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Thin film membranes for molecular separations

Andrew Livingston
Imperial College London, London SW7 2AZ UK, a.livingston@ic.ac.uk

Thin Film Membranes for Molecular Separations

Separations Technology IX: New Frontiers in Media, Techniques, and Technologies
March 5-10, 2017, Algarve, Portugal

Andrew Livingston

Barrer Centre
Department of Chemical Engineering
Imperial College London

- Organic Solvent Nanofiltration (OSN)
- OSN Membranes – aging and operation temperature
- OSN Membranes – higher permeance
- OSN – speedy membranes, fast processes?
- Concluding remarks

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Organic Solvent Nanofiltration (OSN)

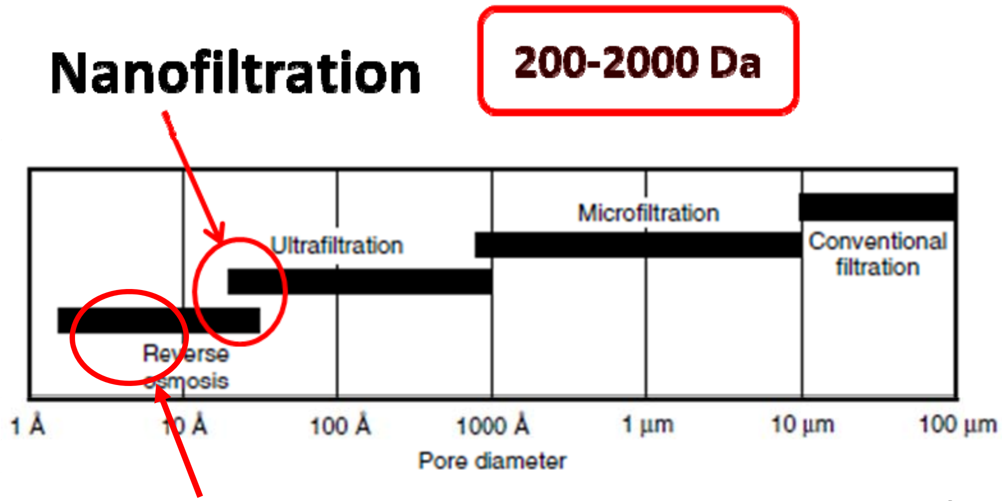
- Water processing - Desalination – Reverse Osmosis (RO) dominates the market over multiple effect evaporation (high energy).
- Can membranes produce the same paradigm change for organic liquids processing?

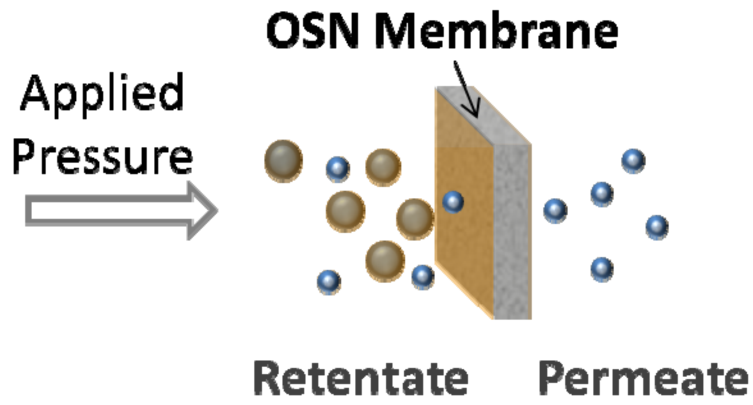
World Scale RO Plants
100,000 – 300,000 $m^3\ d^{-1}$

World Scale Oil Refineries
50,000 – 100,000 $m^3\ d^{-1}$

Organic Solvent Nanofiltration (OSN)

OSN → Emerging membrane technology for separation and purification processes involving organic solvents.





Organic Solvent Reverse Osmosis OSRO – Ryan Lively – Science 335 (2016) pp 804-807

OSN membranes must preserve their separation characteristics in contact with **organic solvents**.

Organic Solvent Nanofiltration (OSN)?

First Generation OSN Membranes - Polyimides

- Stable in non-polar solvents such as toluene, heptane, ethyl acetate (Steve White and colleagues)
- Largest industrial success so far has been W.R. Grace's lube oil dewaxing process at ExxonMobil Beaumont Refinery using polyimide OSN membranes (operational in 2001)

- Capacity ***11,000 m^3 d^{-1}*** solvent
- Project cost $6 million in 2000
- Net benefit $6 million per annum

Lube Oil Dewaxing Unit at ExxonMobil Beaumont Refinery

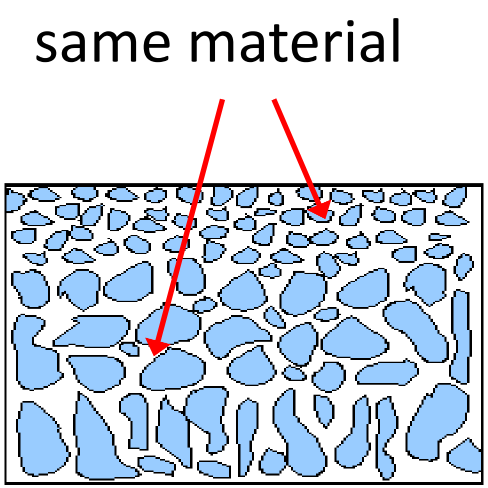
Organic Solvent Nanofiltration (OSN)
Challenges for Molecular Separations in Organic Systems

- **OSN Membranes**
  - **Achieve chemical stability in solvents,** including in acidic and basic organic solutions, and at high T
  - **Enhance permeance to reduce required membrane area**
  - Reduce flux decline over service lifetime (aging, fouling)
  - Improve separation accuracy
- **OSN System Engineering**
  - **Membrane transport modelling**
  - Improve separation accuracy
  - Process simulation and modelling
  - Concentration polarisation and module design

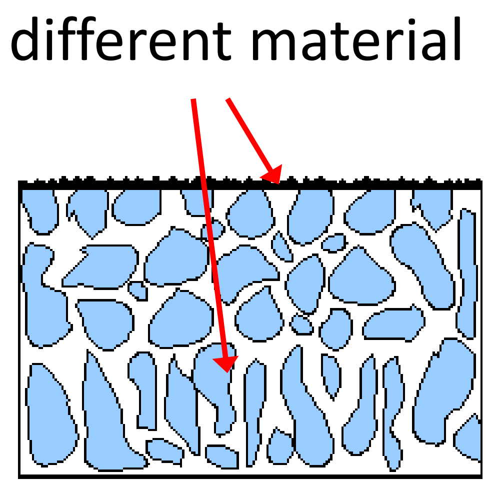
■ Lots of focus since 2000 ■ Little focus since 2000

OSN Membrane Fabrication

Integrally skinned asymmetric (ISA) membrane
ONE step process



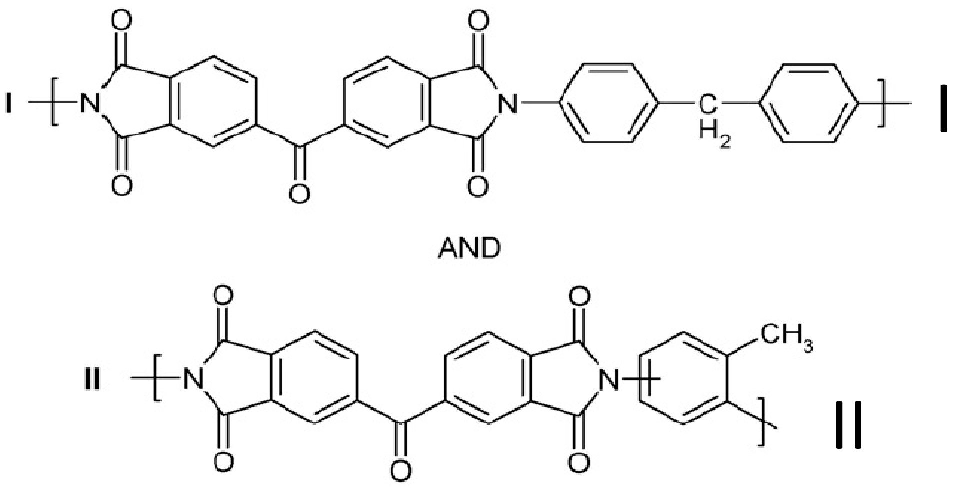
Thin Film composite (TFC) membrane
MULTIPLE step process



ORGANIC SOLVENT NANOFILTRATION (OSN)
Membrane Fabricatrion

ORGANIC SOLVENT NANOFILTRATION (OSN)
Membrane Fabrication

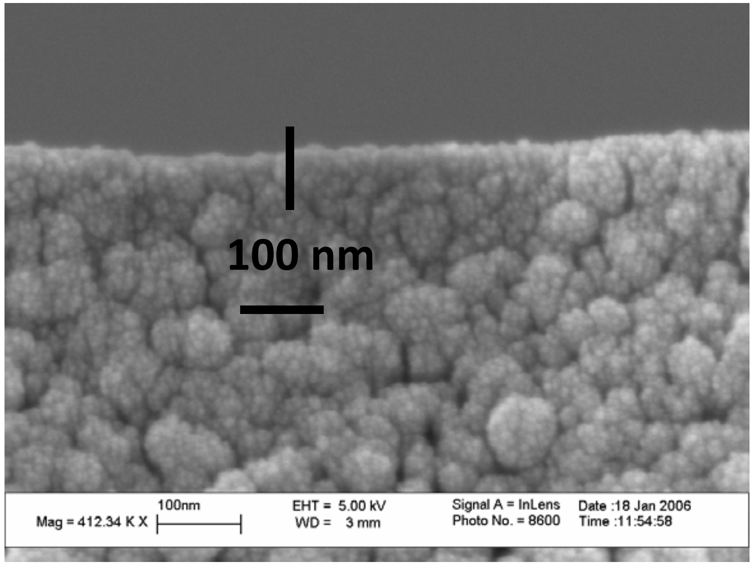
Integrally skinned asymmetric membranes from P84 polyimide

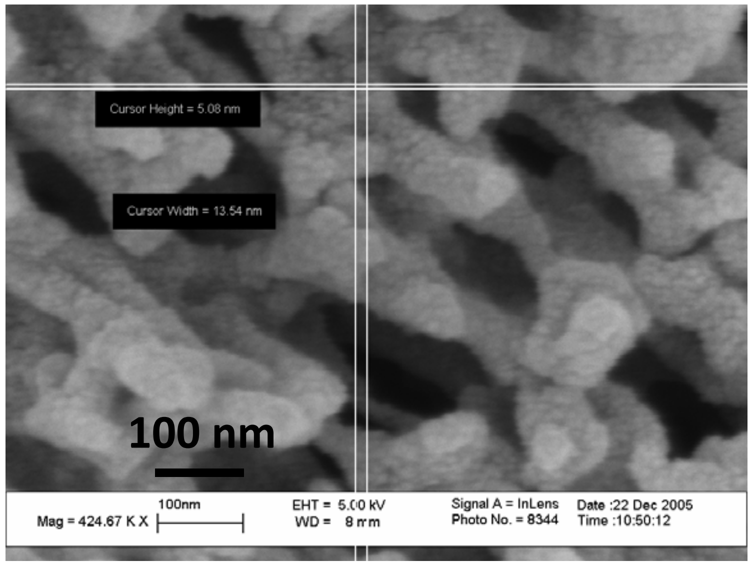


P84 polyimide

20% I

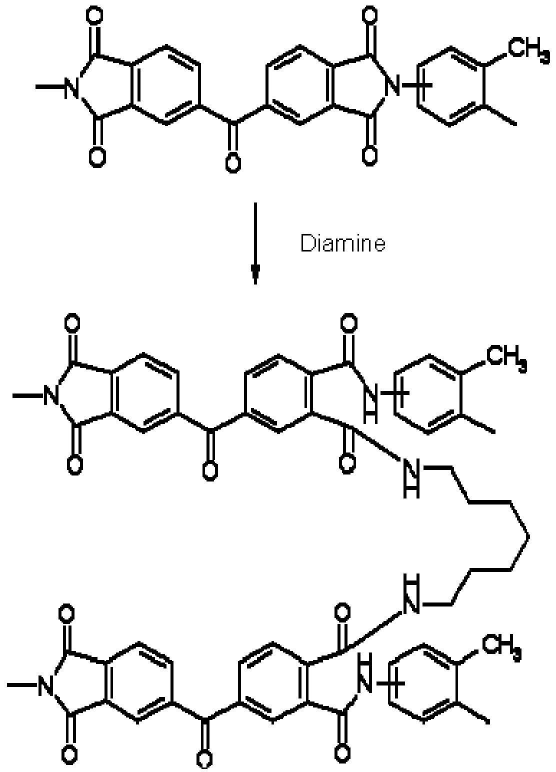
80% II





OSN Membrane Fabrication : Chemical Stability

Post-formation cross-linking of polyimide membranes via diamines using established chemistry



Non-crosslinked P84

BEFORE

AFTER IMMERSION IN DMF

Crosslinked P84

BEFORE

AFTER IMMERSION IN DMF

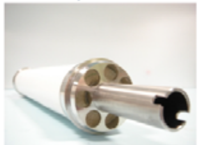
See-Toh et al., J. Membr. Sci. **301** (2007) 1-10

Development of Crosslinked PI OSN Membranes

1990-2000
Max Dewax
STARMEM™ Polyimide membranes

Membrane Extraction Technology (MET), Imperial Spin-out company, licensed OSN technology from Imperial College and developed the **DuraMem™** range

STEP 1: Dope Solution Preparation → STEP 2: Membrane Casting → STEP 3: Chemical Crosslinking → STEP 4: Membrane Drying → STEP 5: Membrane Element Fabrication → STEP 6: Quality Control



- DuraMem™ membrane cartridge
- ALL components are solvent stable
- Cartridges are leak free
- RSF – Regulatory Support File

MET

2007-2008 MET Ltd
Scaleup Crosslinked PI Duramem™

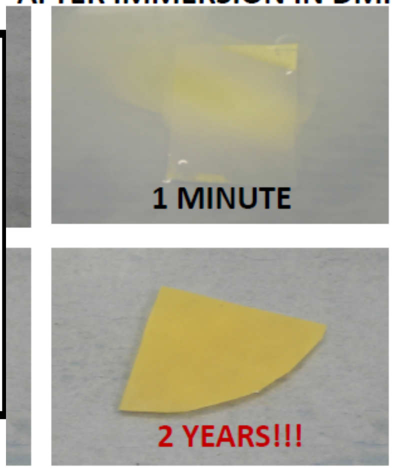
Evonik MET Ltd

- MET acquired by Evonik AG 1 March 2010
- Evonik have invested in new facilities and space for production of membranes and membrane modules
- Operational since June 2012
- Fabrication of a range of membranes and modules up to 8" x 40" spiral modules

2010 Evonik Acquisition of MET Ltd

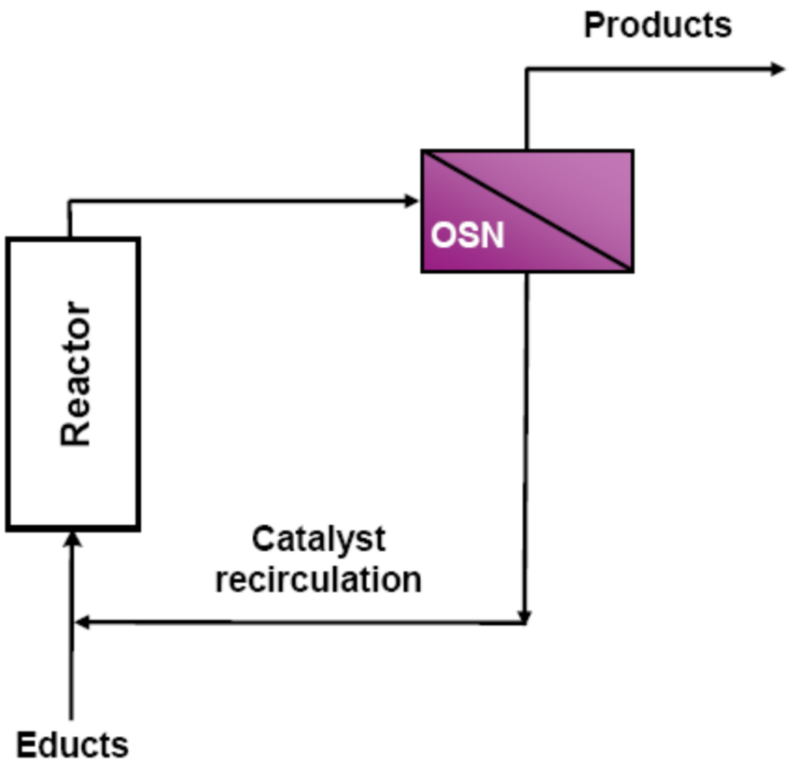
2006-2007
Invention of Crosslinked Polyimide Membranes
US Patent 8,894,859

