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# Hollow fiber membrane fabrication

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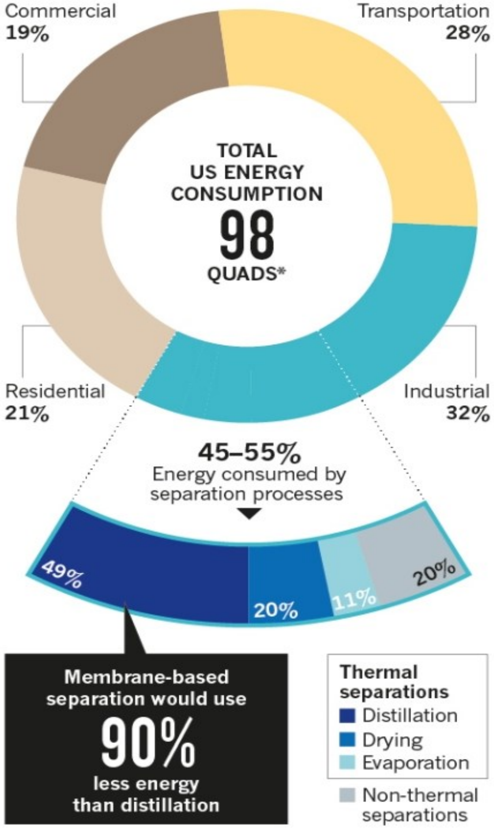
Membrane Technology and Process Intensification

# MEMBRANE TECHNOLOGY




## MEMBRANE SEPARATION

- No require a gas-liquid phase change
- Smaller separation units → small footprint
- Lack of mechanical complexity
- Operate under continuous, steady-state conditions

# GAS SEPARATION WITH MEMBRANES

## APPLICATIONS

- $CO_2$ capture
- $CH_4$ purification
- $H_2$ purification
- Olefin / paraffin separation
- Water separation

## TYPE OF MEMBRANE

### MATERIAL

**Inorganic**
- Metallic
- Ceramic
- Carbon
- Zeolite

**Organic**
- Polymeric

### STRUCTURE

**Symmetric**

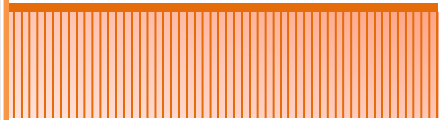
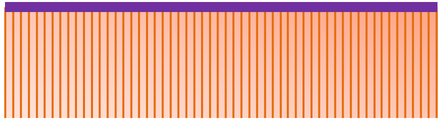
**Asymmetric**
- Integral asymmetric
- Composite

### GEOMETRY

- Flat sheet
- Tubular
- Hollow fiber (< 0.5mm)

# MEMEBRANE STRUCTURE AND GEOMETRY

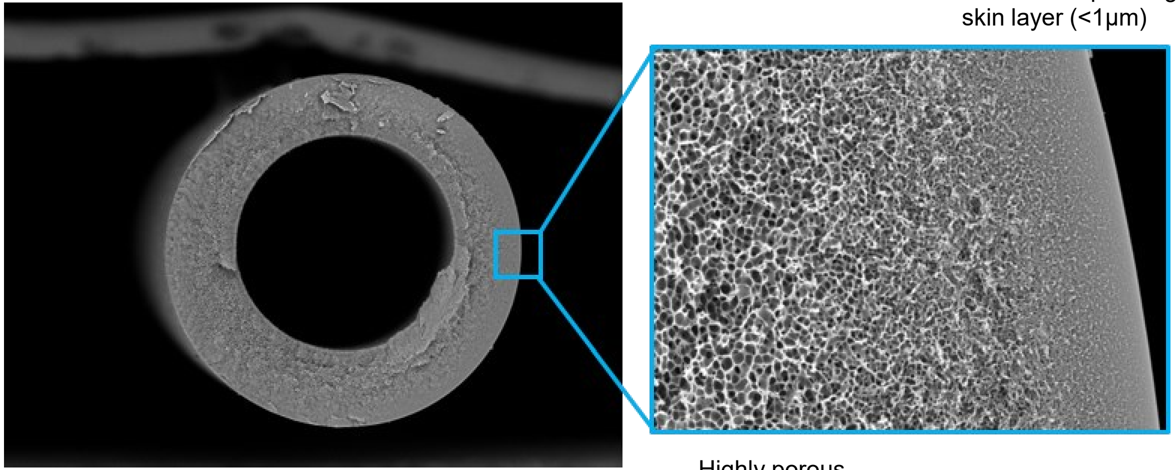
## Commercial membranes

| | | Asymmetric | |
|---|---|---|---|
| | | **Monolithic** | **Composite** |
| **Membrane structure** | **Homogeneous**  |  |  |
| **Membrane processing** | **Polymeric melt extrusion:** temperature phase separation **Solution film casting:** Evaporation induced phase separation | **Solution film casting or Hollow fiber spinning:** Evaporation followed by non-solvent induced phase separation | **Dip-coating:** Evaporation induced phase separation **Interfacial polymerisation** |
| **Geometry** |  |  |  |

$$J_i = \frac{P_i \cdot \Delta p_i}{l}$$

# MEMEBRANE STRUCTURE AND GEOMETRY

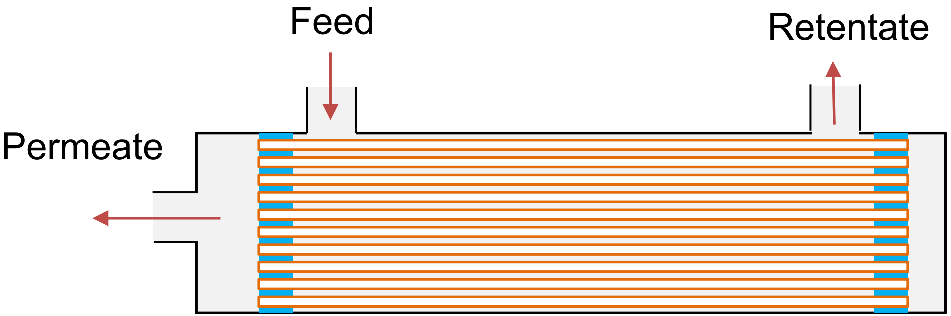
**Monolithic and asymmetric hollow fiber membrane**




$$J_i = \frac{P_i \cdot \Delta p_i}{l}$$

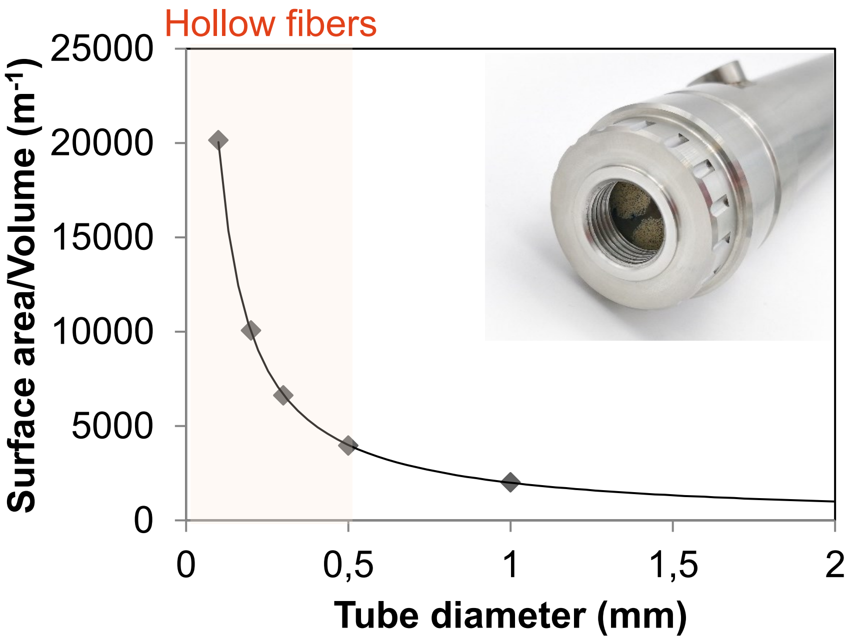
# HOLLOW FIBER MEMBRANES - Geometry

Separation Module




## HOLLOW FIBER MEMBRANES - Geometry

Membrane packing density inside the permeation module = 50 %




**Advantages of HF**

- High packing density (over 10000 $m^2/m^3$), 10 times higher than plate and frame modules

