Czaplewski *et al.*, 2001 Zhou *et al.*, 2005

- Common drawbacks
  - Difficult to manufacture
  - Very low flux

Graft copolymers for size-selective NF membranes

- Thin film composite membranes: graft copolymer as selective layer
  - Hydrophobic backbone (PVDF)
  - Hydrophilic side-chains (PEG)

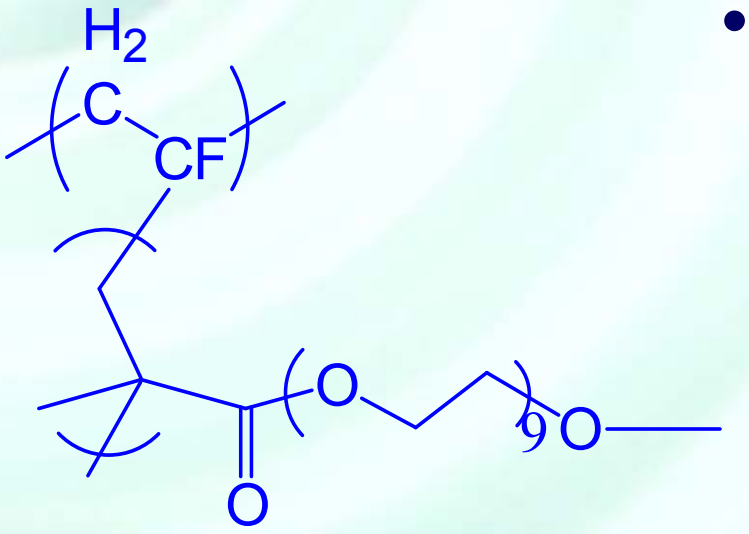
- Microphase separation → "nanopores"[1]
- Hydrophilic side-chains form interconnected "nanochannels"
- Uncharged → separation based on size
- Complete resistance to irreversible fouling[2]



[1]Akthakul et al., *Macromolecules* (2004) **37** , 7663

[2]Asatekin et al., *Journal of Membrane Science* (2006) **85**, 81

Graft copolymer: PVDF-*g*-POEM

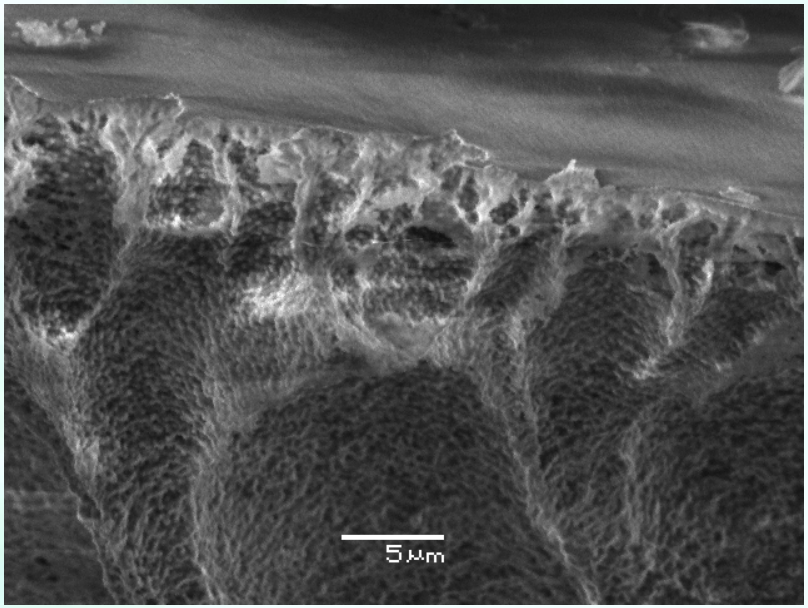


- PVDF-*g*-POEM
  - Poly(vinylidene fluoride) (PVDF) backbone – semi-crystalline, very hydrophobic
  - Effective poly(ethylene glycol) side-chains
  - M_n~180 kg/mol, 40 wt% POEM
  - Insoluble in water
  - Synthesized by ATRP-like reaction[1]