AFTER IMMERSION IN DMF



2008 onwards
Duramem™ Commercial Installations

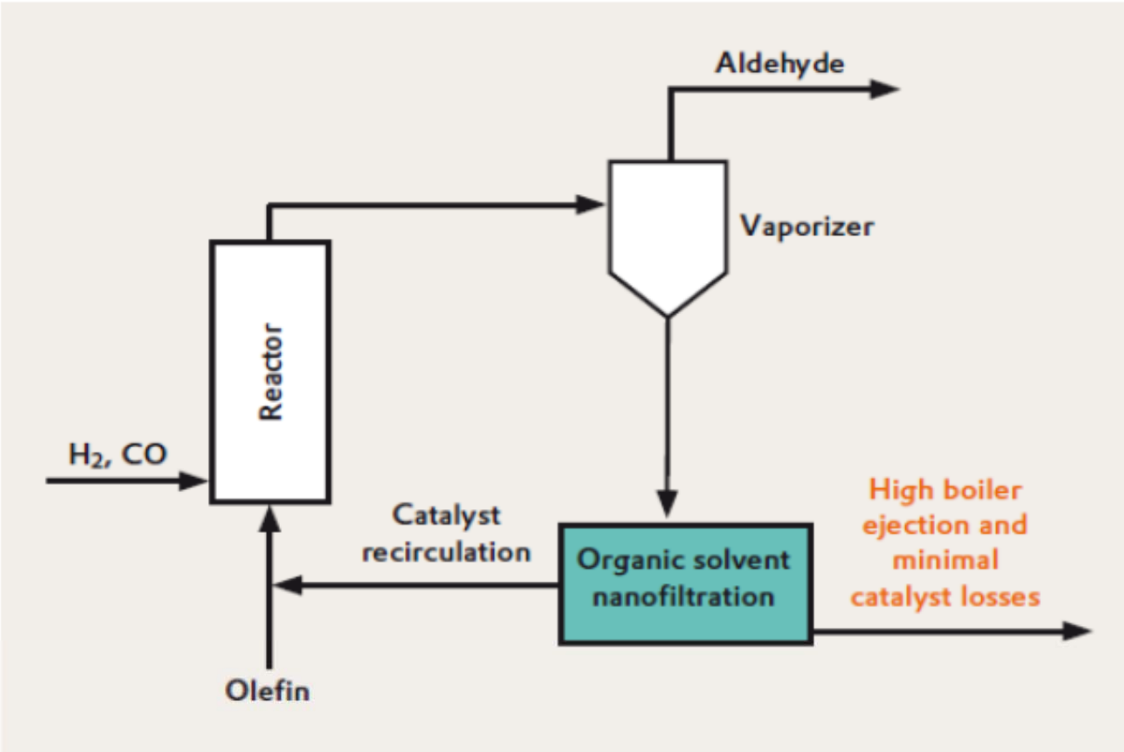
CASE STUDY @ Evonik
Recycling of homogeneous catalysts

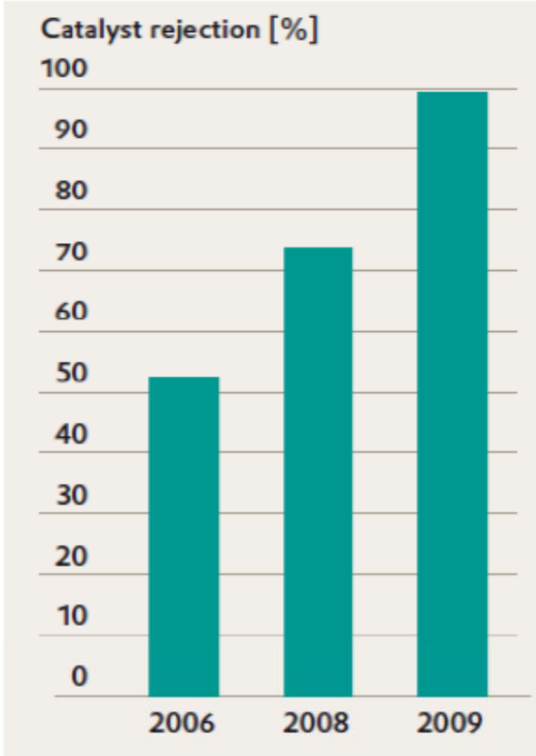


Processes …

- Metathesis
- Suzuki coupling
- palladium catalyzed cross-coupling
- Hydroformylation
- Telomerisation
- …….

Evonik Innovations Award 2010
Benefit: OSN recovers homogeneous catalyst



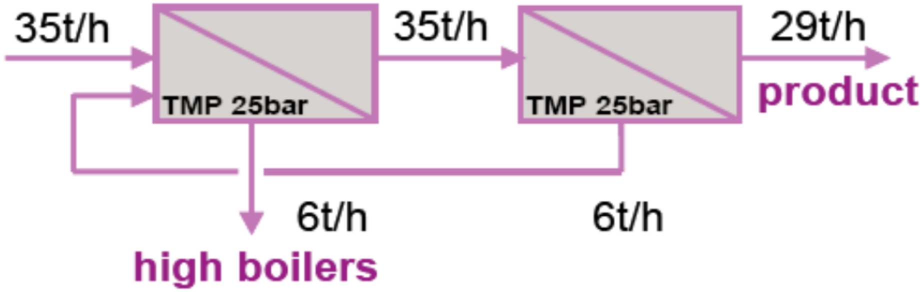


OSN customer benefit: Energy savings

Membrane process:

Membrane costs: 220 T€/a

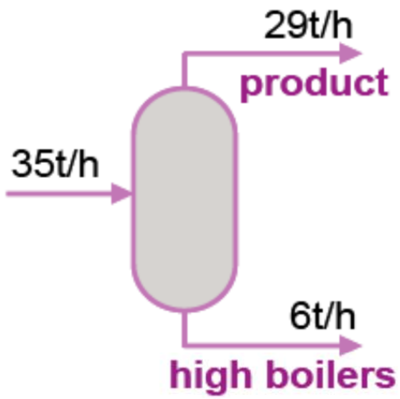
Investment costs: 1,7 Mio. €



Thermal separation

Energy costs: 1,2 Mio. €/a

Investment costs: 2,2 Mio. €



OSN

→ **30% lower investment costs**
→ **75% lower operational costs**

} **Savings > 1 Mio. €/a**

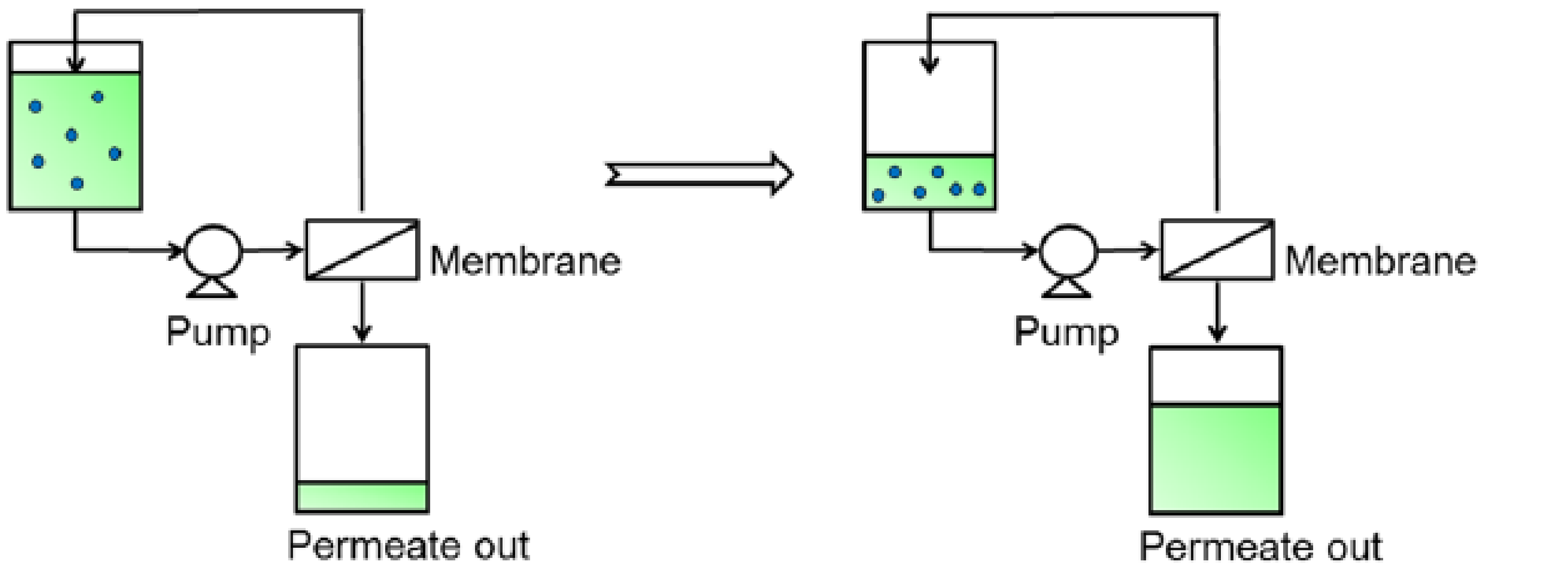
OSN – APPLICATIONS IN REFINING AND CHEMICALS

KEY POINTS

- OSN is an emerging technology in the large scale refining and chemicals sector
- In this sector, plants may cost > £1 million, and membrane replacement may average > £0.2 million per annum
- Since plants are high capital cost, and since membrane replacement costs and downtime costs are signifciant, applications in this sector have been characterised by long pilot testing periods
- For example, development of MaxDewax™ started in 1993, plant finally installed in 1999.
- Applications in this sector are likely to have a major long term impact on the energy efficiency of refining and chemicals processing

OSN – APPLICATIONS IN PHARMACEUTICALS
Concentration

(a) Concentration *Defining feature: at least **one solute** and **one solvent***



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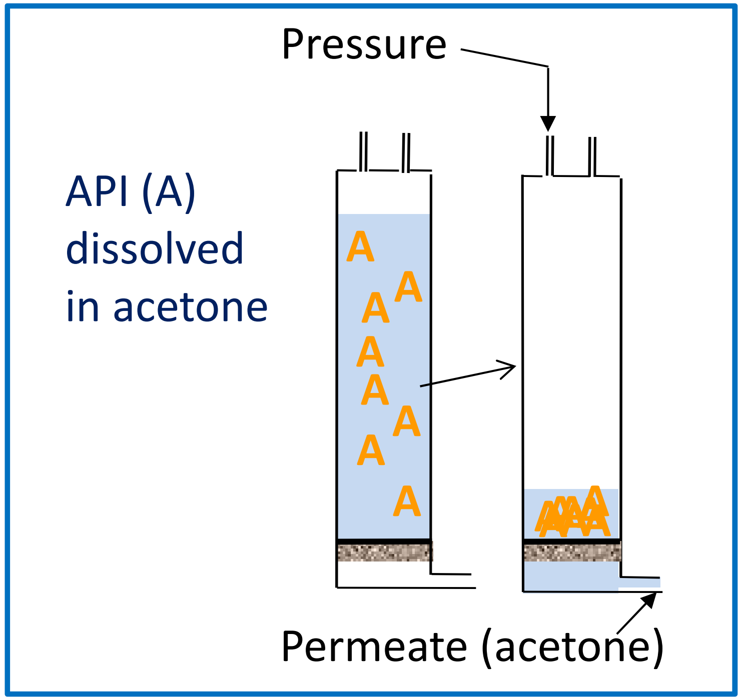
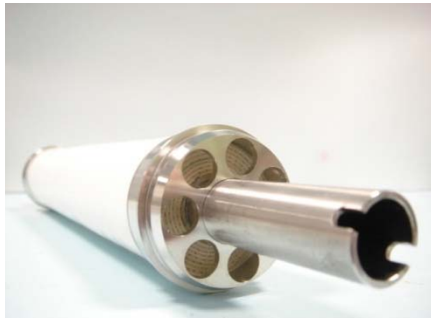
API Recovery/Concentration

Process Scale Example: Product Recovery

- Acetone solution containing ~1 wt% of valuable, final API (MW=420 g/mol)
- Nanofilter solution at sub-ambient temperature so that ~90% of volume passes through membrane, retain ~10% starting volume
- Final retentate ~10wt% API recycled
- Key issues addressed – stability of membrane and module components; satisfy regulatory requirements for GMP

Product Concentration Filtration





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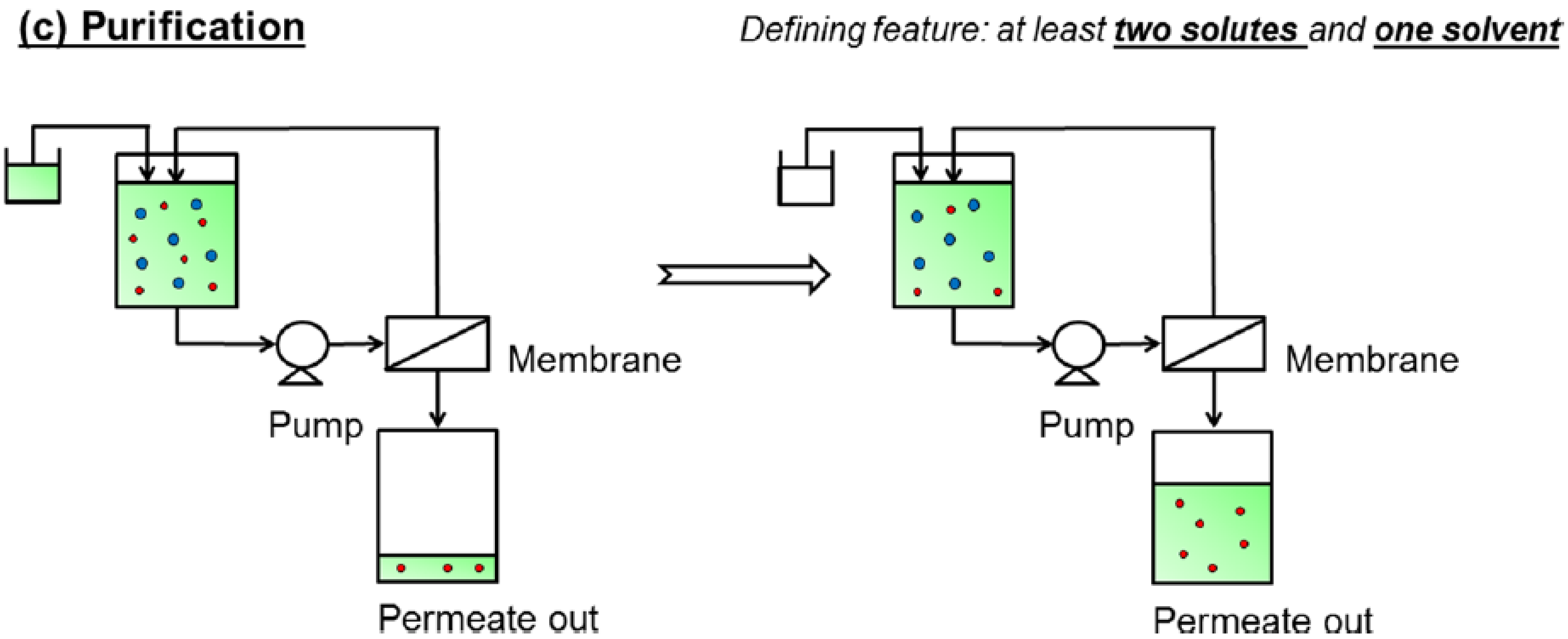
OSN – APPLICATIONS IN PHARMACEUTICALS
Purification



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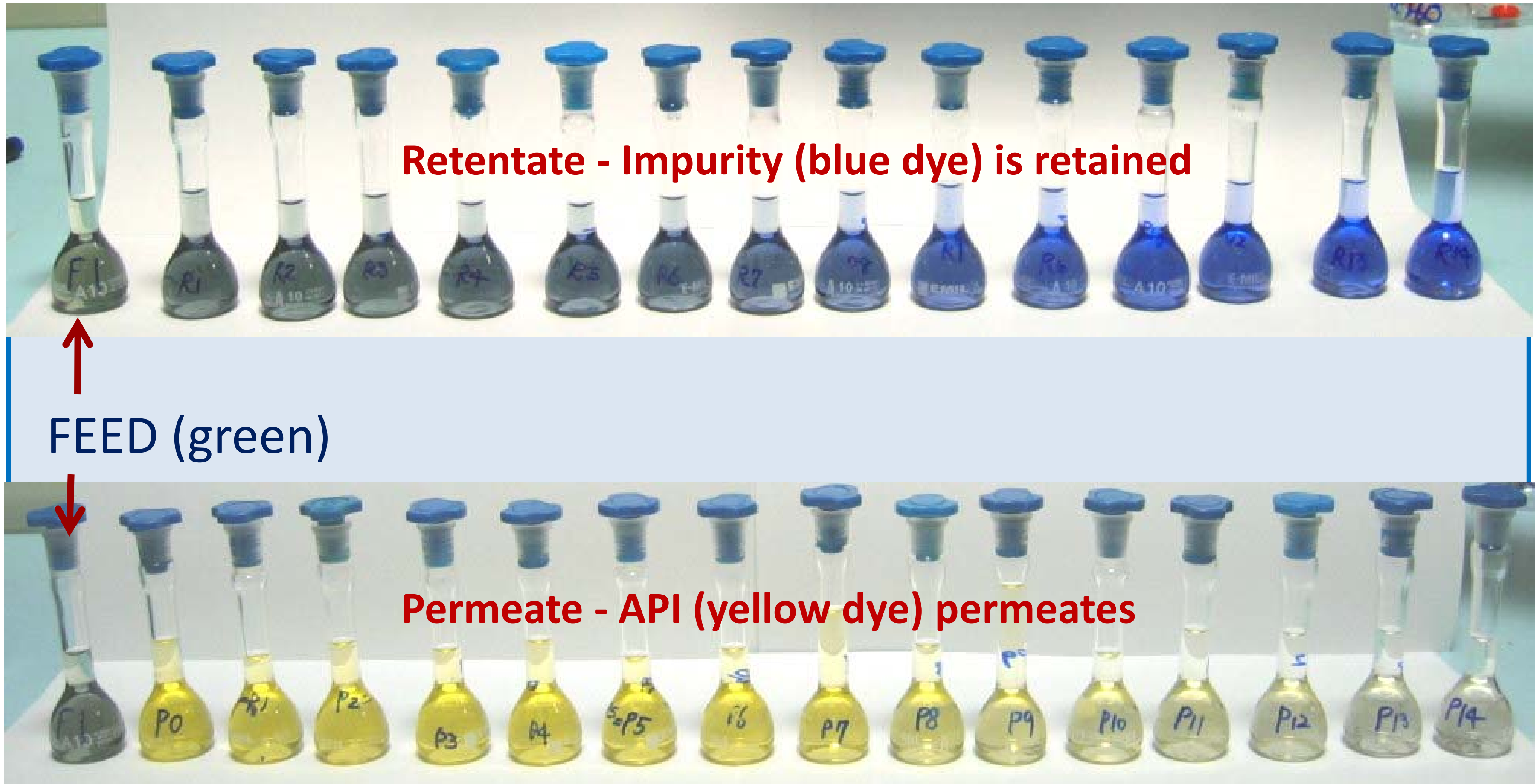
OSN – APPLICATIONS IN PHARMACEUTICALS
Purification

Constant Volume Diafiltration → separate model API (yellow dye, MW=274) from model large Impurity (blue dye, MW=826) in methanol.