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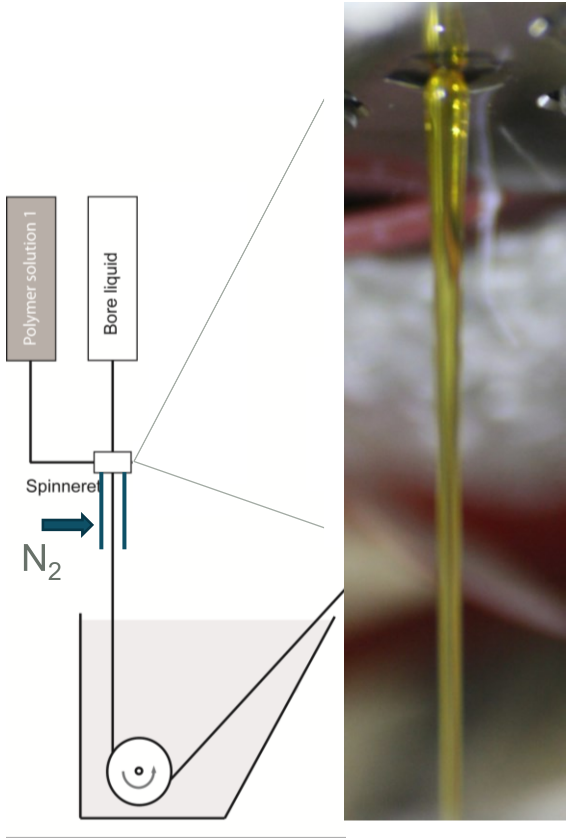
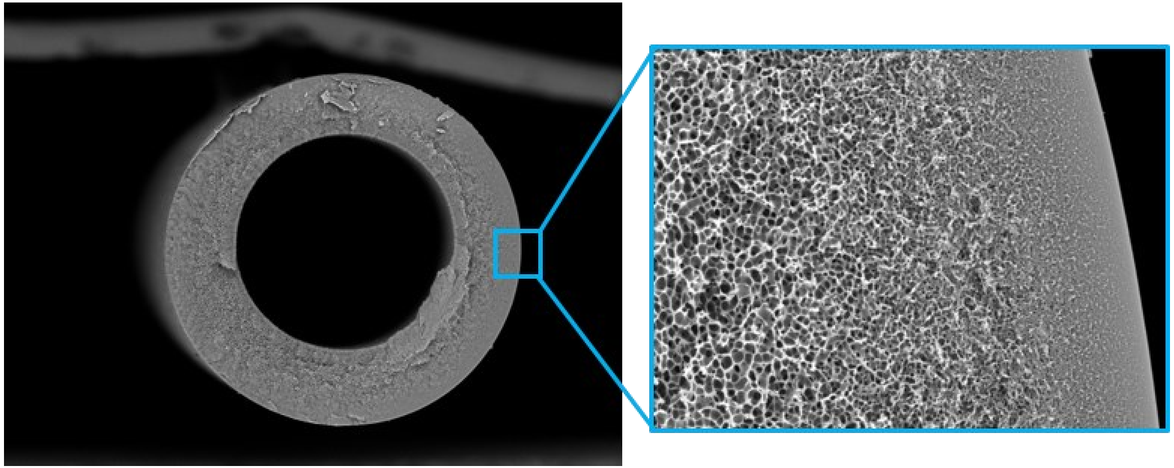
# HOLLOW FIBER PREPARATION METHODS -spinning

Single step process: simultaneous formation of the

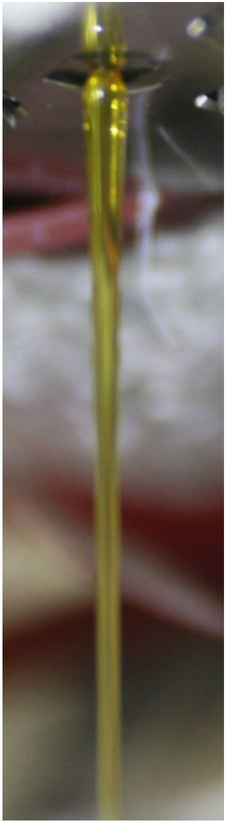


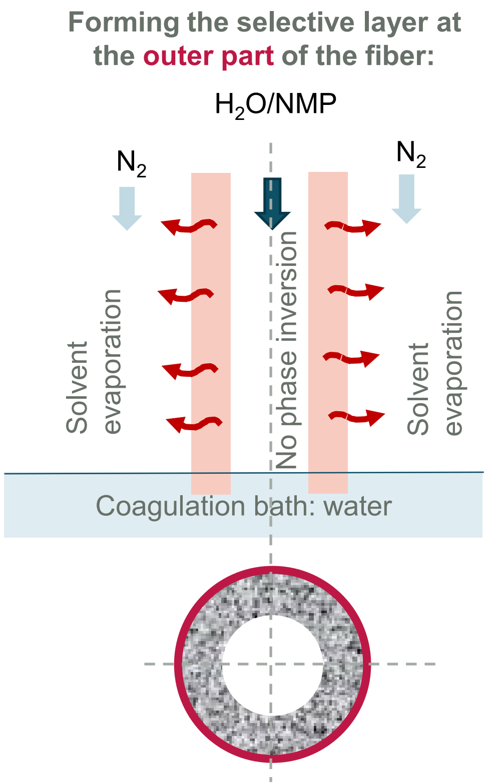



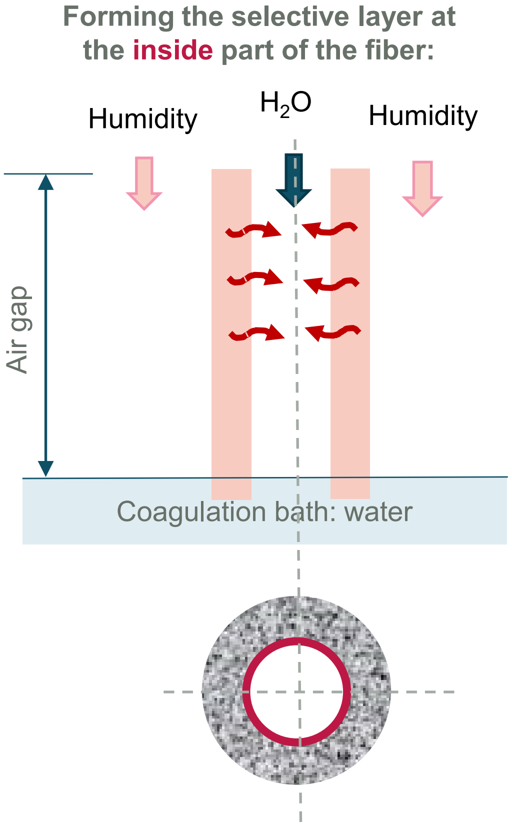
**Process parameters:**
Dope and bore composition and flow rate
Spinneret and coagulation bath temperature
Air gap height and atmosphere
Take up-rate
Room temperature and humidity