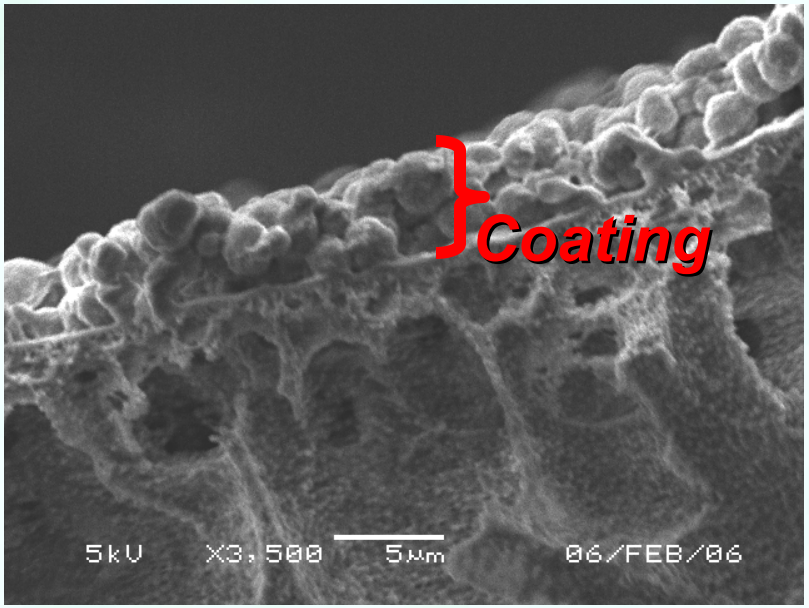
[1]Hester et al., *Macromolecules* (2002) **35** , 7652