OSN – APPLICATIONS
Purification by Diafiltration

- Separation of coloured impurity from API at Astra Zeneca by OSN *

(3a) Starting material containing high MW coloured compound

(3b) Coloured impurity difficult to remove via extraction

(3c) Product after OSN purification. Nice white powder!

Nanofilter solution so that API passes through membrane with solvent and impurity is retained

The Chemical Engineer, August 2006

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OSN APPLICATIONS: Molecular Fractionation
Can membranes replace distillation columns?

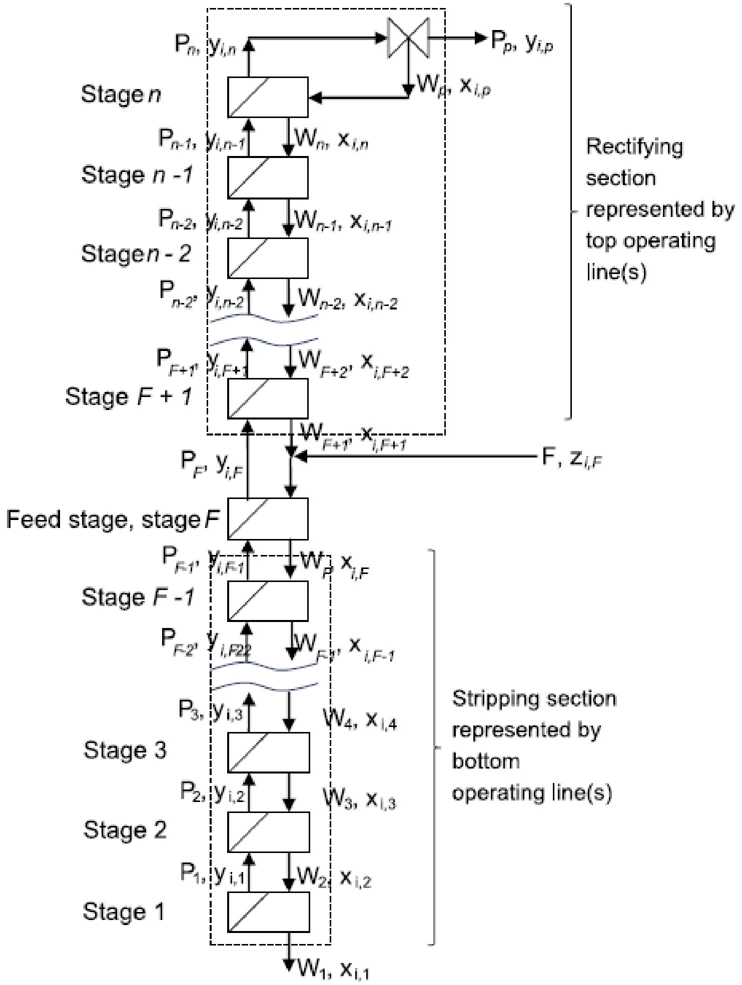
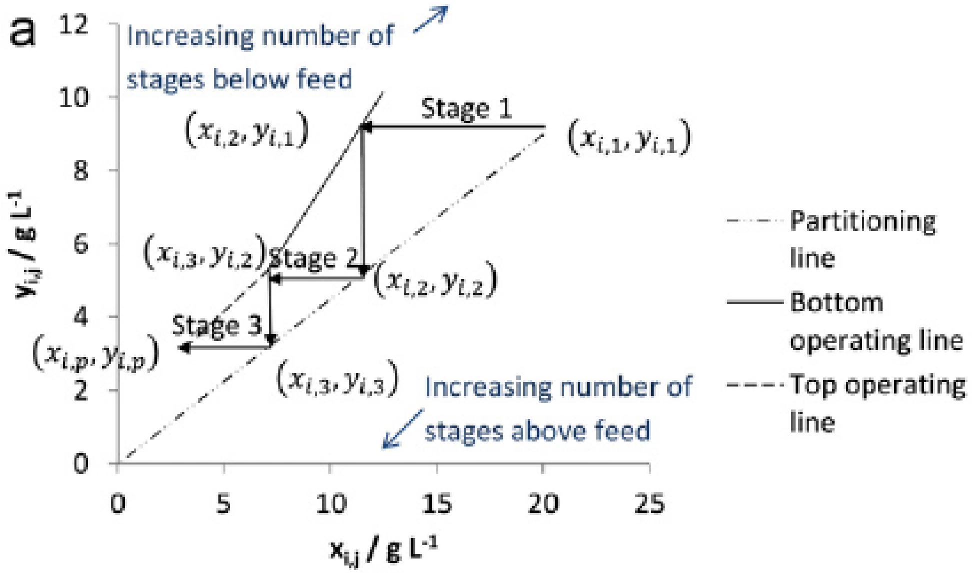


Fig. 4. Schematic of a multipass membrane cascade with n stages. Cascade stages in the rectifying section decrease solute content in the recovered solvent while stages in the stripping section enrich solute content in the concentrate stream. In this cascade, $x_{i,product} = x_{i,1}$ and $y_{i,product} = y_{i,p}$.



Isothermal Refining – Liquid phase fractionation of hydrocarbon streams at constant T

Siew et. al., Chem.Engng.Sci. 90 (2013), 299-310

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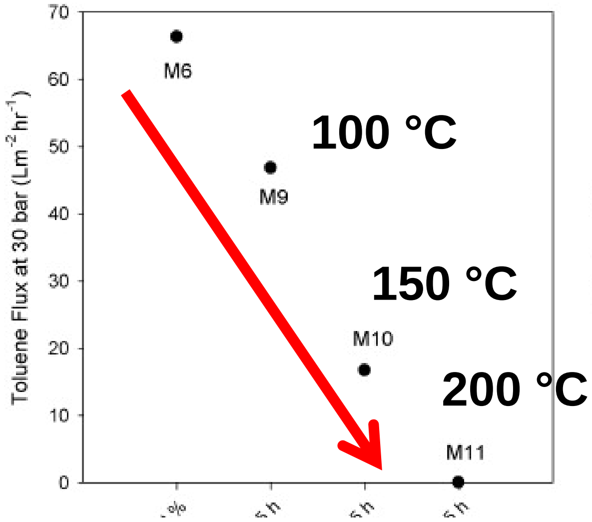
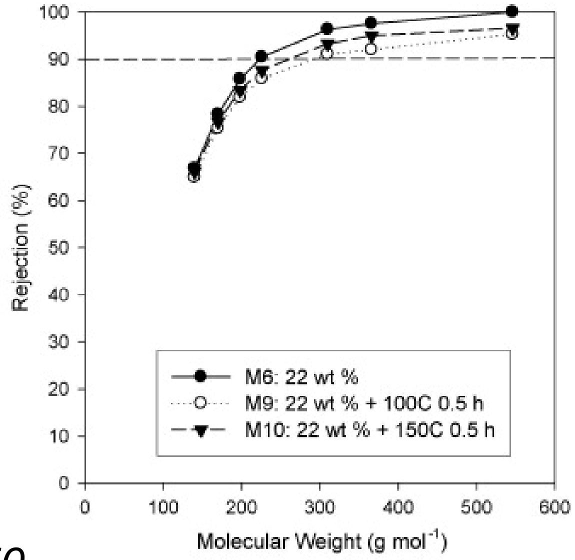
Physical aging in ISA Polyimide P84 membranes

Polymers “frozen” in a non-equilibrium state relax over time, compressing and clogging permeation pathways.