*Membranes 2021, 11(8), 557; https://doi.org/10.3390/membranes11080557*

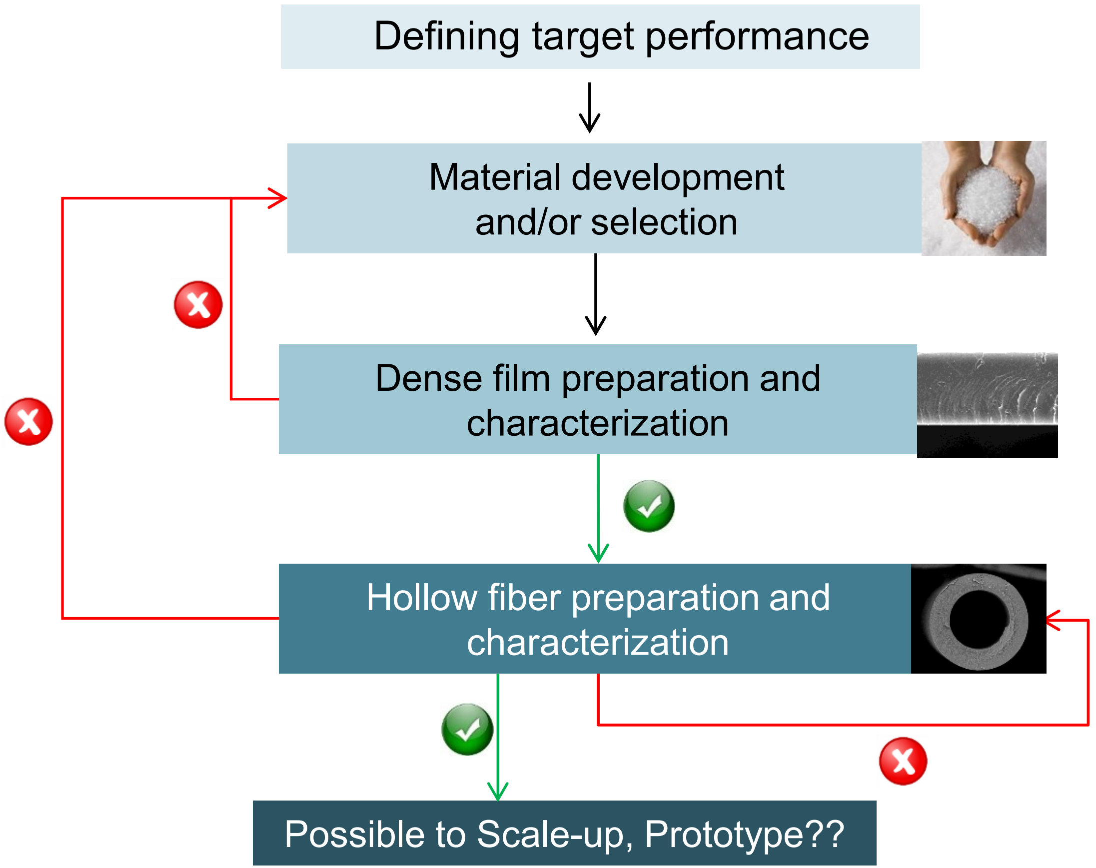
# HOLLOW FIBER PREPARATION METHODS -spinning





# MEMBRANE DEVELOPMENT STRATEGY




*Intrinsic separation properties*
*Permeability and selectivity*

*Separation properties*
*Permeance and selectivity*

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# BENCHMARK

| Polymeric materials used |
| --- |
| Polyaramide |
| Polysulfone |
| Poly(phenilene oxide) |
| Cellulose acetate |
| Polyimides: |
| P84 |
| PBI |
| 6FDA-DAM |
| PI-Extem |

Bio-based copolymers for membrane end products for gas separations

# Bio-Based HF membranes

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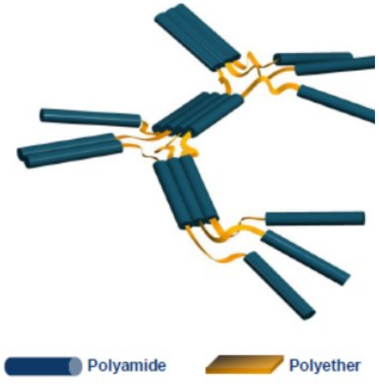
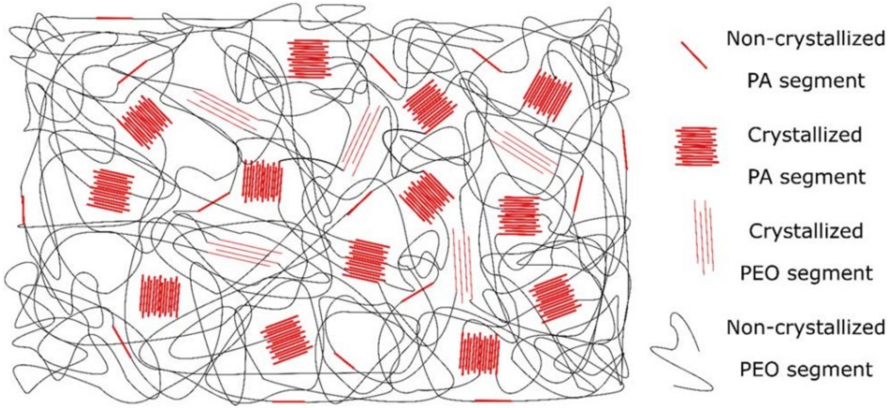
# Material development and/or selection



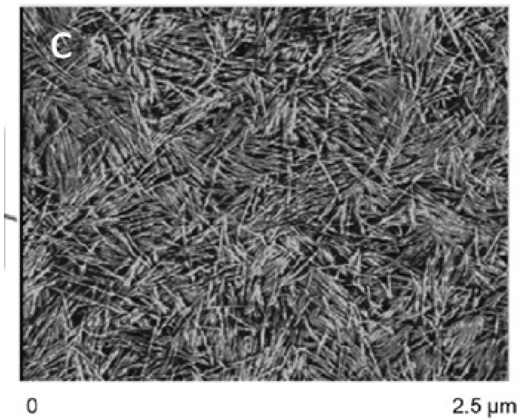
## PEBA type Polymers




Arkema



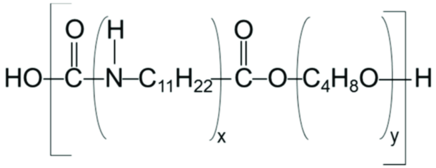

Didden, Jeroen; Thür, Raymond; Volodin, Alexander; Vankelecom, Ivo F. J. (2018), Journal of Applied Polymer Science, 46433