SEM

Base

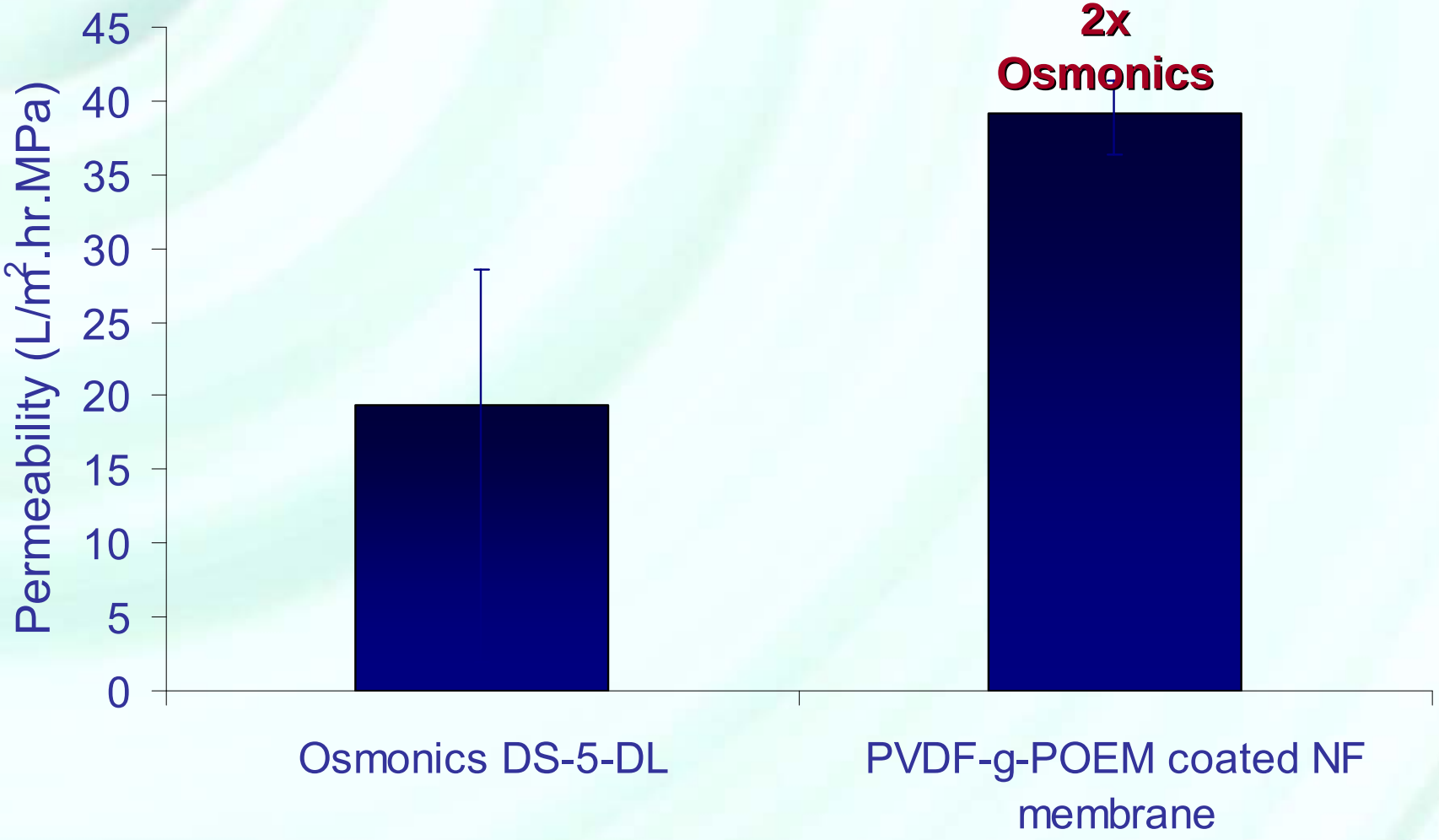


Coated



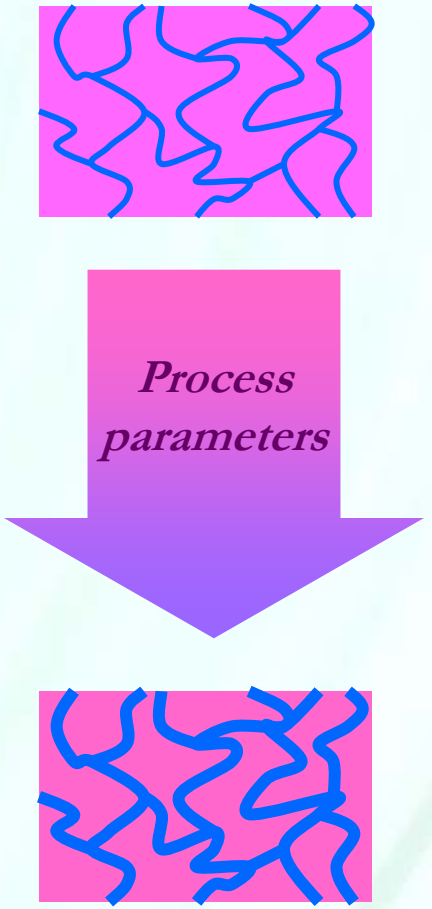
Coating thickness ~2 µm

Pure water permeability

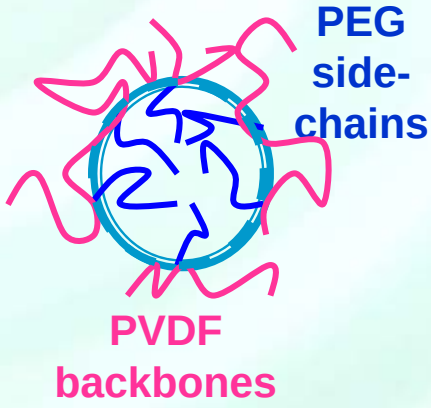


Tunable pore size

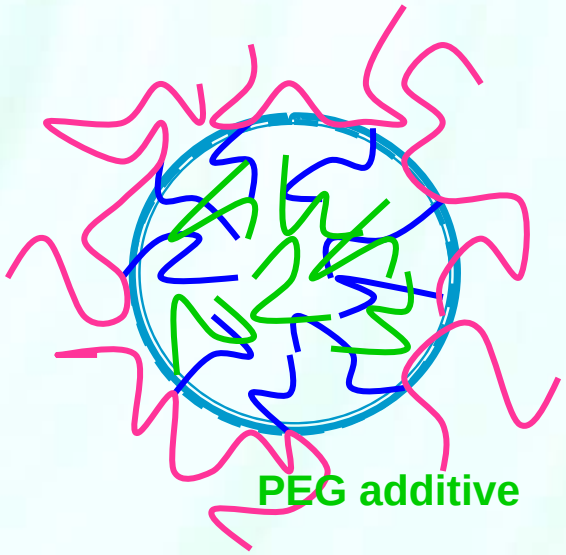
- Tuning channel size with simple processing parameters
  - Easy modification for different separations
  - Extends the range of applications
- What makes the pore size tunable?
  - Microphase separation ⇨ Pore size
- Possible parameters
  - During membrane manufacture
    - PEG addition to casting solution
    - Casting bath non-solvent
  - After membrane is manufactured
    - Solvent quality of the feed