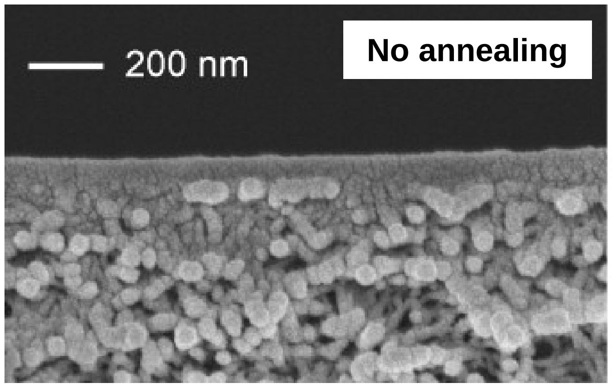
Annealing for 30 min

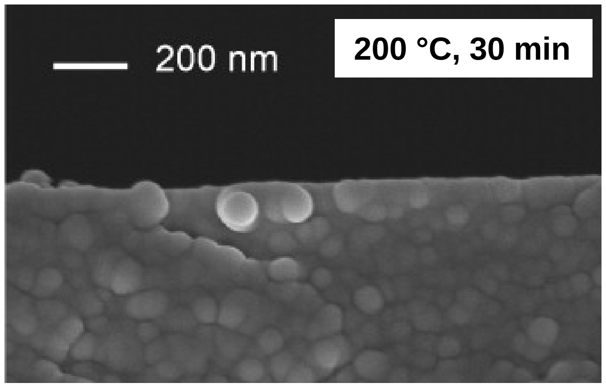


MWCO curves for PS/toluene at 30 bar

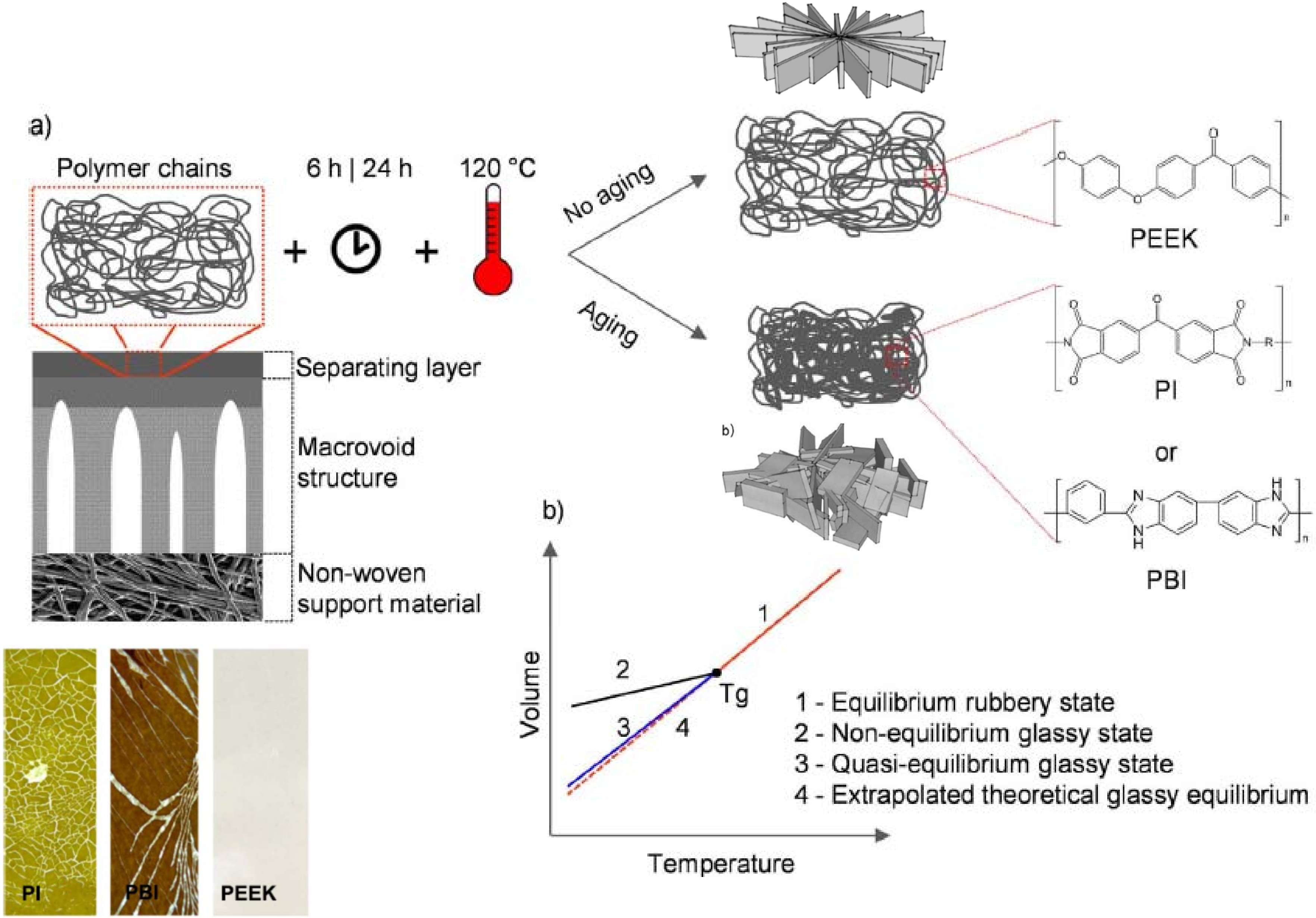


Y.H. See-Toh et. al., JMS, 299 (2007) 236-250

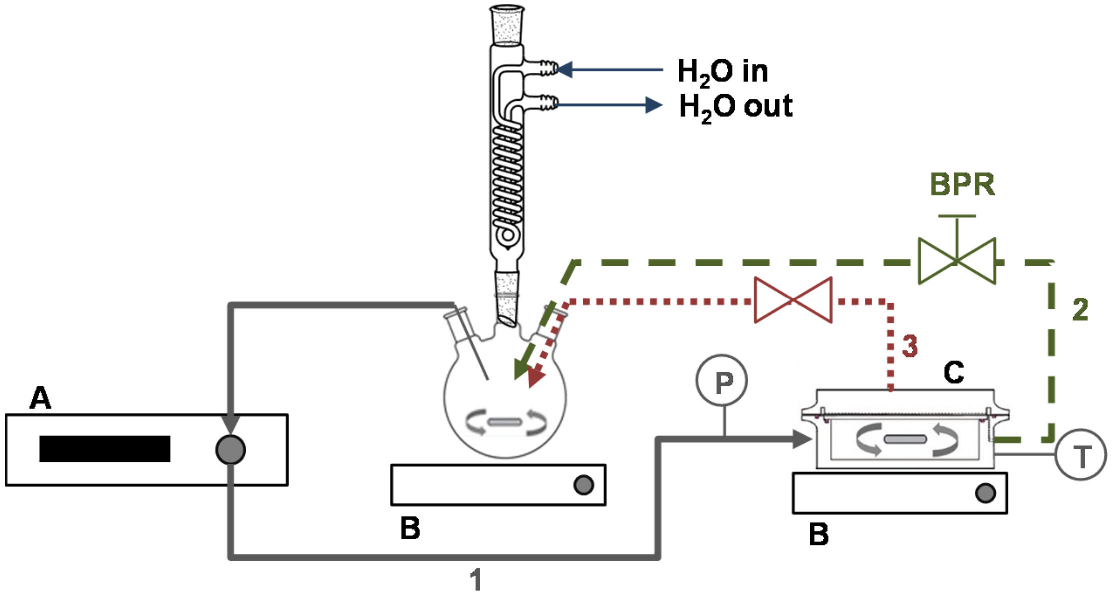


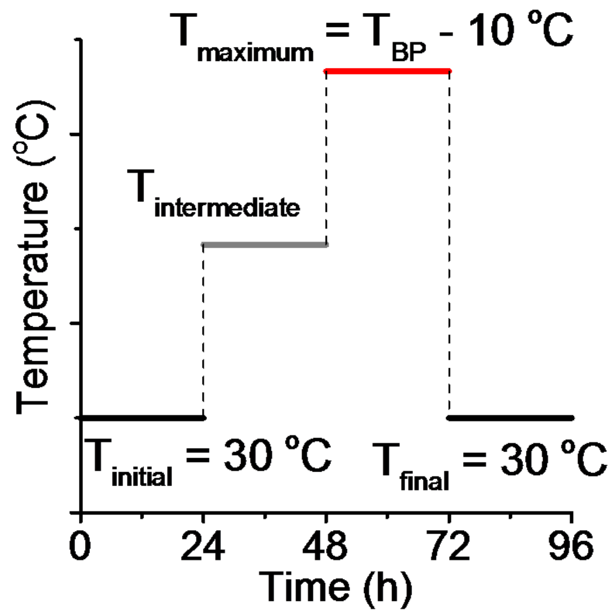


Physical Aging - Integrally Skinned Asymmetric Membranes



Polyether ether ketone (PEEK) membranes – high T filtration





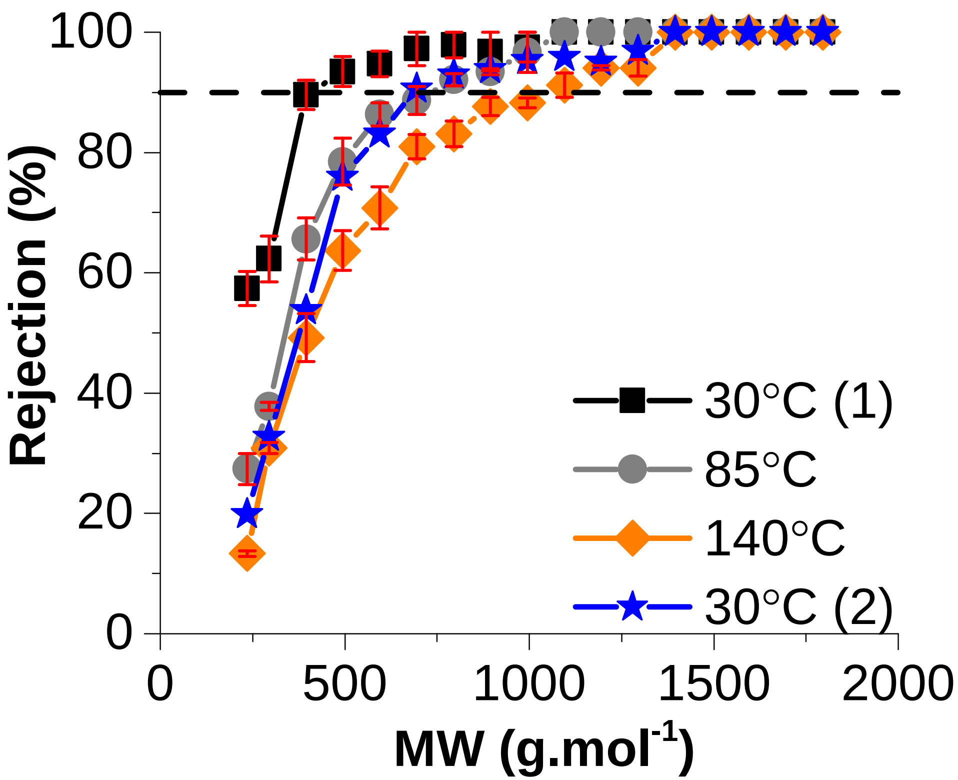
High temperature cross-flow rig
A: HPLC pump; **B:** hot stirring plate;
C: cross-flow cell; **P:** pressure gauge;
T: thermocouple;
BPR: back pressure regulator.

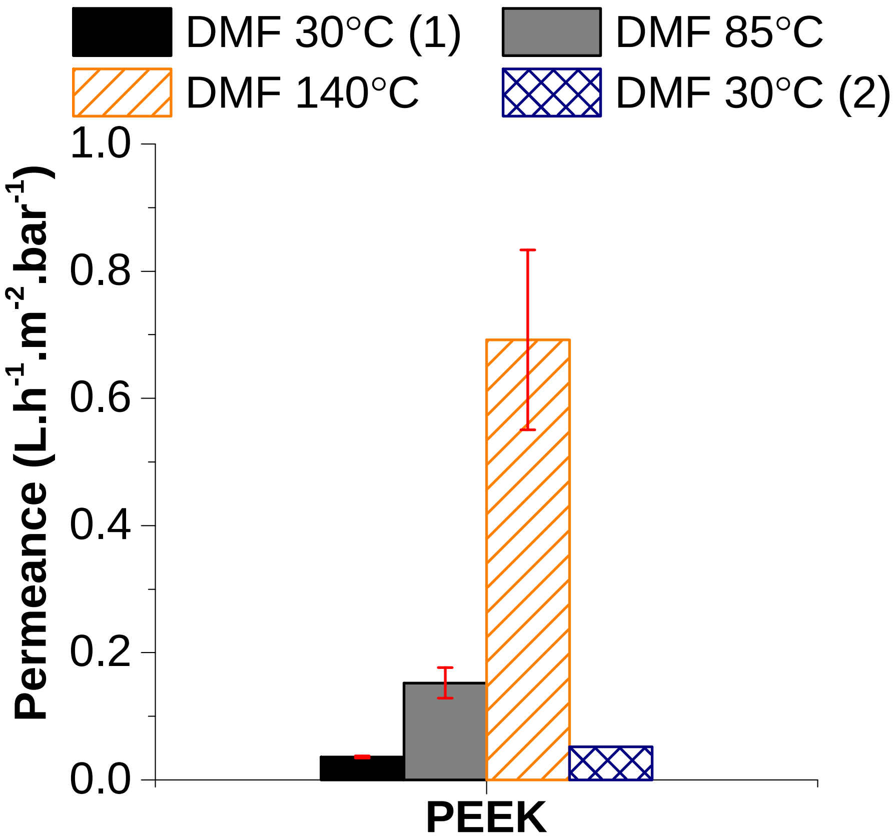
Temperature cycles over time.

Da Silva Burghal et al., J. Membr. Sci. **525** (2017) 48-56

Polyether ether ketone (PEEK) membranes – high T filtration

Filtering solvent: DMF; P = 30 bar



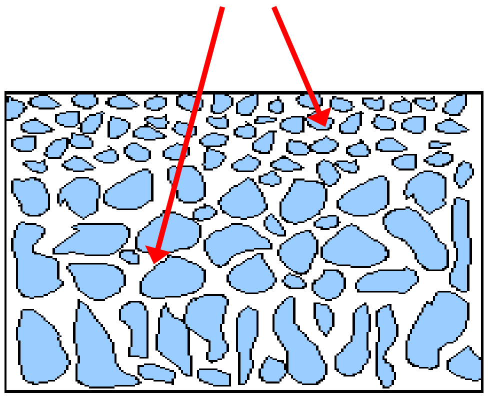


- Membrane becomes looser with temperature but it is partially reversible after cooling down.
- **Membrane survived 140 °C in DMF (Tg PEEK = 140ºC)**

OSN Membranes – Search for permeance

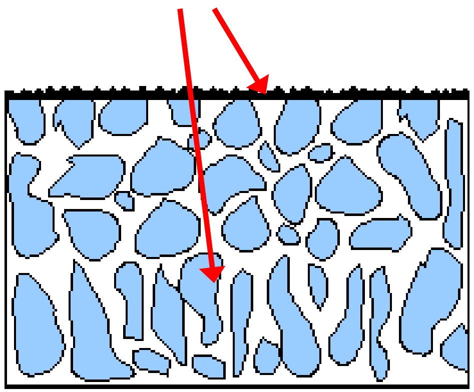
Integrally skinned asymmetric (ISA) membrane
ONE step process

same material



Thin Film composite (TFC) membrane
MULTIPLE step process

different material

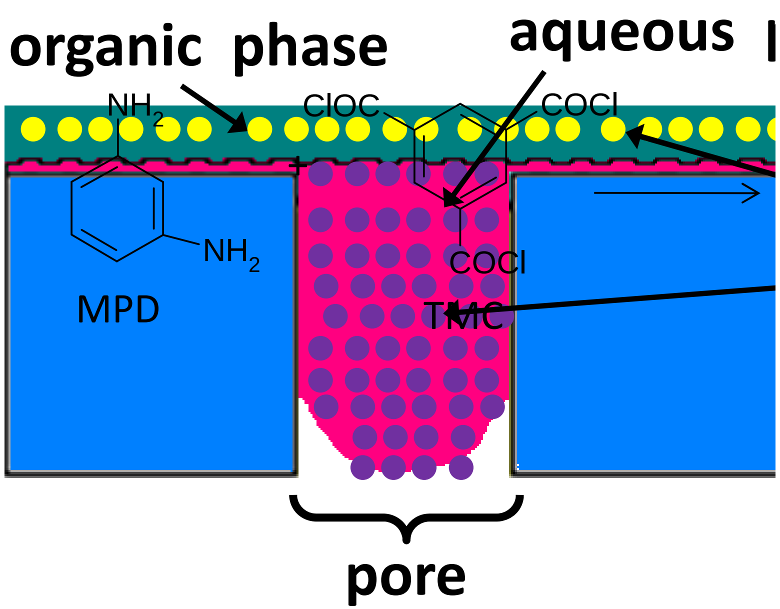


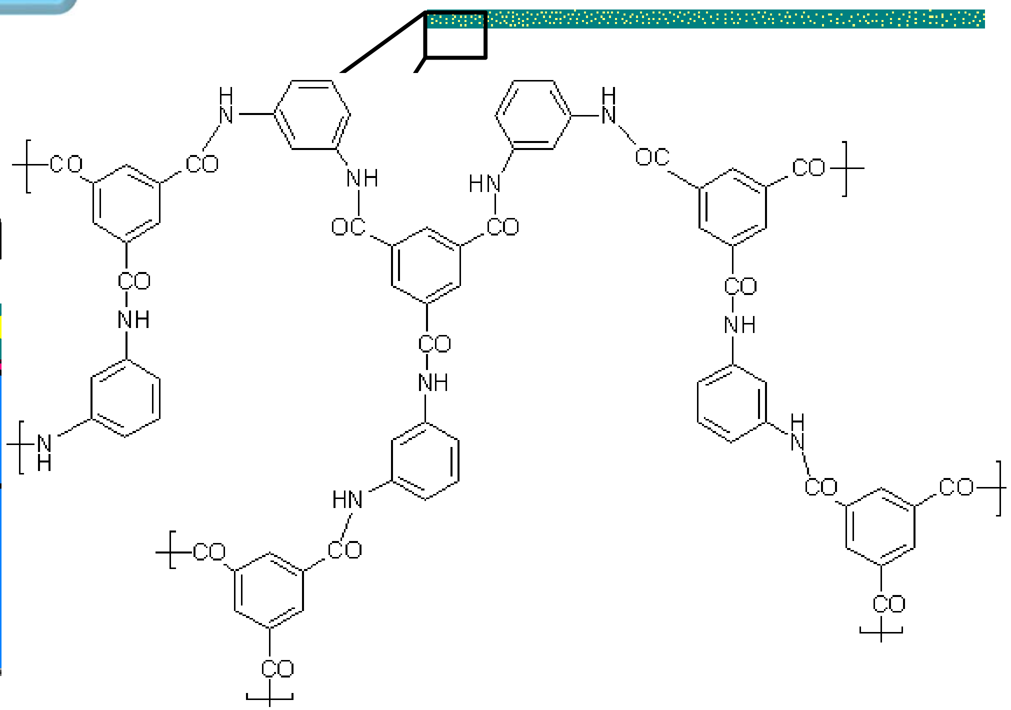
Thinner makes faster!
Thin Film Composites By Interfacial Polymerisation

aqueous amine solution

organic acid chloride solution

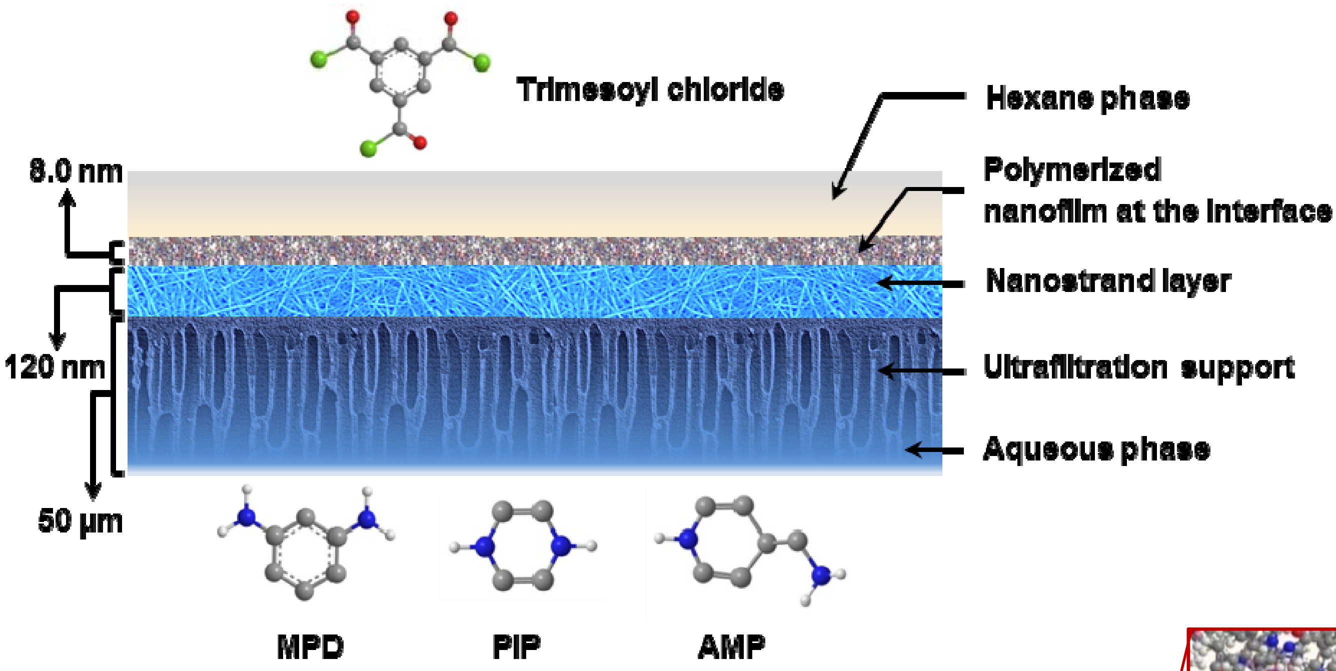
- *m* – phenylenediamine (MPD)
- trimesoyl chloride (TMC) in hexane



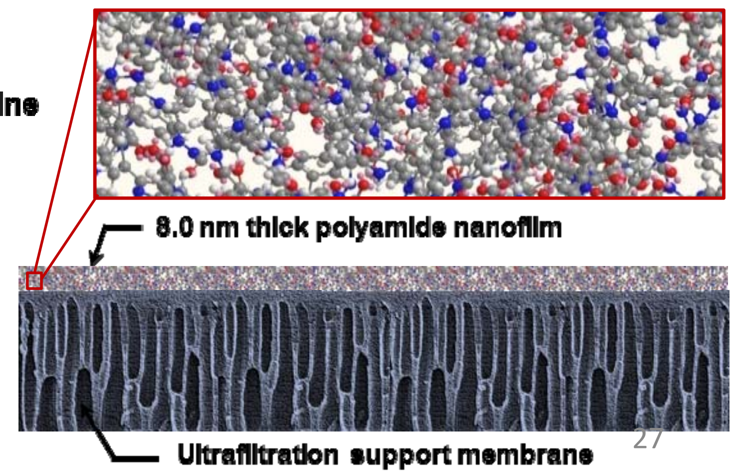


polyamide network

Higher Permeance - Sub 10nm polyamide films
Fabrication of highly cross-linked ultrathin nanofilms