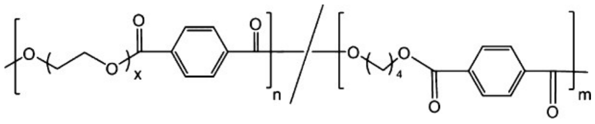



Yave, W., A. Car, and K.-V. Peinemann, J. Membr. Sci. 2010, 350: p. 124-129 (2010)

# Material development and/or selection

| Polymer | P (Barrer) | Permselectivity | | | Ref. |
|---|---|---|---|---|---|
| | $CO_2$ | $CO_2/N_2$ | $CO_2/CH_4$ | $CO_2/H_2$ | |
| **Pebax 1657** PEO with PA6 | 98 | 53,2 | 16,1 | 9,5 | 1 |
| **PEBAX 2533** PTMO with PA12 | 234 -351 | 25 - 41 | | | 2 |
| **PEBAX 1074** PEO with PA12 | 134,74 | 59,61 | 16,16 | 10,28 | 2 |
| **Bio PEBAX** PEO with PA11 | 311,41 | 45 | 14,07 | 9,35 | Bioco mem |




[1] S.R. Reijerkerk et al. / Journal of Membrane Science 352 (2010) 126–135
[2] H. Lin, B.D. Freeman, Gas solubility, diffusivity and permeability in poly(ethylene oxide), J. Membr. Sci. 239 (1) (2004) 105–117

BioCoMem

# RESEARCH LINES

| Co-polymer | Polyamide block | Polyether block | Main expected result |
|---|---|---|---|
| **A**<br>**Reference bio-PEBAs** | Bio-based polyamide 11 derived from castor oil $(PA_{ref}{}^{bio})$ | Fossil based polyether block $(PE_{ref}{}^{fossil})$ | Composite HF Membrane |
| **B**<br>**New bio-PEBAs Pathway 1**<br>aromatic/cycloaliphatic polyamide-b-polyether | Bio-based polyamides derived from new building blocks $(PA_{new}{}^{bio})$ | Fossil based polyether block $(PE_{ref}{}^{fossil})$ | Better processability: (Monolithic HF membrane)<br>*and*<br>Higher gas separation performance |
| **C**<br>**New bio-PEBAs Pathway 2**<br>lignin-g-(polyether-b-polyamide 11) | Bio-based polyamide 11 derived from castor oil $(PA_{ref}{}^{bio})$ | Bio-based polyether block derived from lignin-g-polyether $(PE_{new}{}^{bio})$ | Better processability: (Monolithic HF membrane)<br>*and*<br>Development of PEBA type co-polymer with bio-based components in both blocks |

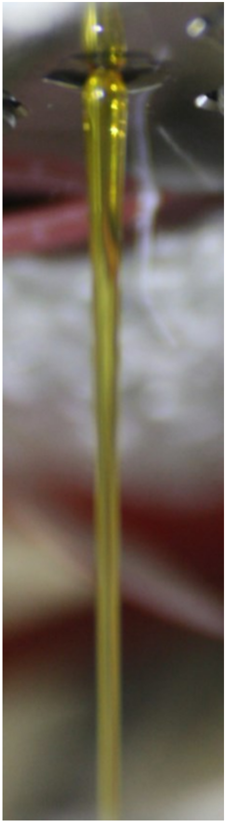
# Preliminary solubility study

| | Concentration wt% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SOL 01 | SOL 02 | SOL 03 | SOL 04 | SOL 05 | SOL 06 | SOL 07 | SOL COMPL. |
| **35 B6** | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| **NMP** | 80 | 78 | 76 | 70 | 74 | 68 | 66 | 64 |
| **LiCl** | | 2 | | | 2 | 2 | | 2 |
| **PVP K30** | | | 4 | | 4 | | 4 | 4 |
| **THF** | | | | 10 | | 10 | 10 | 10 |

**Conclusions:**

1. THF is better solvent than NMP (SOL 01 vs SOL 04).
2. Addition of PVP does not form a homogeneous blend (SOL 03, SOL 05, SOL 07 and SOL COMPL), therefore is not a viable approach.
3. At Polymer/LiCl=10, adding THF induces lower gel formation speed at RT (~2 h for SOL 02 vs ~8 h for SOL 06).
4. Gel formation could not be prevented at room temperature. Therefore, the solution should be kept at minimum 40 ºC within the spinning vessels and lines.
5. A good dope composition could be SOL 06 and SOL 04.
6. Spinning with SOL 02 instead of SOL 06 will determine a higher contribution of crystallization phenomena to phase inversion phenomena during the coagulation of the fibers.

# Polymer spinning



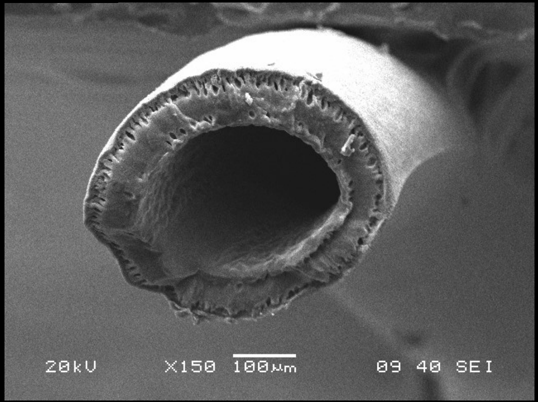
**Polymer dope composition:**

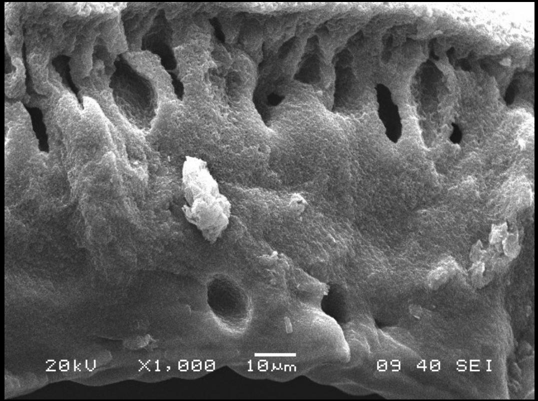
| | |
|---|---|
| **035 B5** | 20 and 23 wt% |
| LiCl | 3.67 wt% |
| NMP | 73.33 wt% |

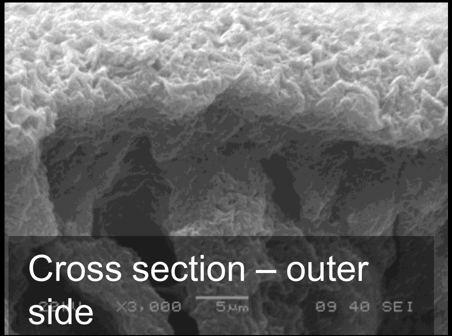
Gel at RT liquid at 40 ºC

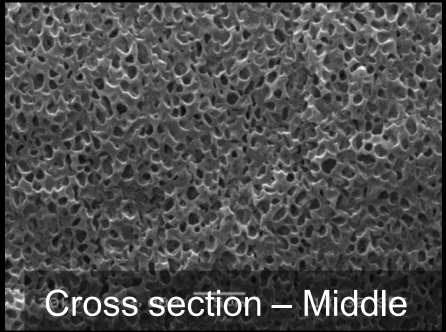
| Pump temperature (ºC) | Spinneret temperature (ºC) | Bore liquid composition $H_2O$/NMP wt% | Air gap (cm) | Air gap environment | Hollow fiber? |
|---|---|---|---|---|---|
| 50 | 50 | 100/0 | 26 | 78% RH | ✓ |
| 50 | 50 | 30/70 | 5 - 20 | $N_2$ | ✗ |
| 50 | 21 | 50/50 | 5, 11 | $N_2$ | ✓ |