Method 1: PEG addition to casting solution – During manufacture

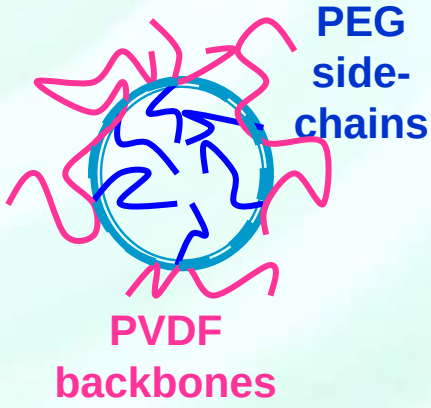


Without PEG addition

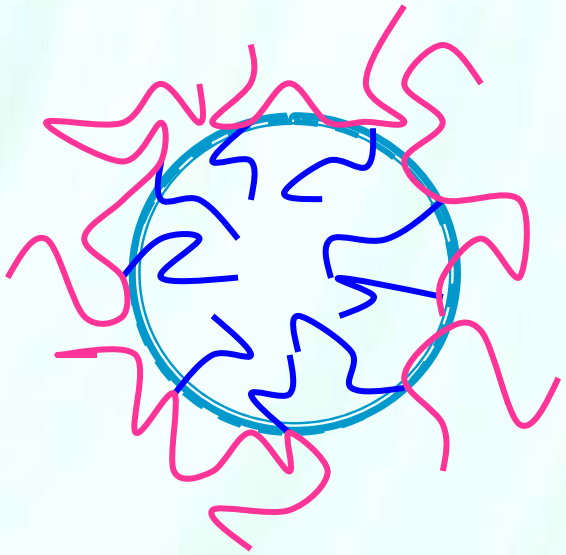


With PEG addition

Method 1: PEG addition to casting solution – During manufacture



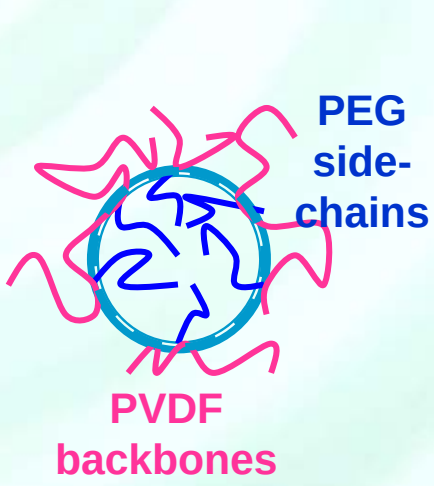
Without PEG addition



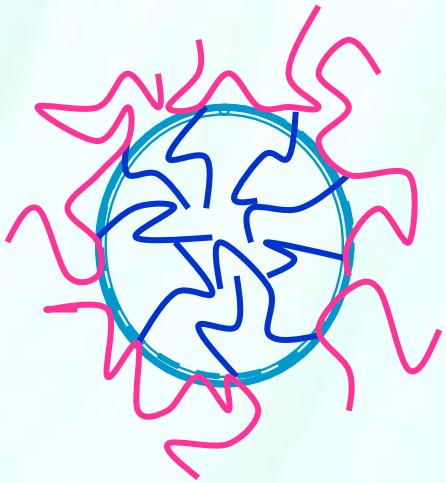
With PEG addition

Wider channels