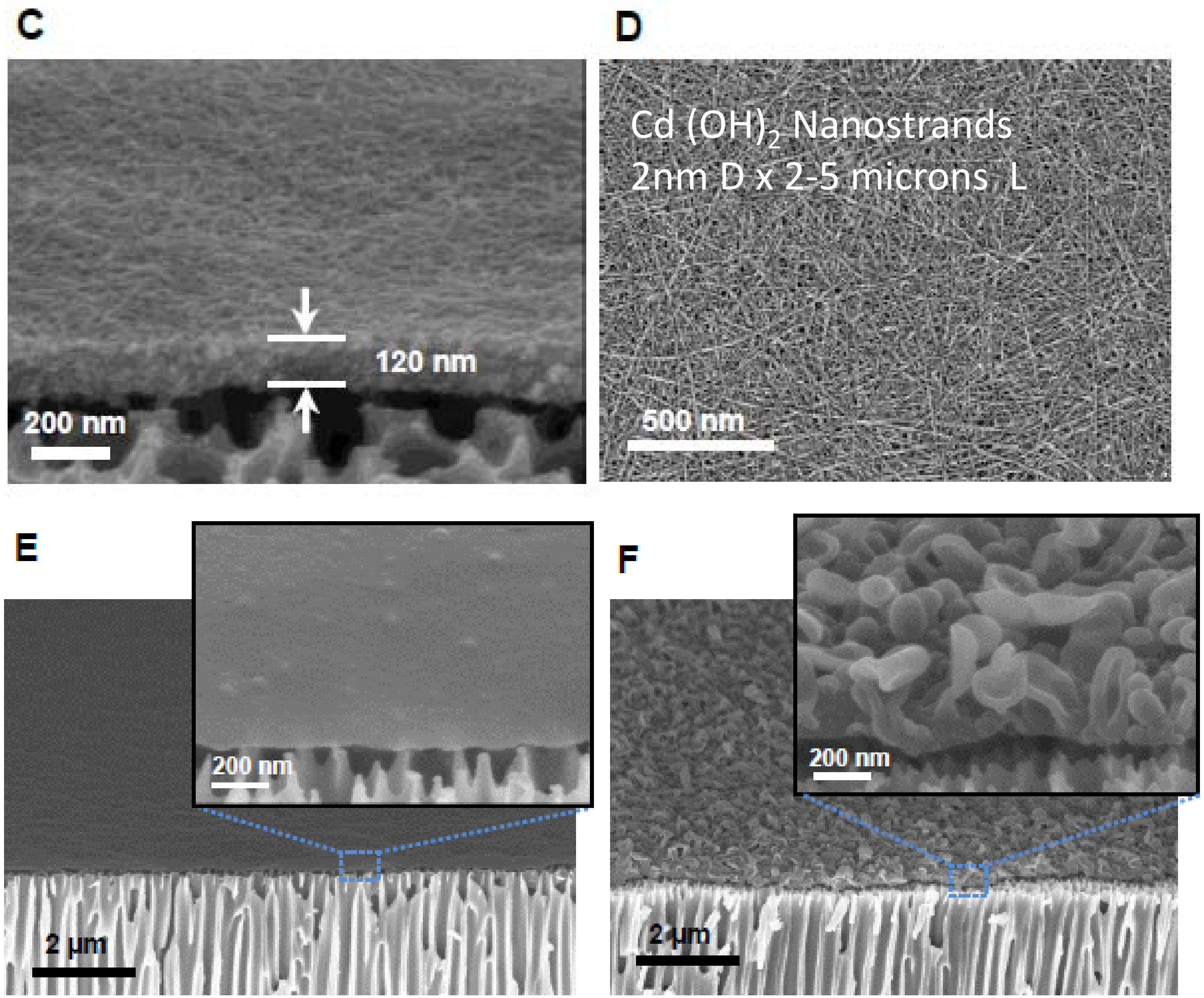


MPD: m-Phenylenediamine; PIP: Piperazine; AMP: 4-(Aminomethyl)piperidine



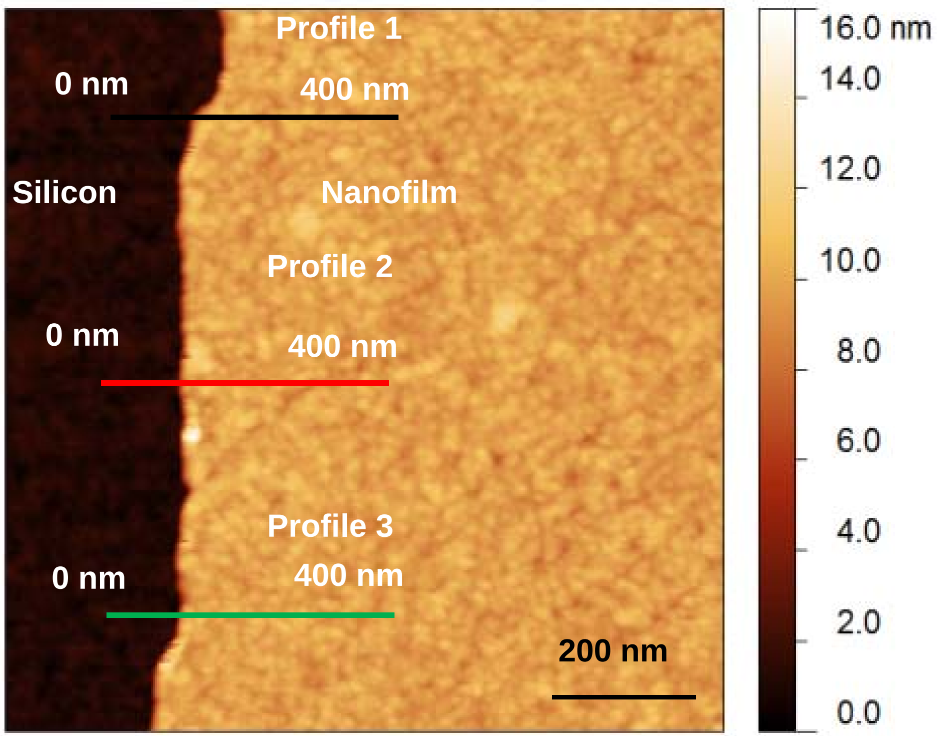
Higher Permeance - Sub 10nm polyamide films
Fabrication of highly cross-linked ultrathin nanofilms

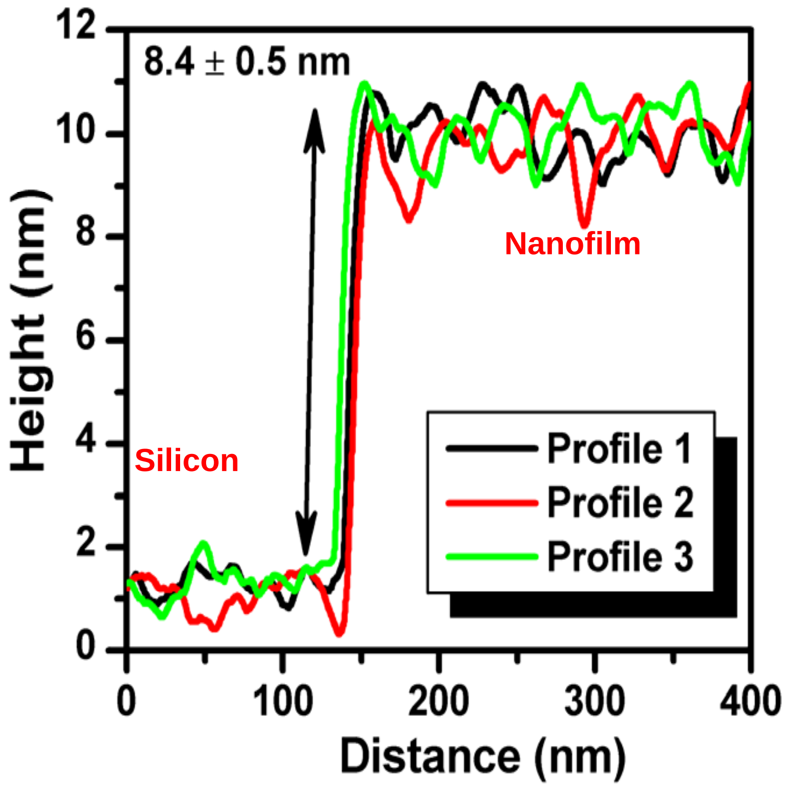
0.1% MPD
0.005% TMC



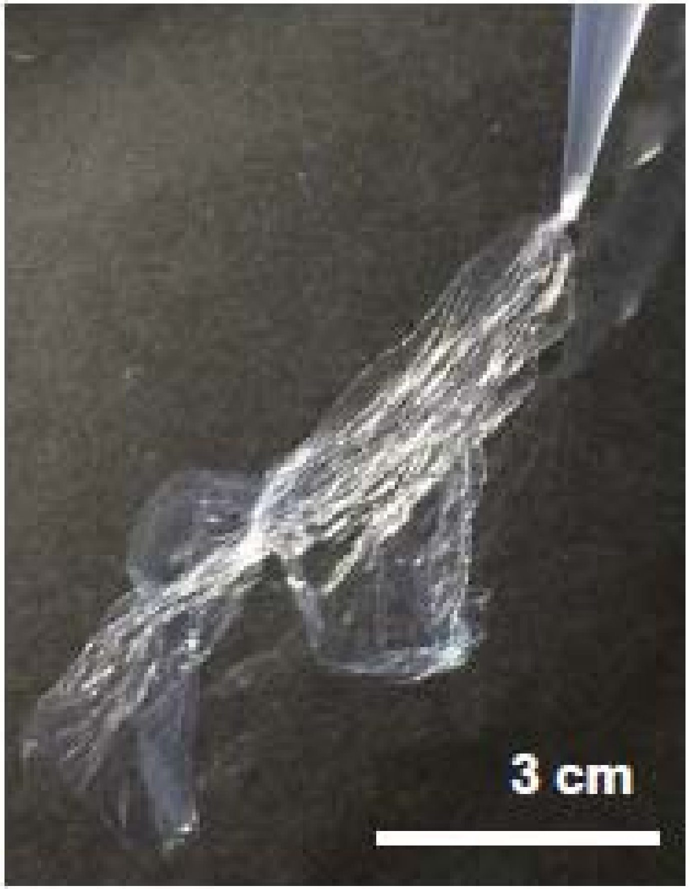
3% MPD
0.15% TMC

Higher Permeance - Sub 10nm polyamide films
Properties of highly cross-linked ultrathin nanofilms



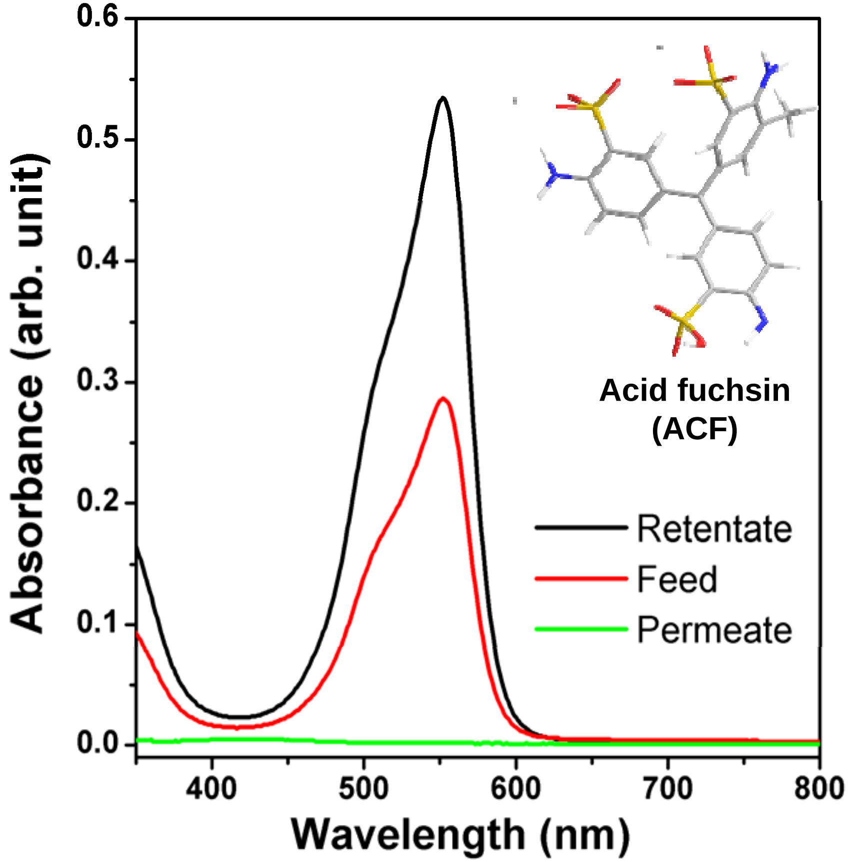


Higher Permeance - Sub 10nm polyamide films
Properties of highly cross-linked ultrathin nanofilms

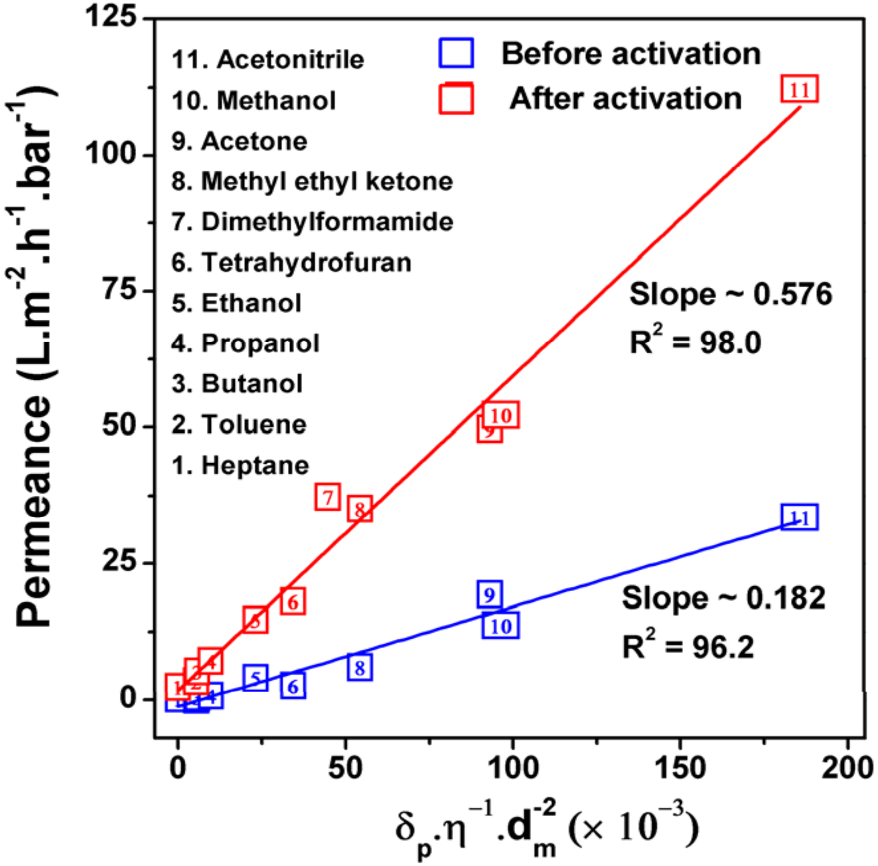


High Permeance - Sub 10nm polyamide films
Performance of highly cross-linked ultrathin nanofilms

Rejection of dye
(ACF - 585 g mol^{-1})

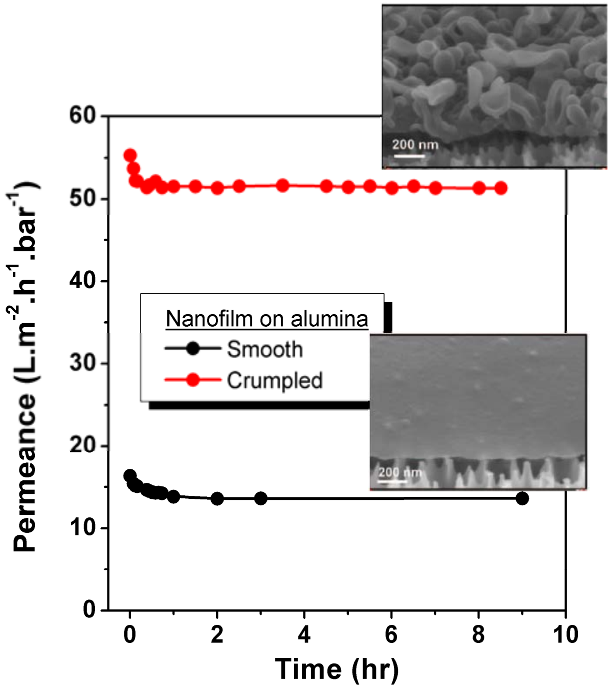


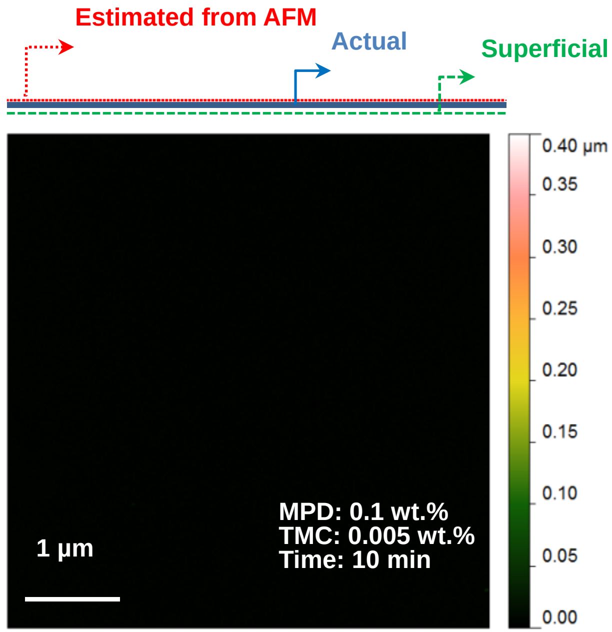
Solvent permeance



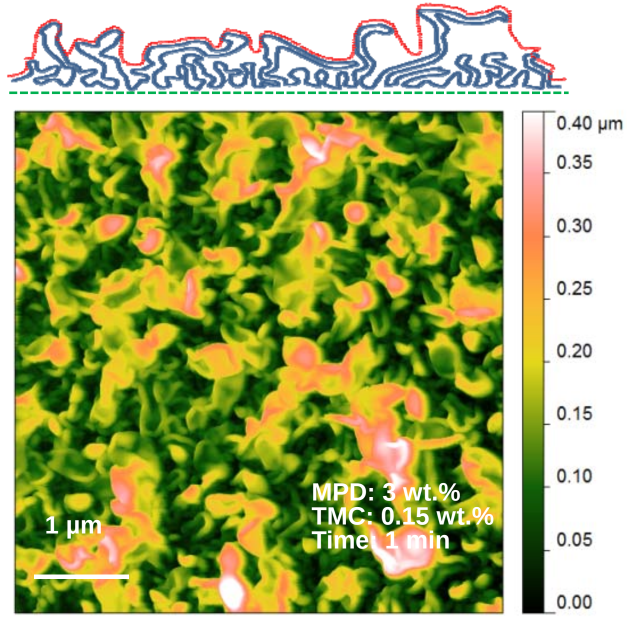
Higher Permeance - Sub 10nm polyamide films
Performance of highly cross-linked ultrathin nanofilms