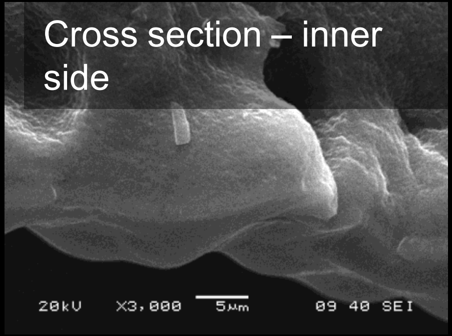
Bio Co Mem

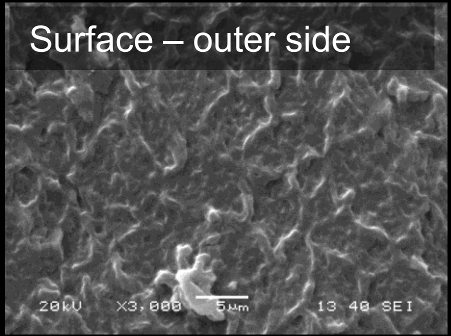

20kV X150 100µm 09 40 SEI

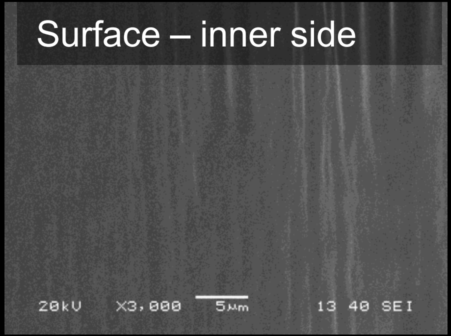

20kV X1,000 10µm 09 40 SEI


Cross section – outer side
X3,000 5µm 09 40 SEI


Cross section – Middle


Cross section – inner side
20kV X3,000 5µm 09 40 SEI


Surface – outer side
20kV X3,000 5µm 13 40 SEI

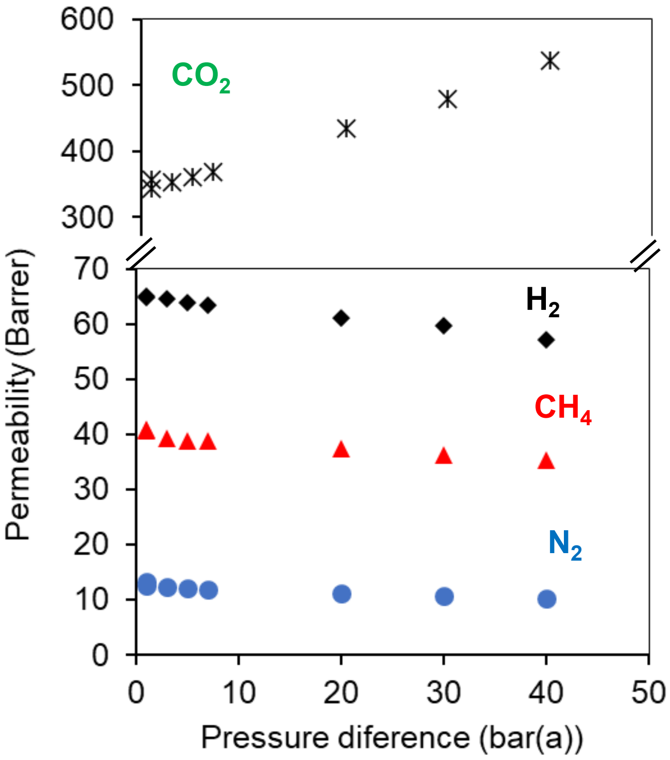

Surface – inner side
20kV X3,000 5µm 13 40 SEI

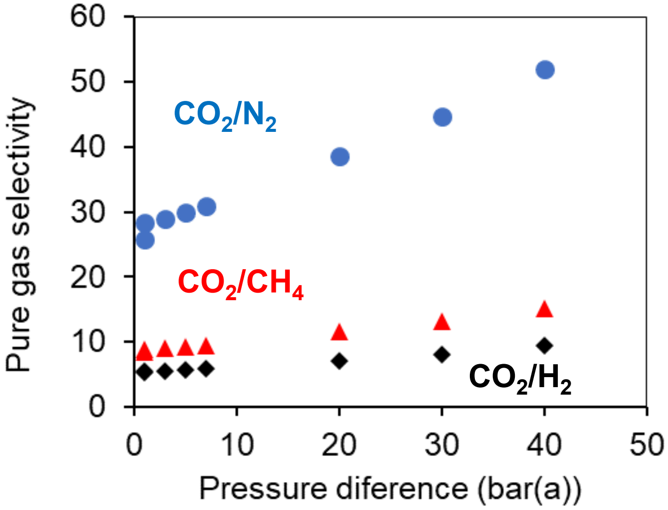
## Polymer scale - up

| Conditions | PA structure | $T_g$ [°C] | $T_m$ [°C] PEO/PA | $CO_2$ permeability (Barrer) | $CO_2/N_2$ Selectivity | $CO_2/CH_4$ Selectivity | $CO_2/H_2$ Selectivity |
|---|---|---|---|---|---|---|---|
| 35 ºc and 3 bar(a) Δp | **Prototype A** | **<-50** | **25/160** | **311,41** | **45** | **14,07** | **9,35** |
| | MS-2021-035 | <-40 | 16 / 80 | 228,8 | 27,5 | 9,2 | |
| | Prototype B *(scaled-up)* 2021-1449TLT500 | n.d | 13/77 | 353,99 | 28,83 | 8,99 | 5,48 |
| | Prototype B *(scaled-up)* 2021-1449TLT502 | n.d | 20/94 | 342,77 | 30,13 | 9,25 | 5,37 |
| 30 ºC, 300 mbar | Polyactive (1500PEO77PBT23) | **-49** | **27/110** | **115** | **45,6** | | **n.d.** |

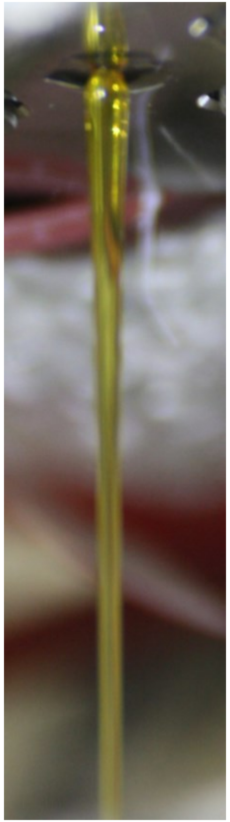
Objective for HF membrane:
PCO2= 1000 GPU
$\alpha_{CO2/N2}$ = 30