Method 2: Changing non-solvent bath – During manufacture

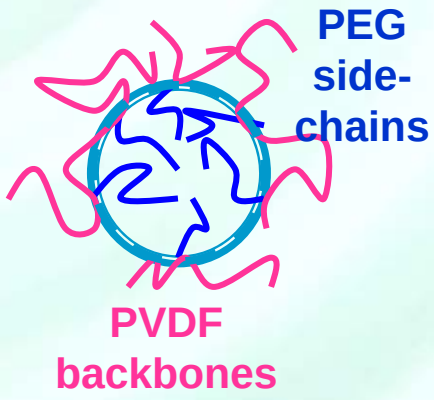


Isopropanol



Ethylene glycol

Method 2: Changing non-solvent bath – During manufacture



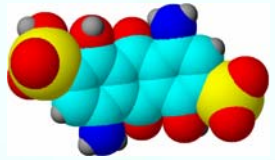
Isopropanol

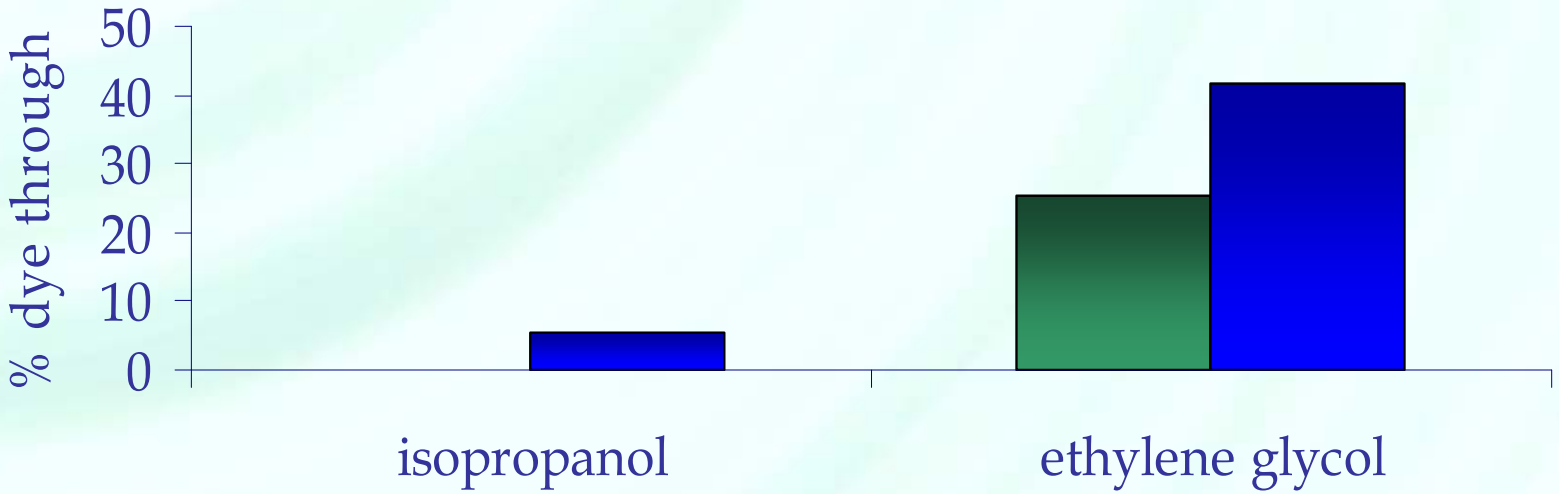
Ethylene glycol

Wider channels

Pore size tuning during manufacture: Results

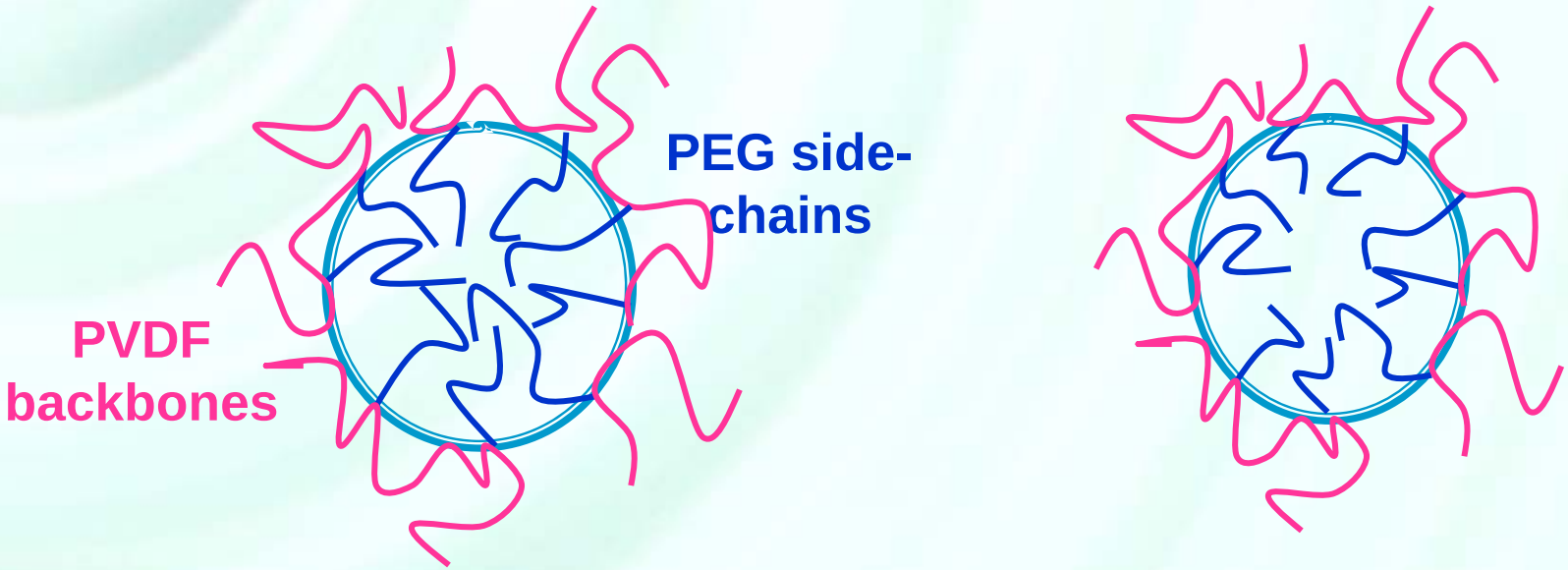
Acid blue 45 - 474 g/mol, 8.41 Å