Permeance of crumpled nanofilms 4 x higher than smooth nanofilms





Estimated length / superficial length ~ 1.0



Estimated length / superficial length ~ 1.8

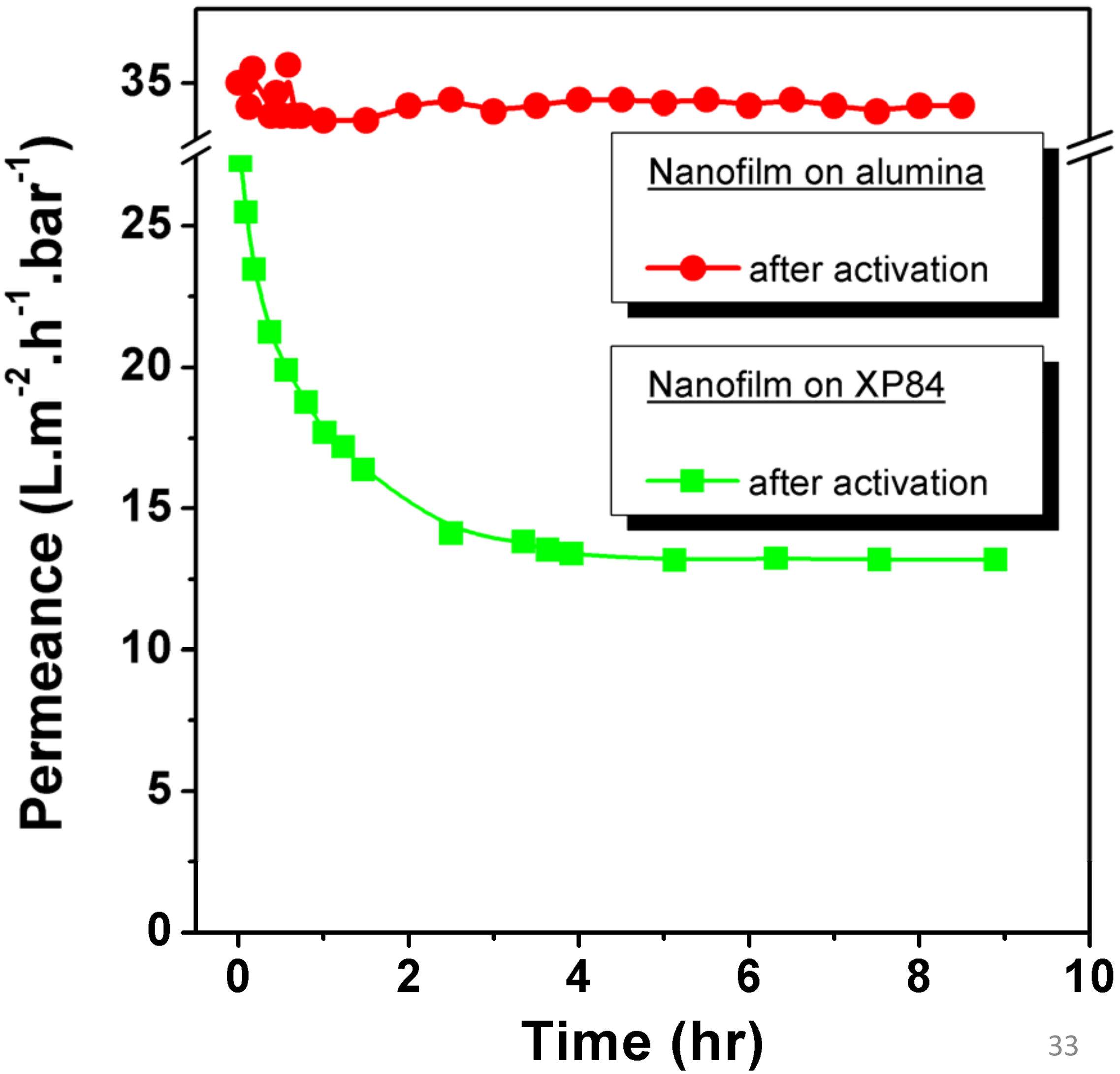
-> crumples are hollow and add permeable surface area

Higher Permeance - Sub 10nm polyamide films
Performance of highly cross-linked thin films

PHYSICAL AGING OF NANOFILMS

Effect of support
Alumina vs Polymer (polyimide)

-> Support is aging, not nanofilm



Science AAAS

S. Karan, Z. Jiang, A. Livingston
Science 348, 1347, 2015.

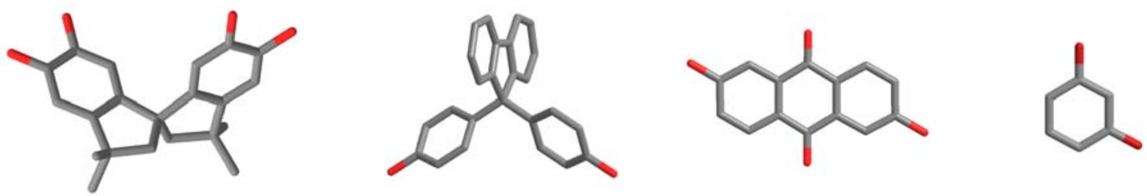
Polymer nanofilms with engineered microporosity by interfacial polymerisation

- Nanofilms of highly crosslinked polymer networks can achieve high flux.
- Interfacial polymerization (IP) can provide very thin network nanofilms.

Approach → **Further increase permeance - design nanofilms at a molecular level to enhance porosity**

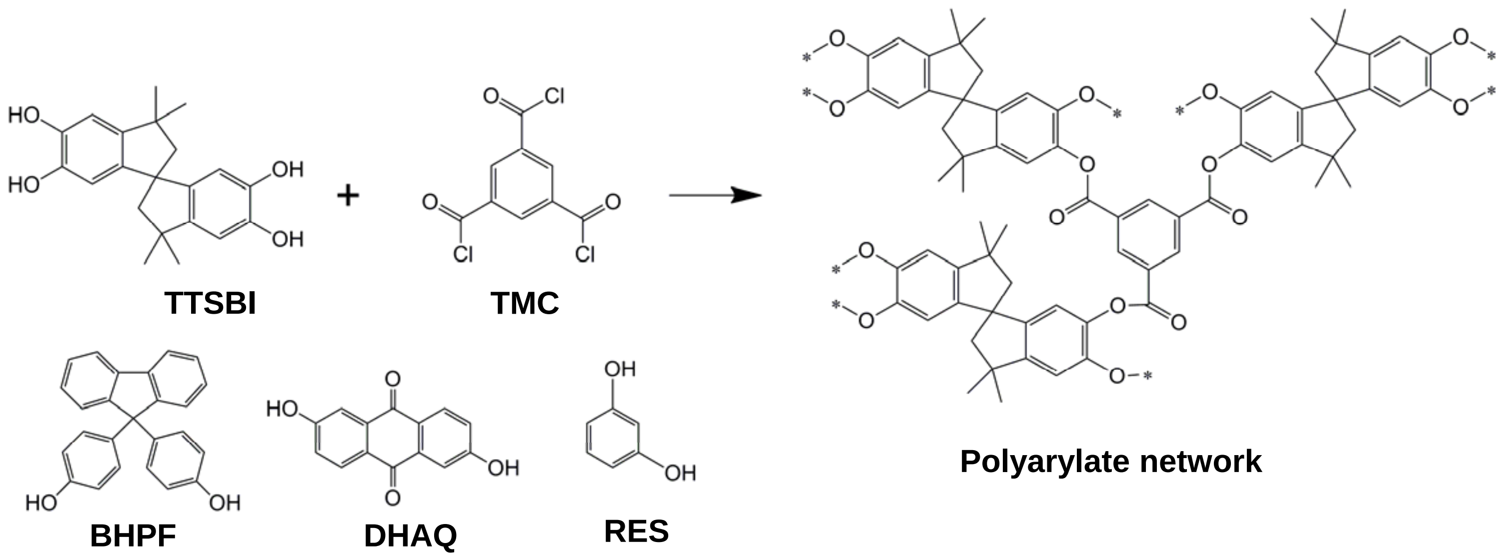
- Introduce contorted monomers during the IP to enhance porosity in the polymer network.
- Compare performance and properties of nanofilms and polymer powders made via IP using contorted or planar monomers.

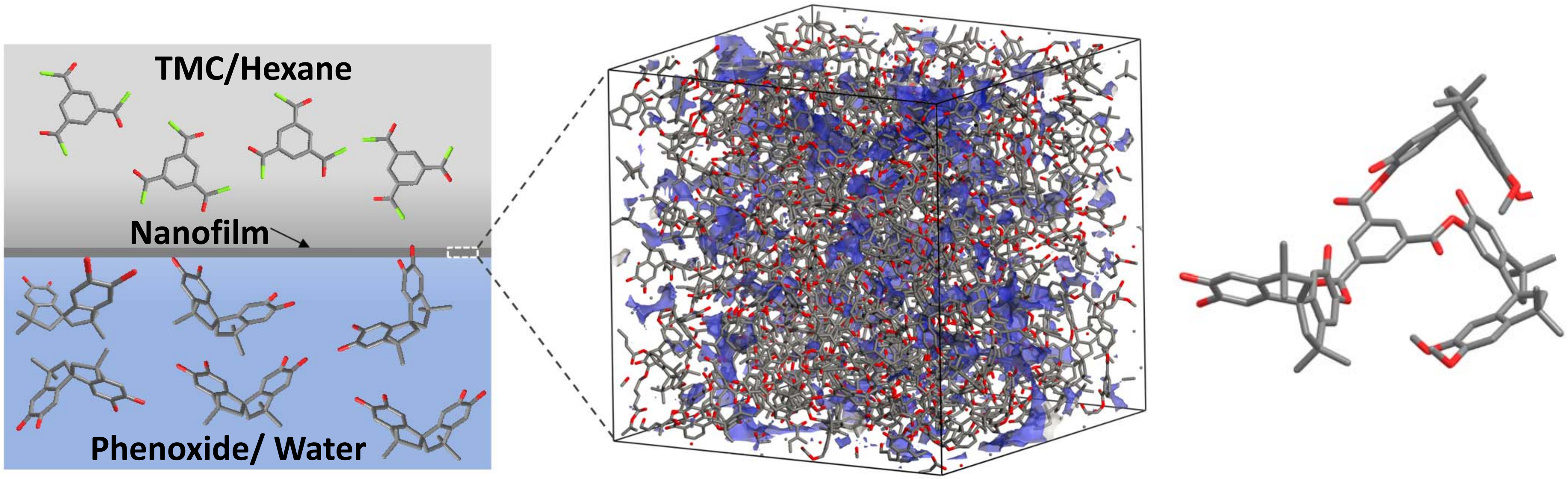
TTSBI **BHPF** **DHAQ** **RES**



Spi **Cardo** **planar (controls)**

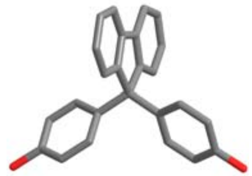
Polymer nanofilms with engineered microporosity by interfacial poymerisation



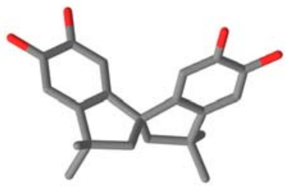


Polymer nanofilms with engineered microporosity by interfacial polymerisation - Simulation

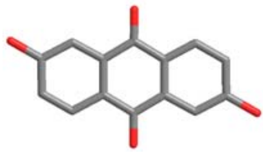
Visualisation model- Materials studio



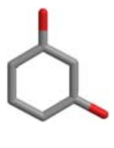
BHPF



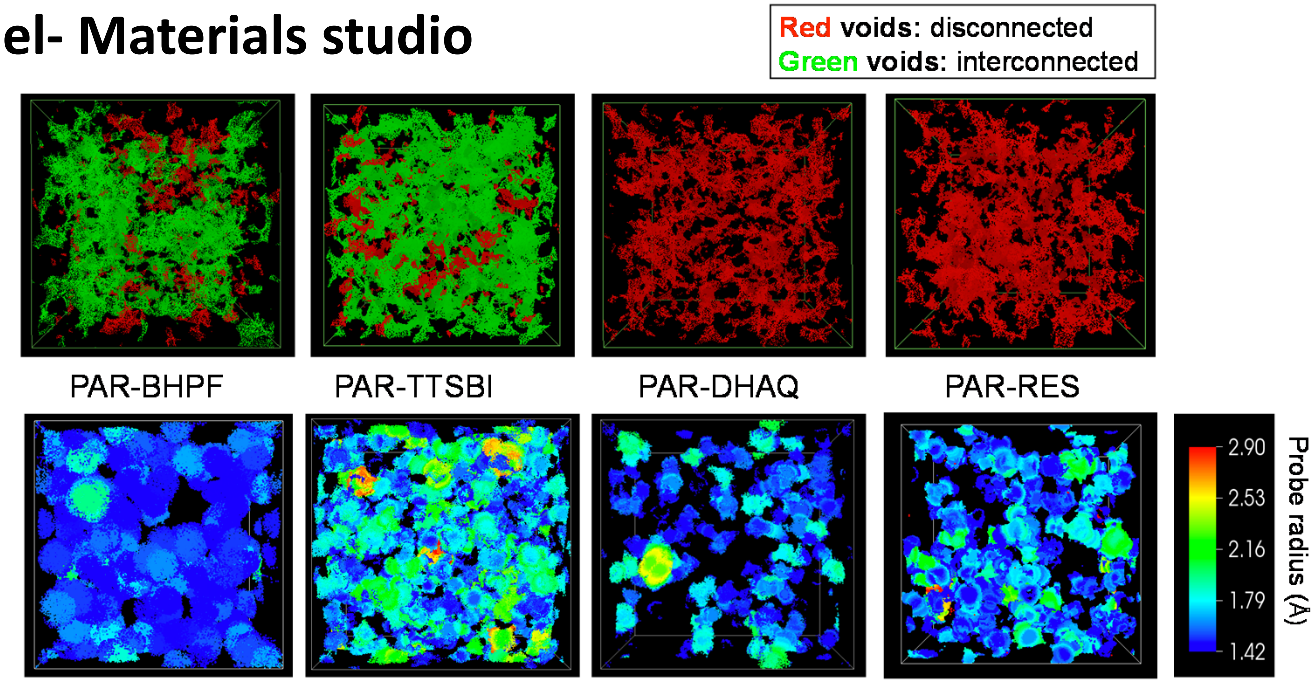
TTSBI

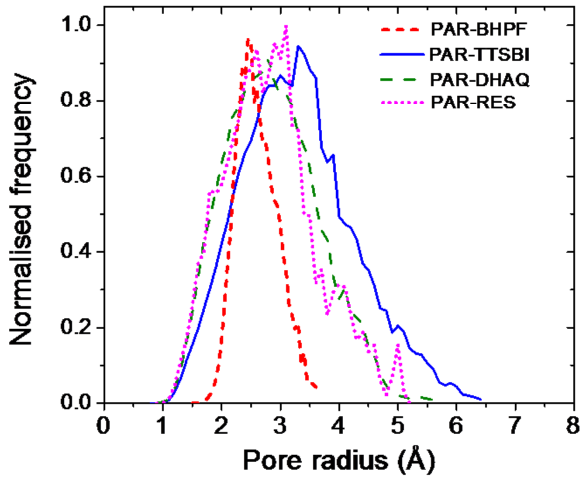


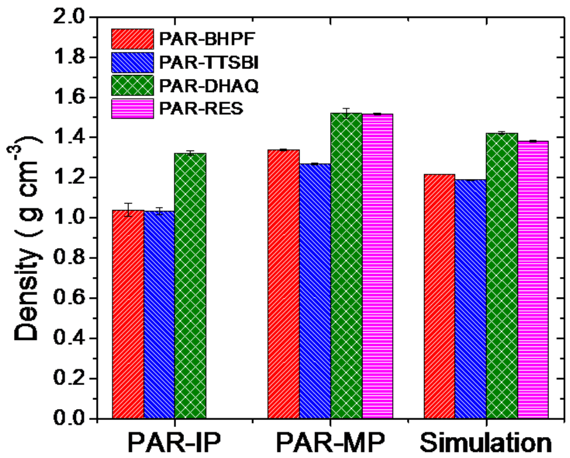
DHAQ



RES





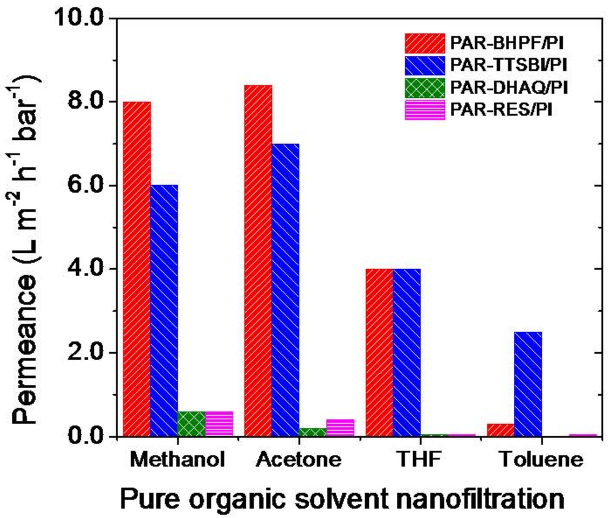


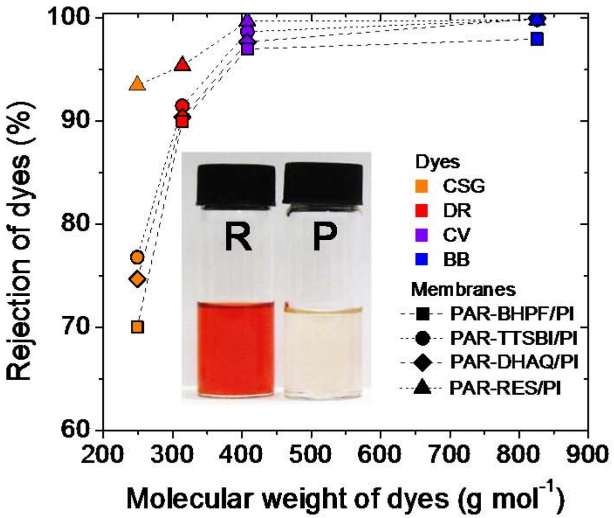
Polymer nanofilms with engineered microporosity by interfacial polymerisation – OSN performance