Gas permeation Properties: 2021-1449TLT500

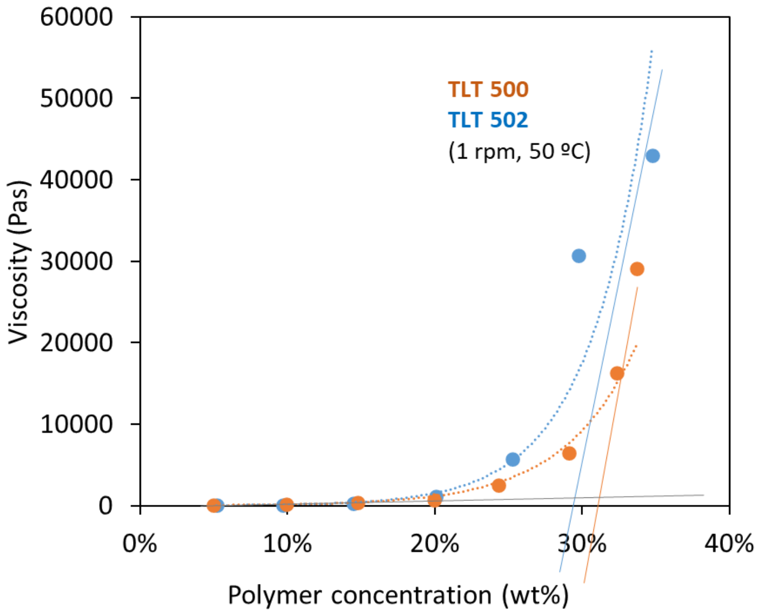


# Solubility study



| | Conc. (wt%) | | | | | |
|---|---|---|---|---|---|---|
| **TLT 500 or TLT 502** | **5** | **10** | **15** | **20** | **25** | **30** |
| **NMP** | 92,5 | 85 | 77,5 | 68 | 62,5 | 55 |
| **LiCl** | 0,5 | 1 | 1,5 | 2 | 2,5 | 3 |
| **THF** | 2,5 | 5 | 7,5 | 10 | 12,5 | 15 |

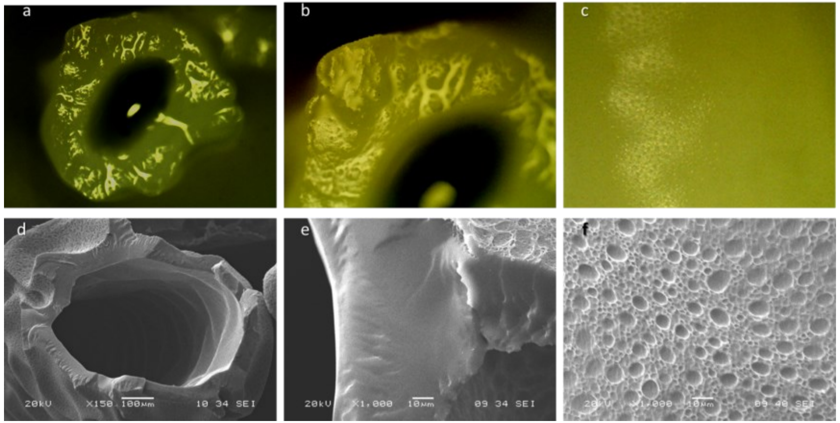



- All solutions are liquid at 40 ºC
- All solutions form a gel at room temperature.
- At RT, gel formation is 3 h for TLT 502 and takes longer time for TLT 502
- Gel formation is faster at lower concentrations (see below)

Polymer spinning

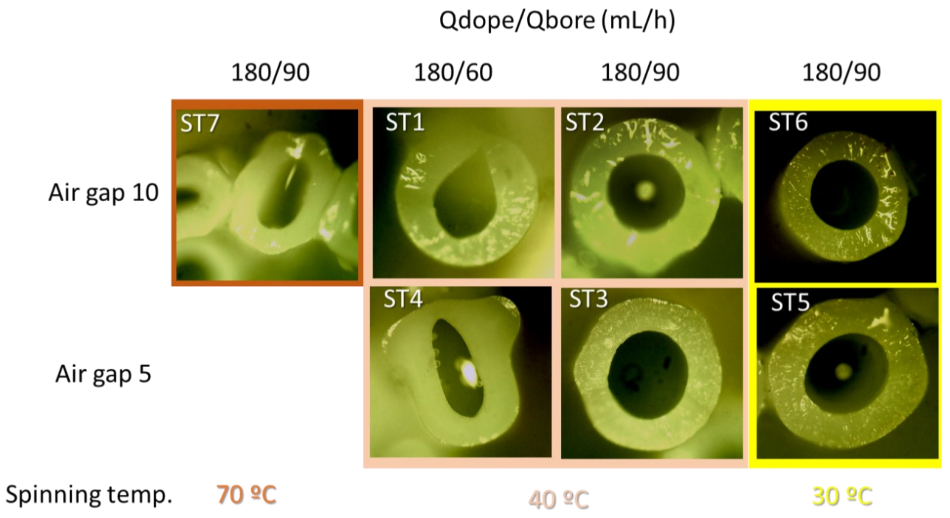
28 wt% TLT 502 ;  14 wt% THF; 2,8 wt% LiCl in NMP

Qdope/Qbore=180/90




- bore liquid composition H2O/NMP=90/10 wt%,
- spinning temperature: 30 °C,
- air gap height = 50, humidity in the air gap,
- take up rate = 8 m/min.