PVDF-g-POEM contains 48 wt% POEM, tests performed at 150 psi

Method 3: Changing feed solution chemistry – After manufacture



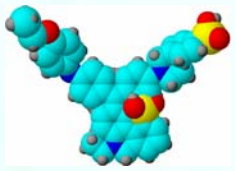
Water → swollen PEG chains

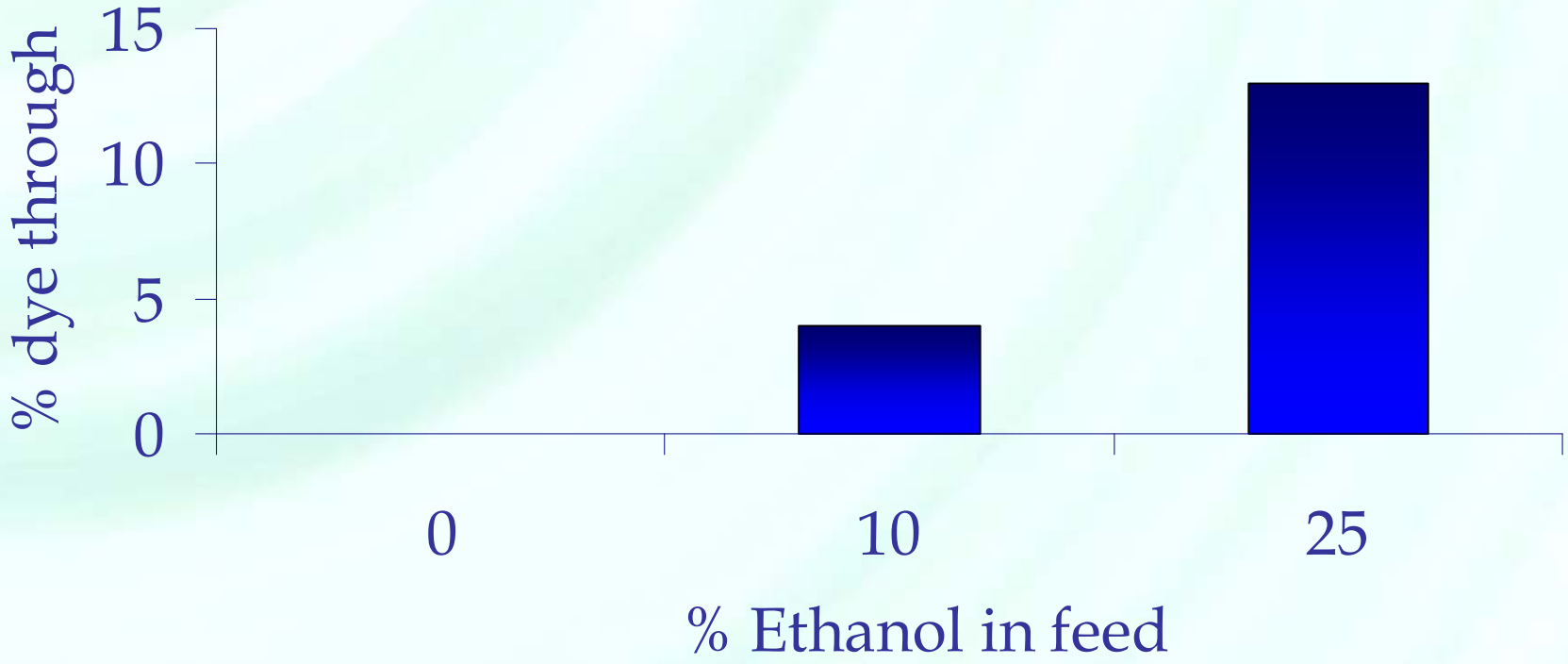
Poorer solvent → collapsed PEG chains

⇨ ***Same membrane for different separations***

Method 3-a: Addition of a poor solvent (ethanol) to feed