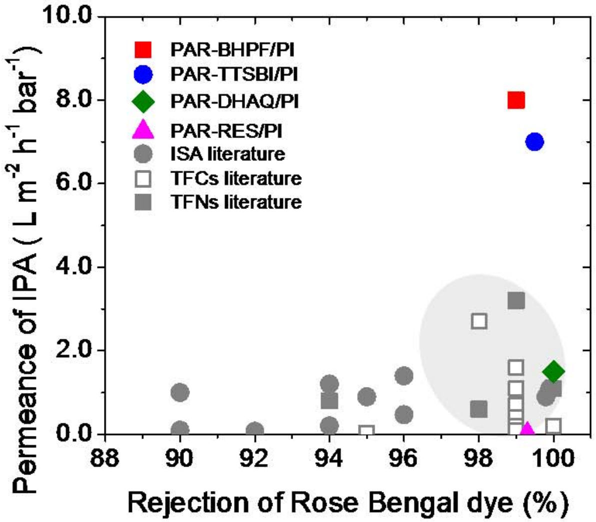
- Filtration experiments at 30 bar and room temperature, 4 repeats for each experiment.

Permeance and rejection
Solvent : THF
Solutes : Dyes

Permeance and rejection
Solvent : IPA
Solutes : Rose Bengal
(1,017 g mol^{-1})







Nanofilms from Spiro and Cardo 100 times higher THF permeance than non-contorted

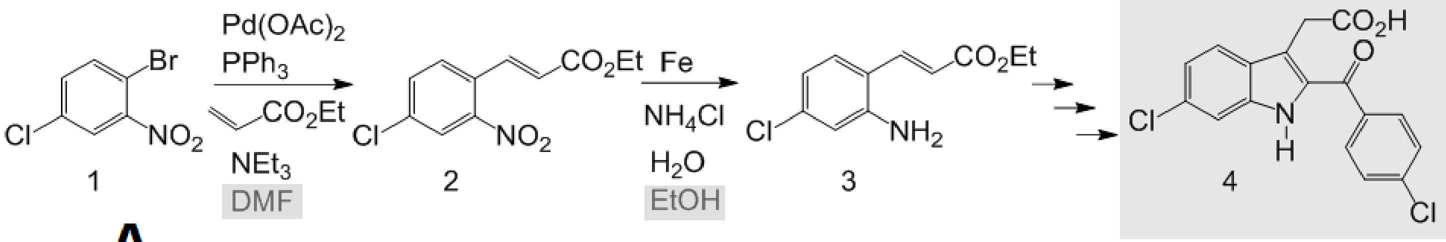
nature materials
ARTICLES
PUBLISHED ONLINE: 2 MAY 2016 | DOI: 10.1038/NMAT4638

Jimenez-Solomon et al *Nature Materials* (2016) 514 pp 646-65.

OSN – APPLICATIONS to Sequential Reactions
Reaction→Solvent Exchange→ Reaction in Flow Chemistry

Synthesis route for a COX-2 inhibitor candidate drug published by Pfizer

Multi-step synthesis that require solvent exchange – DMF to Ethanol



A

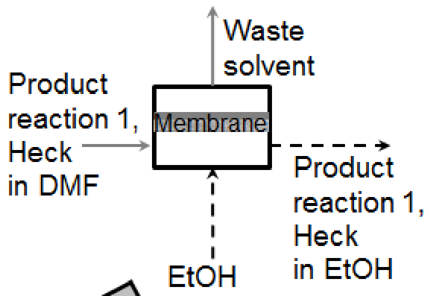
API

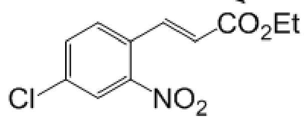
Published procedure for solvent exchange

1. Extraction with toluene
2. Wash with 1 N HCl
3. Wash with water
4. Wash with water
5. Concentration to oil via evaporation
6. Crystallisation in hexane
7. Dissolution in ethanol

B

Membrane cascade solvent exchange





Ethanol solution of cinnamate

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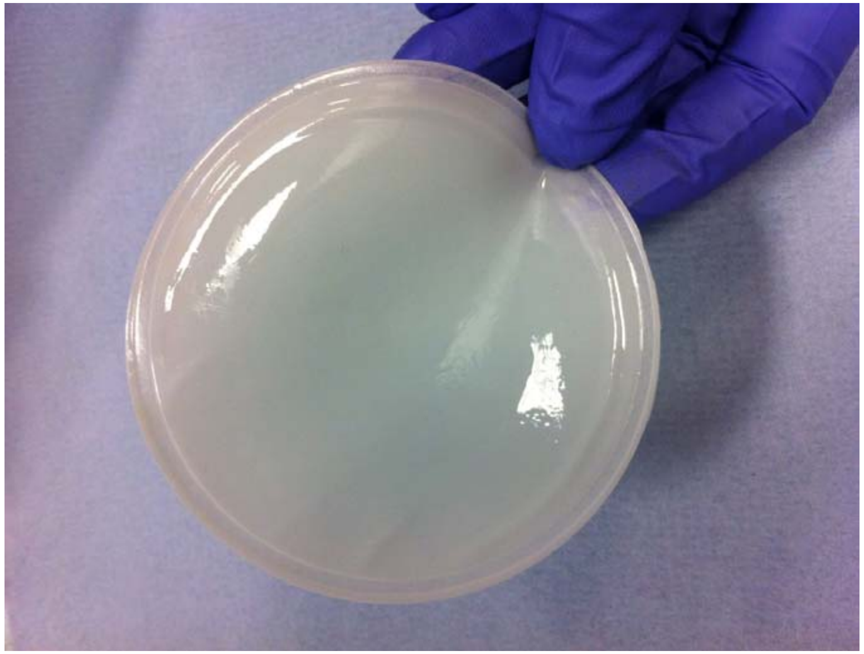
OSN – APPLICATIONS to Sequential Reactions
Reaction→Solvent Exchange→ Reaction in Flow Chemistry

Commercial membrane DM 300 after use in continuous Heck reaction in **DMF at 80^0C and 1.5 eq. (0.9 M) NEt_3** - the membrane is completely destroyed



PEEK membrane after two months use in the continuous Heck reaction in **DMF at 80^0C and 1.5 eq. (0.9 M) NEt_3** - the membrane seems stable

Peeva at al, Journal of Catalysis 306 (2013) 190–201

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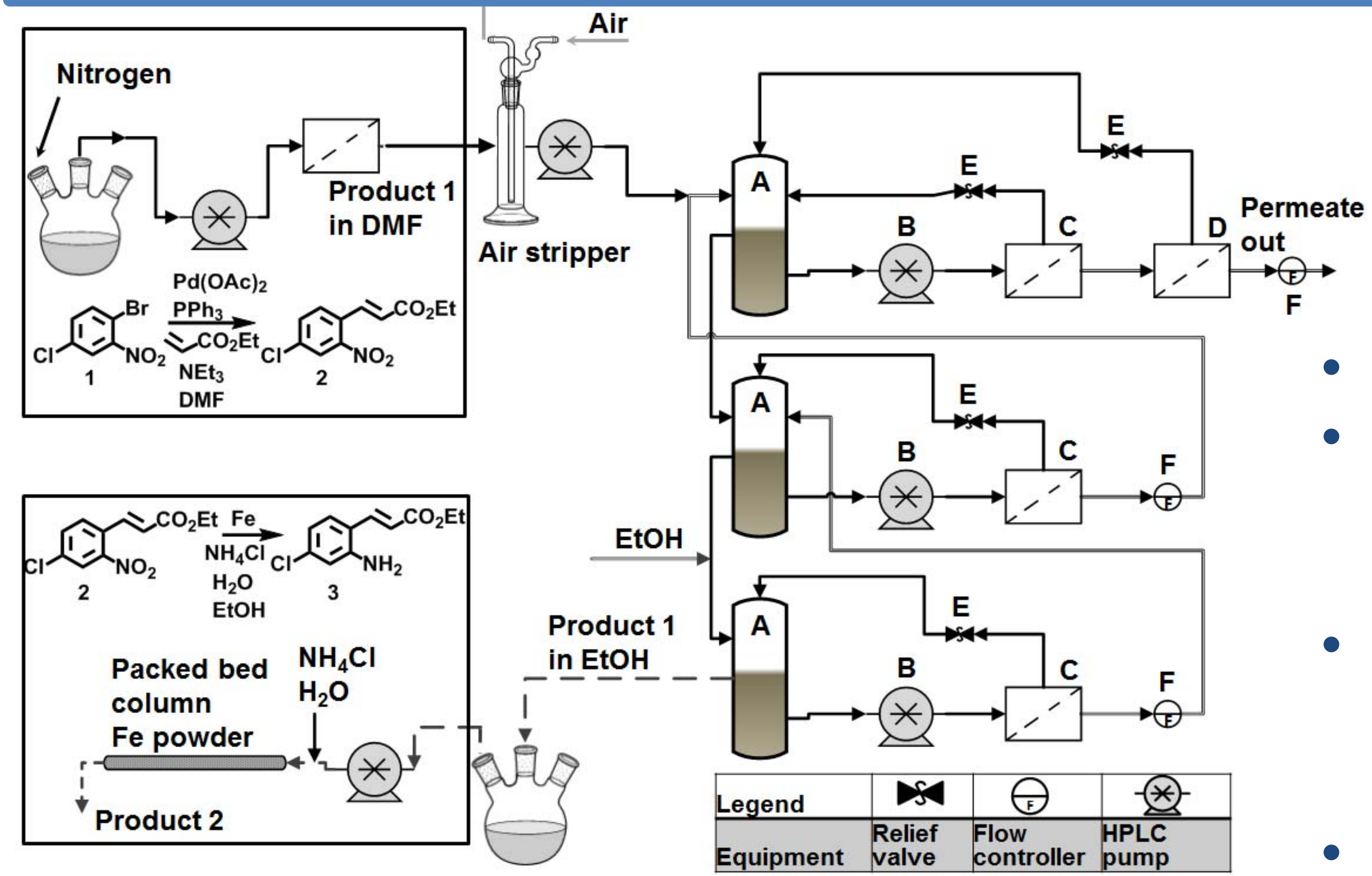
OSN – APPLICATIONS to Sequential Reactions
Reaction→Solvent Exchange→ Reaction in Flow Chemistry

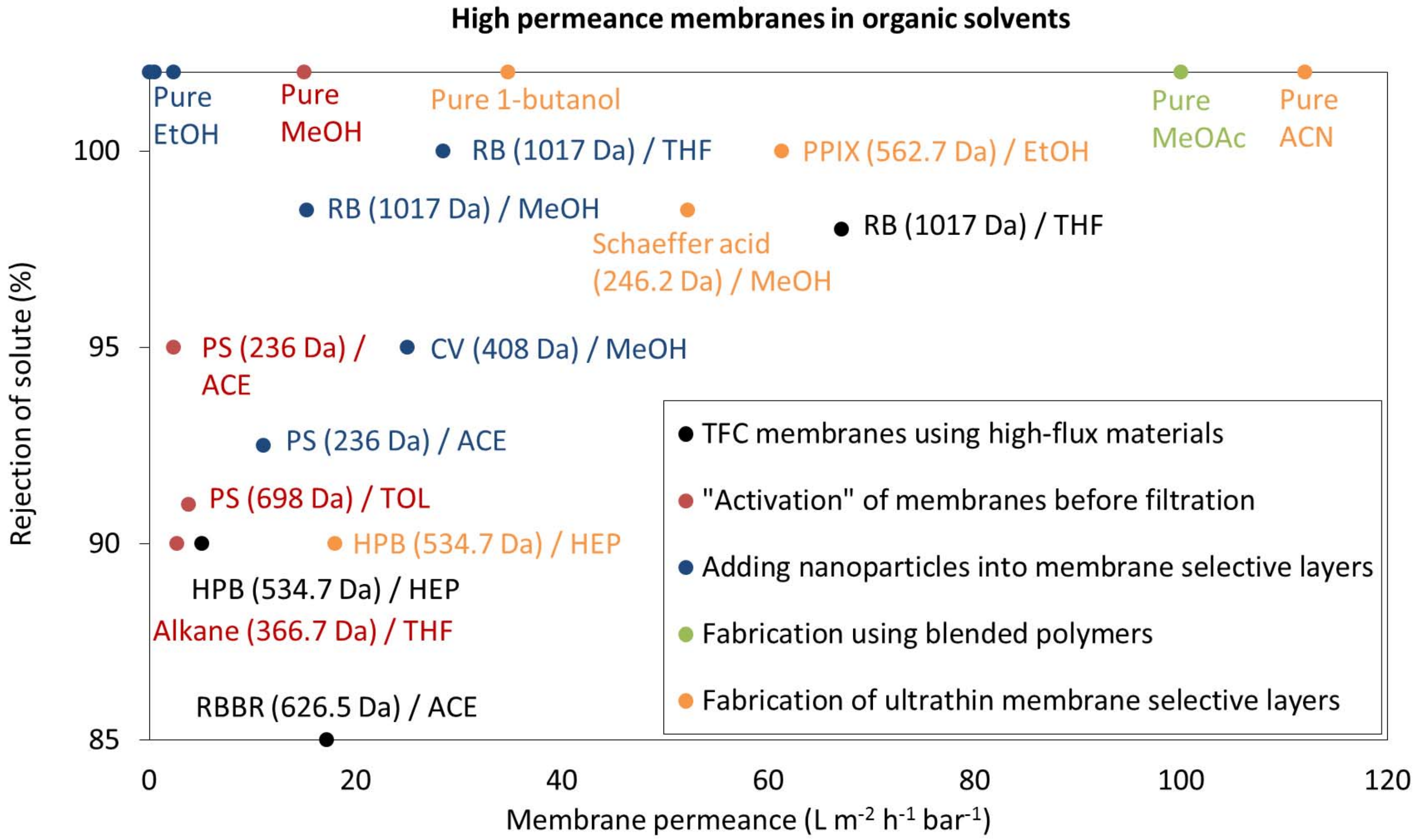


- $15\ ml\ h^{-1}$
- 200 hours continuous operation
- Crude product purity 80%
- Yield > 95%

Peeva at al, Angewandte Chemie Int Edn 55 (2016) pp13576-13579

Imperial College London

OSN - Speedy membranes, fast processes?
Concentration polarisation and osmotic pressure



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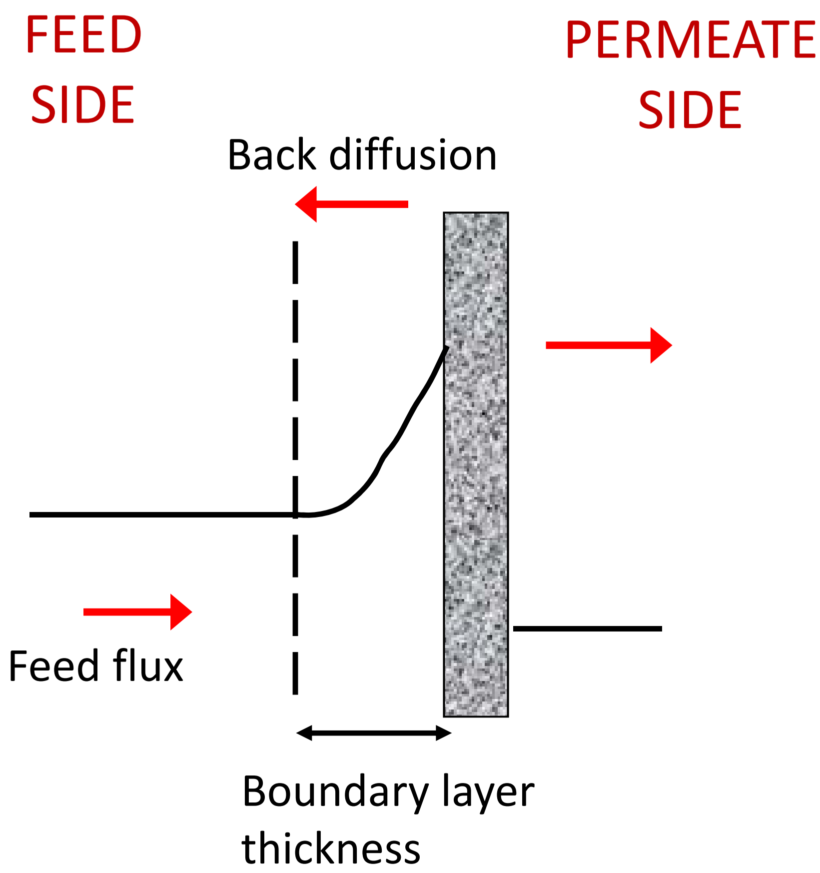
OSN - Speedy membranes, fast processes? Concentration polarisation and osmotic pressure