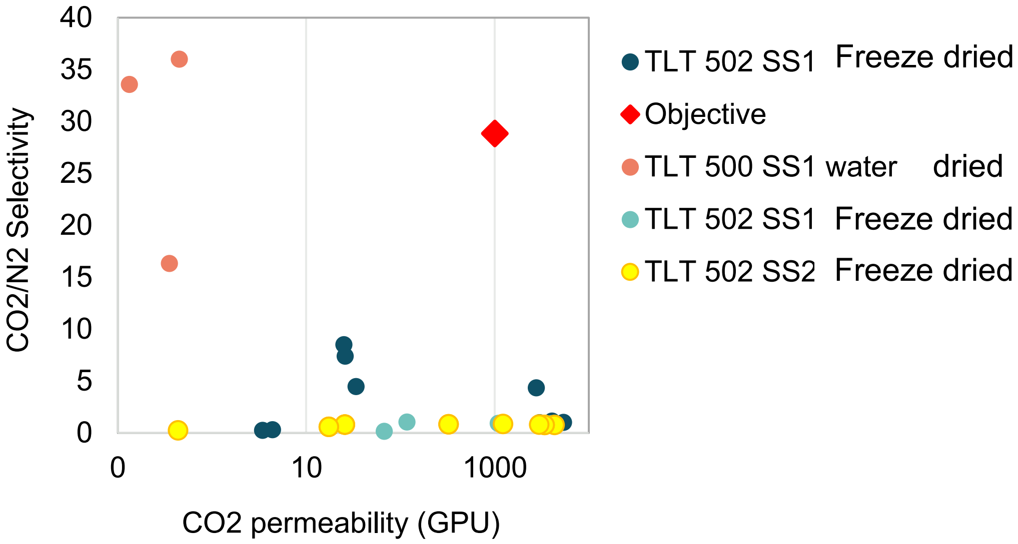
26 wt% TLT 502; 1.3 wt% LiCl in NMP



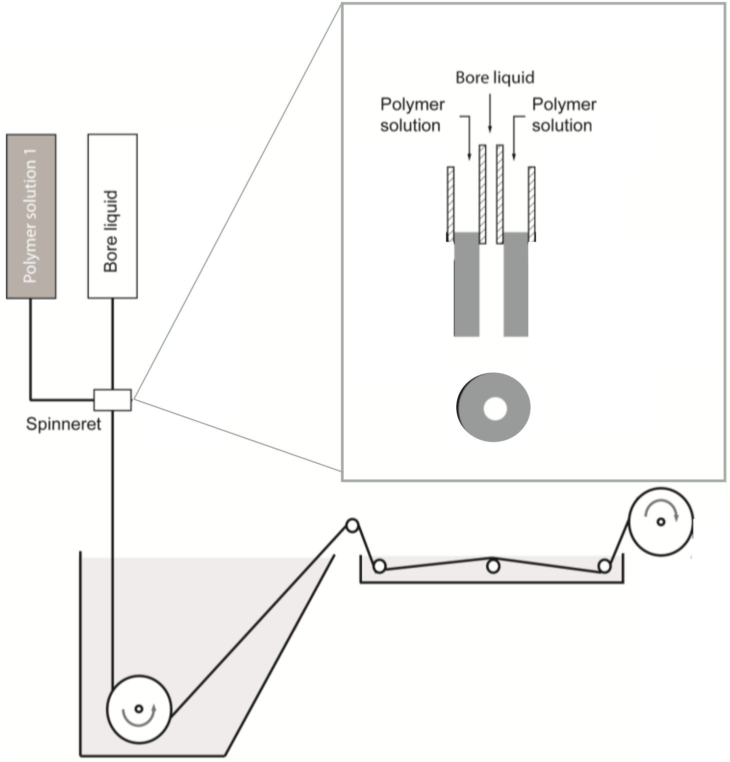

- bore liquid composition H2O/NMP=95/5 wt%,
- take up rate = 8 m/min.

# Gas permeation





# Dual layer Hollow fiber spinning




| PA structure | $T_g$ [°C] | $T_m$ [°C] PEO/PA | $CO_2$ permeability (Barrer) | $CO_2/N_2$ Selectivity | $CO_2/CH_4$ Selectivity | $CO_2/H_2$ Selectivity |
|---|---|---|---|---|---|---|
| **Prototype A** | **<-50** | **25/160** | **311,41** | **45** | **14,07** | **9,35** |
| MS-2021-035 | <-40 | 16 / 80 | 228,8 | 27,5 | 9,2 | |
| Prototype B *(scaled-up)* 2021-1449TLT500 | n.d | 13/77 | 353,99 | 28,83 | 8,99 | 5,48 |
| Prototype B *(scaled-up)* 2021-1449TLT502 | n.d | 20/94 | 342,77 | 30,13 | 9,25 | 5,37 |
| **Prototype B *(scaled-up)* 2021-1449TLT549** | | | **395,88** | **36,13** | **10,9** | **7,46** |
| **Prototype B *(scaled-up)* 2021-1449TLT550** | | | **106** | **21,02** | **7,16** | **2,81** |
| Polyactive (1500PEO77PBT23) | **-49** | **27/110** | **115** | **45,6** | | **n.d.** |

Objective for dual layer fiber approach:
PCO2= 400 GPU
$\alpha_{CO2/N2}$ = 30

Membranes 2021, 11(8), 557; https://doi.org/10.3390/membranes11080557

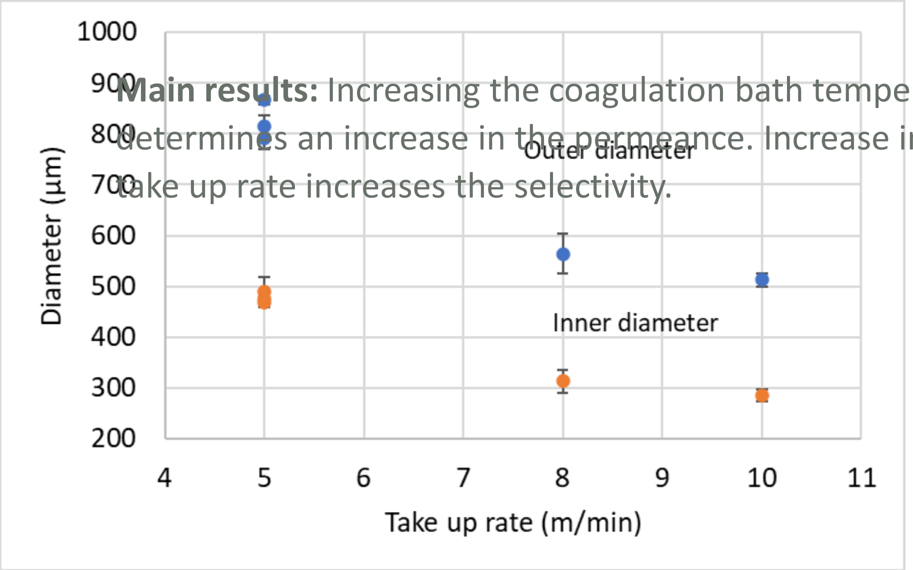
# Dual layer Hollow fiber spinning

| TLT 550 | 20,00% |
|---|---|
| NMP | 72,90% |
| LiCl | 1,10% |
| PEG 1500 | 6,00% |

| TLT 549 | 22,0% |
|---|---|
| NMP | 76,4% |
| LiCl | 1,00% |
| H2O | 0,5% |

**Spinning parameters:**
Outer dope flow rate = 160 mL/min
Inner dope flow rate = 20 mL/min
Bore liquid = 80/20 H2O/NMP
Spinneret Temperature = **50 ºC, 40 ºC for exp 2**
Air gap = chimney in place when air gap of 10, No N2 flow
Freeze drying

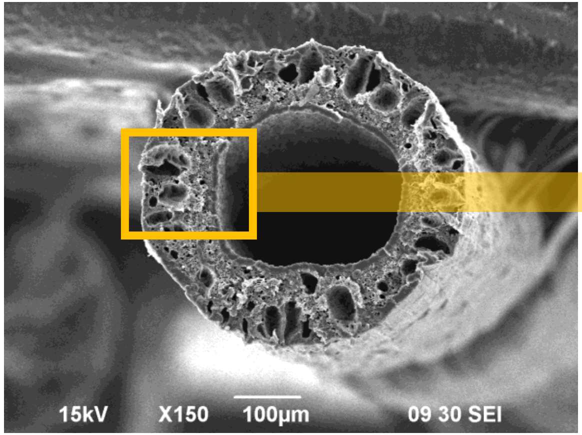
| | Quench Bath Temp | Air gap height | Take up rate |
|---|---|---|---|
| | (ºC) | (cm) | (m/min) |
| ST1 | 22 | 10 | 5 |
| ST3 | 21,5 | 1,5 | 5 |
| ST4 | 21,5 | 1,5 | 10 |
| ST5 | 39 | 10 | 5 |
| ST6 | 38,8 | 1,5 | 8 |