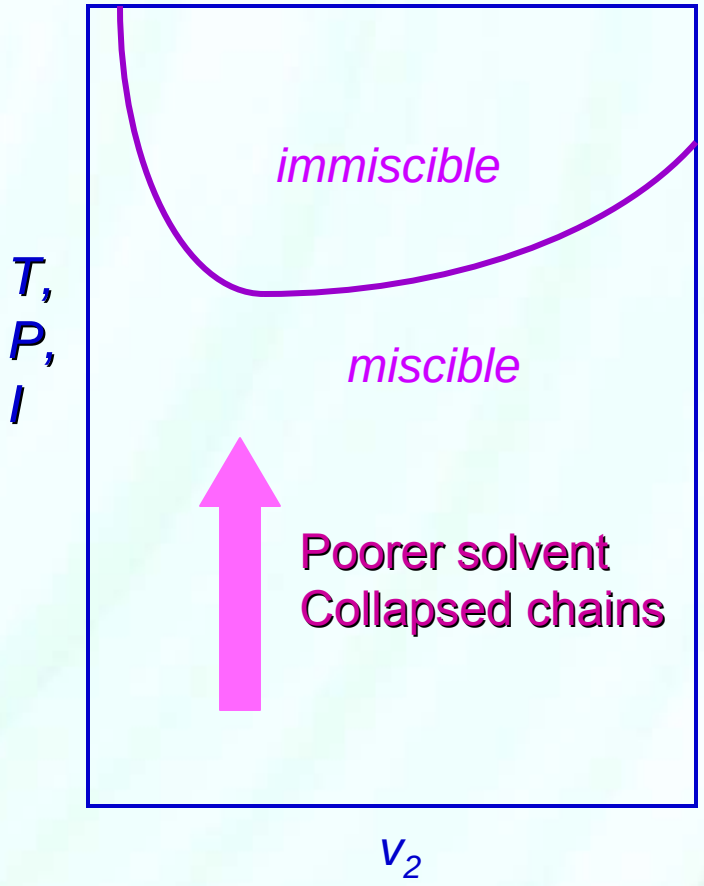
Brilliant blue R - 826 g/mol, 11.08 Å





Method 3-b: Changing the temperature and pressure

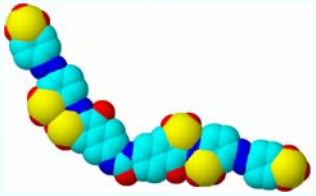
- PEG dissolves because it fits into the H-bonded structure of water
- Disturbed water structure → lower solvent quality
  - Increasing temperature
  - Increasing pressure
  - Increasing ionic strength
- ⇨ Higher temperature & pressure ⇨ larger pores