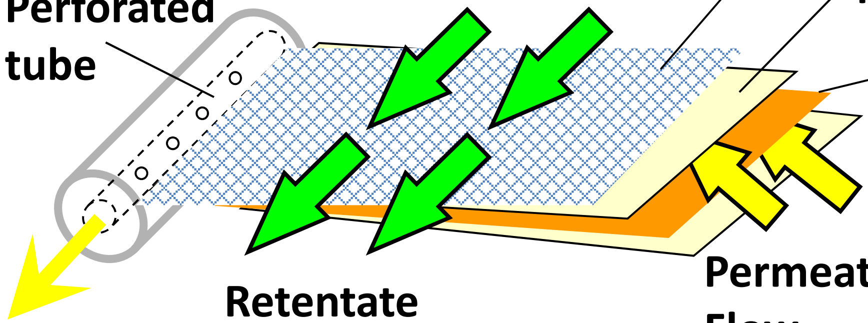
Performance Limitations

- Most studies of OSN are either membrane-focussed or application-focussed
- Major limitations on performance can come from system factors, such as:
  - Chemical stability
  - Aging and Fouling
  - **Concentration polarisation**
  - **Osmotic pressure**
  - **Hydrodynamics**

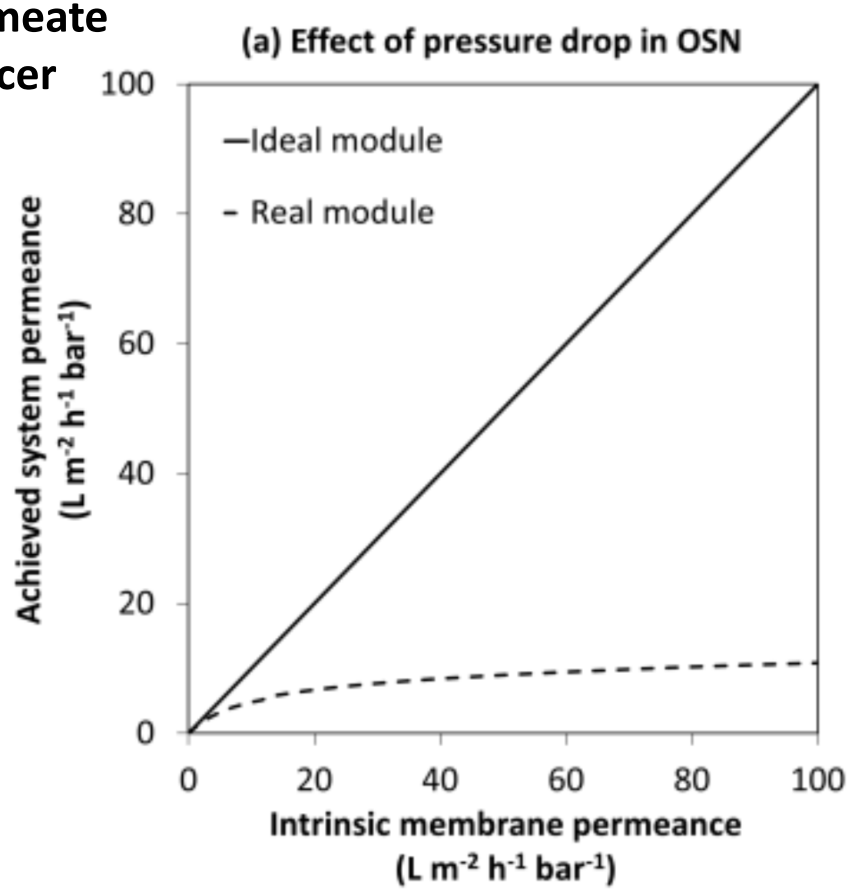
Effects of Mass Transfer



OSN – Speedy Membranes, Fast Processes?
Spiral Wound Modules

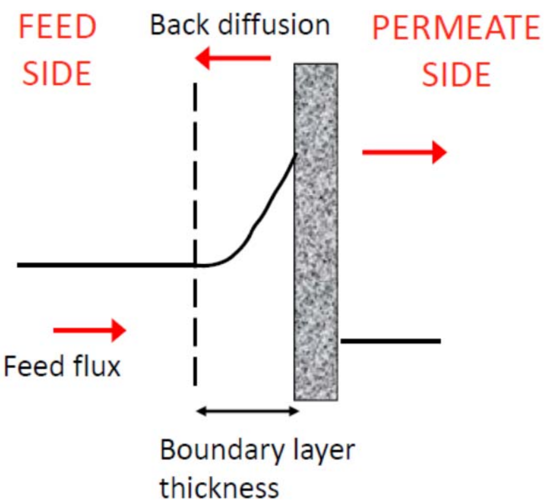


Pure Ethyl Acetate

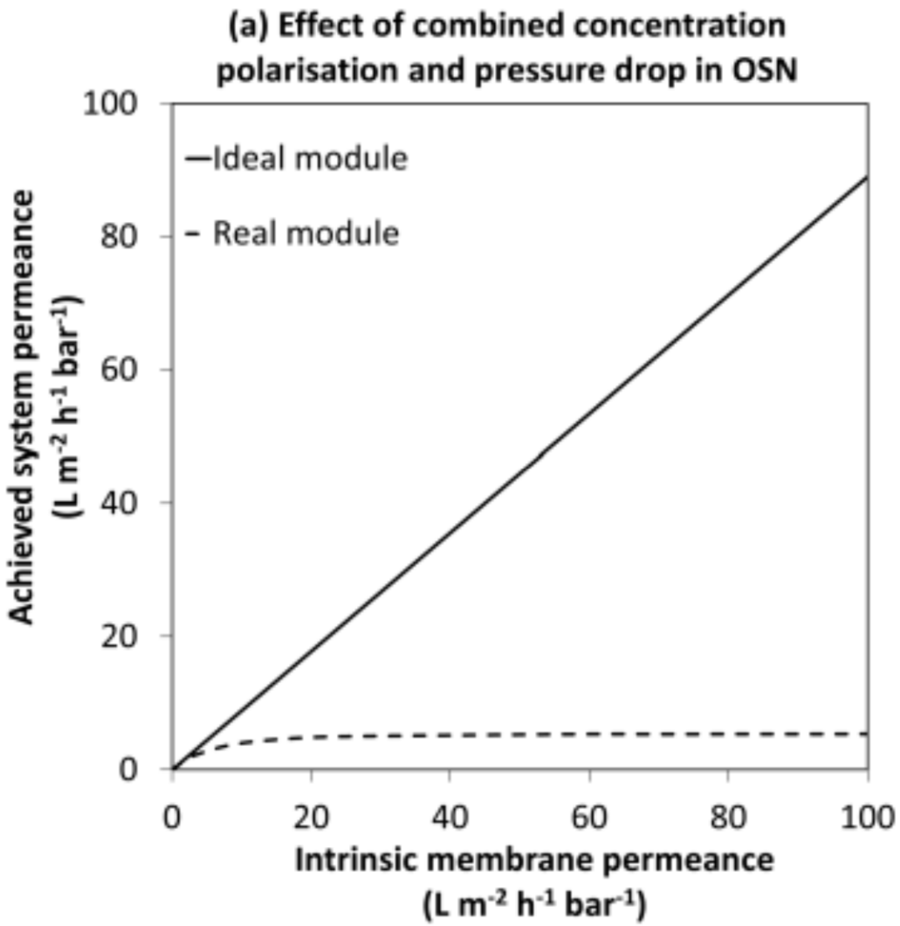


Shi B et al *Journal of Membrane Science* (2015) 494 pp 8-24.

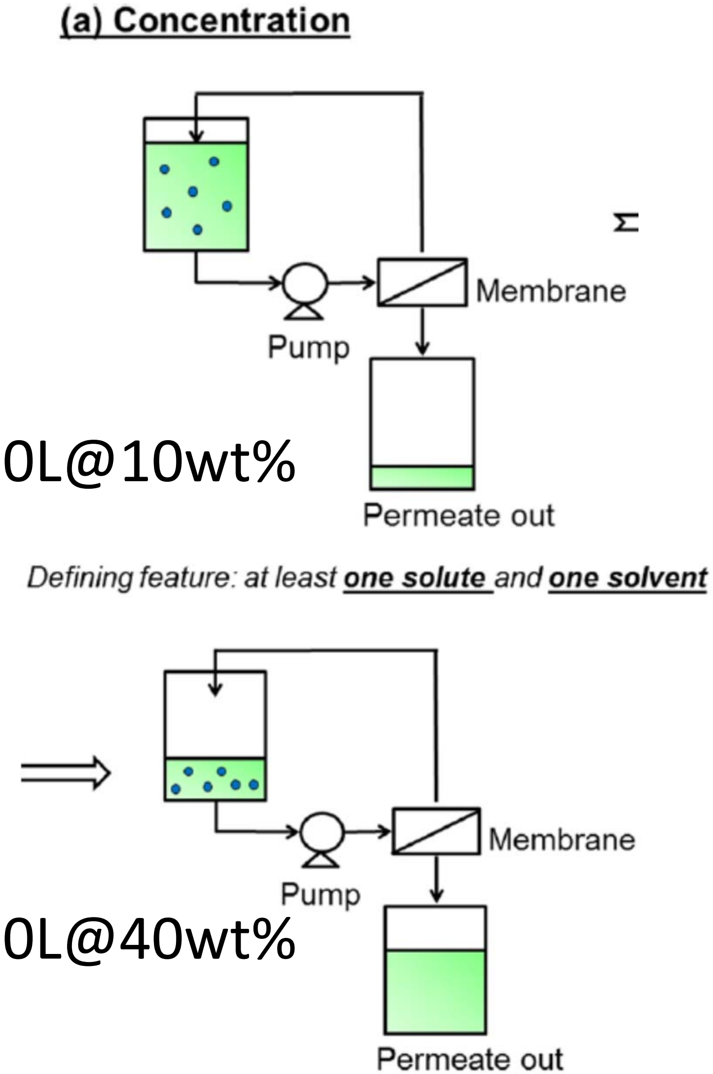
OSN – Speedy Membranes, Fast Processes?
Spiral Modules and Concentration Polarisation



Sucrose Octaacetate in Ethyl Acetate
30 bar / 30°C/10wt%/k = 5 x 10^{-5} m s^{-1}



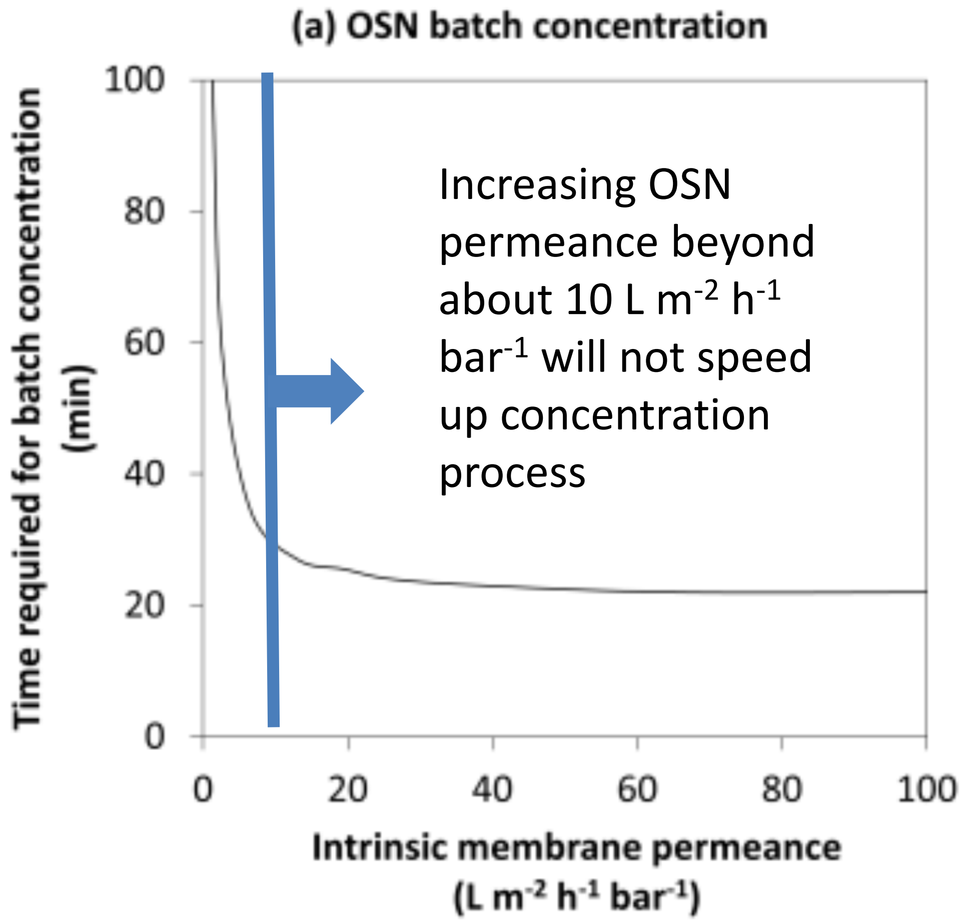
OSN – Speedy Membranes, Fast Processes?
Process time for concentration of solute



80L@10wt%

20L@40wt%

Sucrose Octaacetate in Ethyl Acetate
30 bar / 30^{o}C / k = 5 x 10^{-5} m s^{-1}



Shi B et al *Journal of Membrane Science 525* (2017) pp 35-47.

Concluding Remarks
Challenges for Molecular Separations in Organic Systems

QUO VARDIS?

- There is a "**useful permeance"** above which further permeance increases will not lead to faster or more compact processes
- The"useful permeance" is system specific but for OSN is around 10 L m^{-2} h^{-1} bar^{-1}
- Once useful permeance is achieved, further materials innovations that would result in better processes are in the areas of
  - **More accurate separations**
  - **Better in service lifetime performance (aging, fouling)**
  - **Improved chemical stability**

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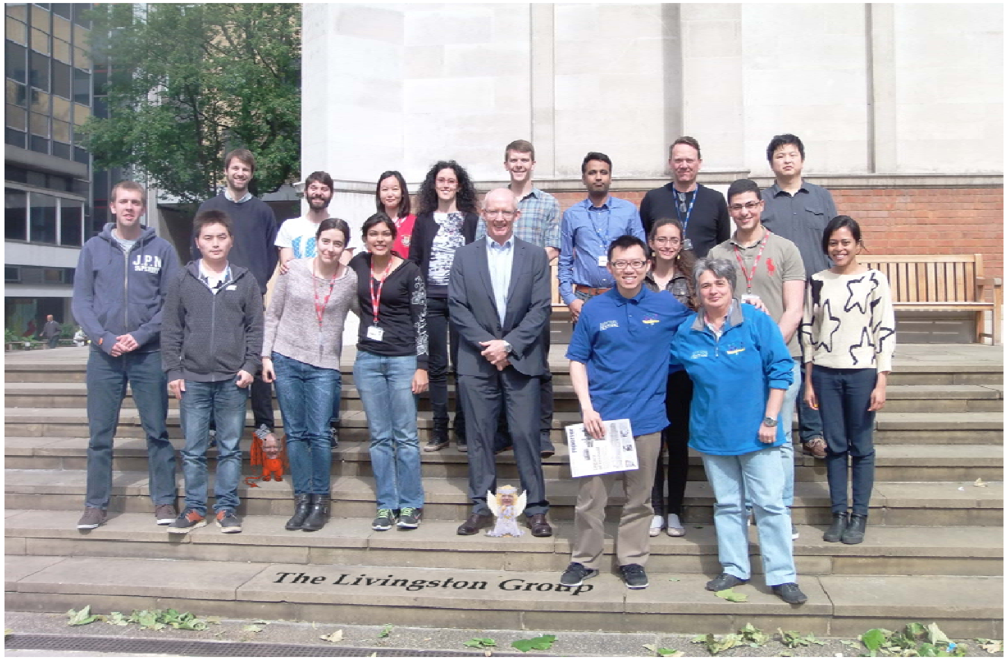
- BP International Centre for Advanced Materials
- Novartis-MIT Centre for Continuous Manufacture (Berthold Schenkel and Klavs Jensen)
- UK Engineering and Physical Sciences Research Council
- The Livingston Group @ Barrer Centre, Imperial College……….



………and to you for listening!