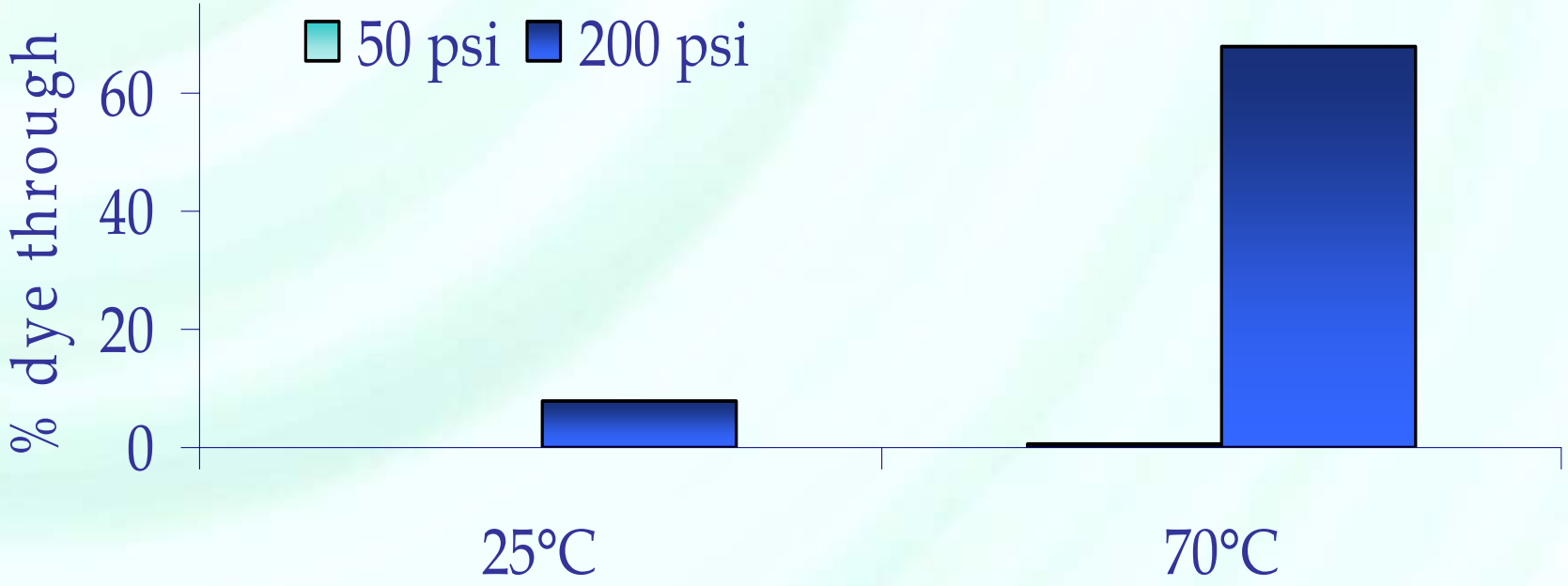


Phase diagram for PEG/water

Method 3-b: Changing the temperature and pressure

Direct red 80 - 1373 g/mol, 10.73 Å





★ 0% → 68% using the same membrane, changing only temperature and pressure!!!

Conclusions

- **PVDF-*g*-POEM coated NF membranes**
  - Uncharged nanochannels ⇨ size selectivity
  - **Pore size tuning** by simple process parameters
    - During casting
    - After manufacture, by changing feed parameters
  - Easy to manufacture
  - High flux
  - Applicable in food and pharmaceutical industries

Acknowledgements

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