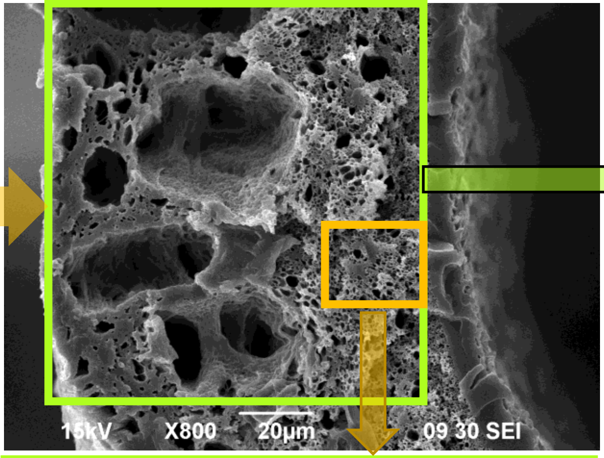


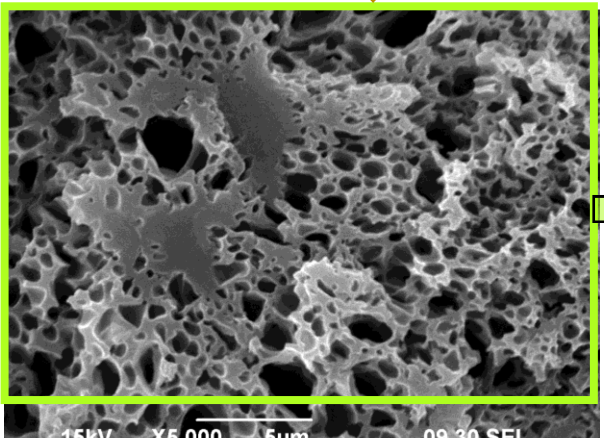

**Main results:** Increasing the coagulation bath temperature determines an increase in the permeance. Increase in the take up rate increases the selectivity.

# Dual layer Hollow fiber spinning

## Porosity

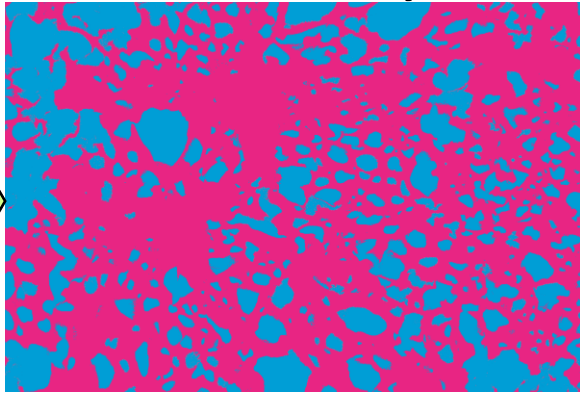


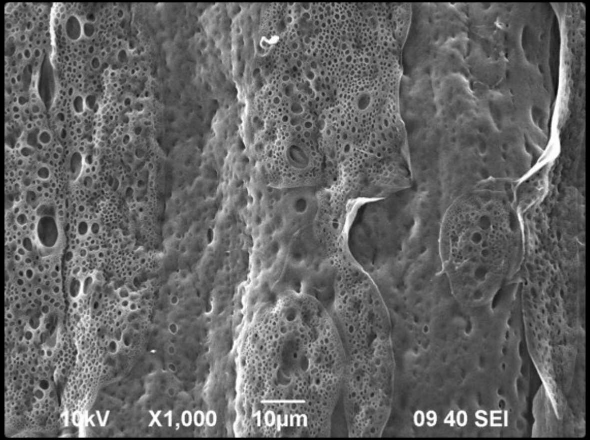



Porosity = 45 %

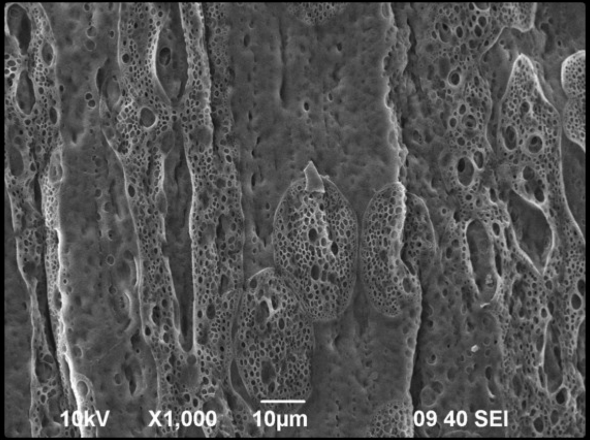
Porosity = 34 %



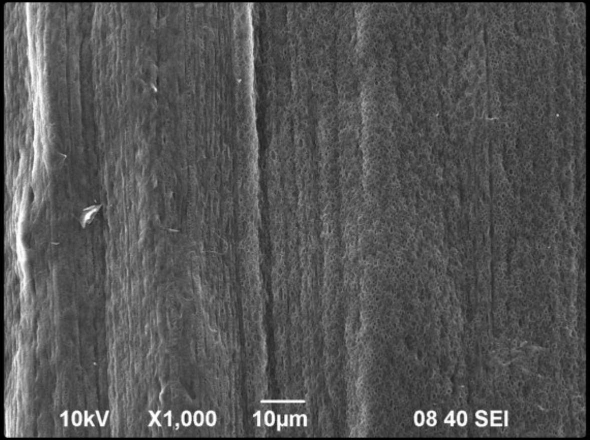
ST1



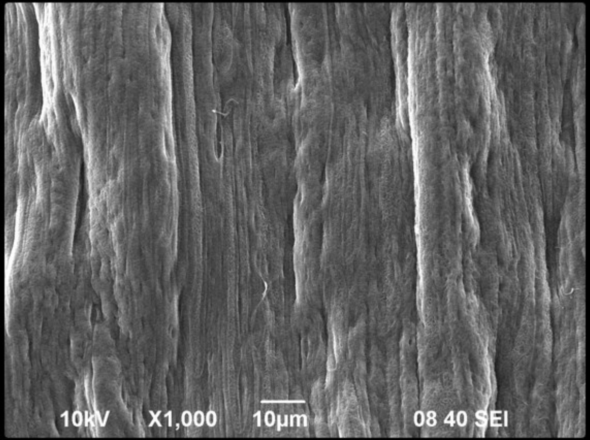

ST2



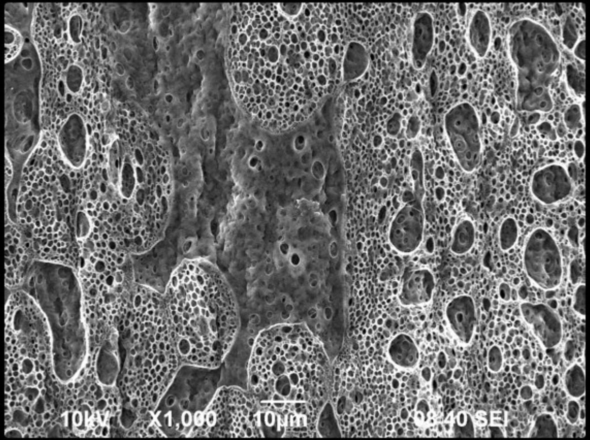

ST3



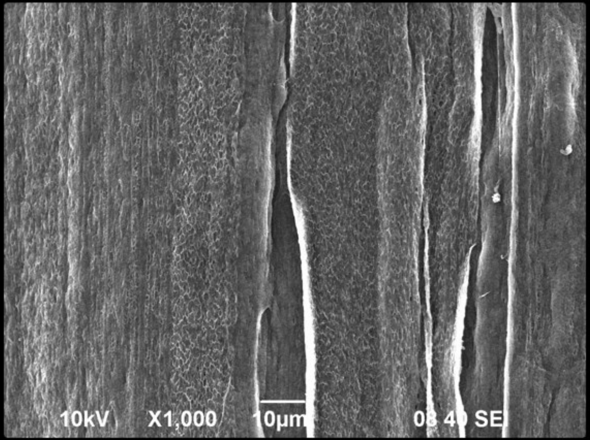

ST4

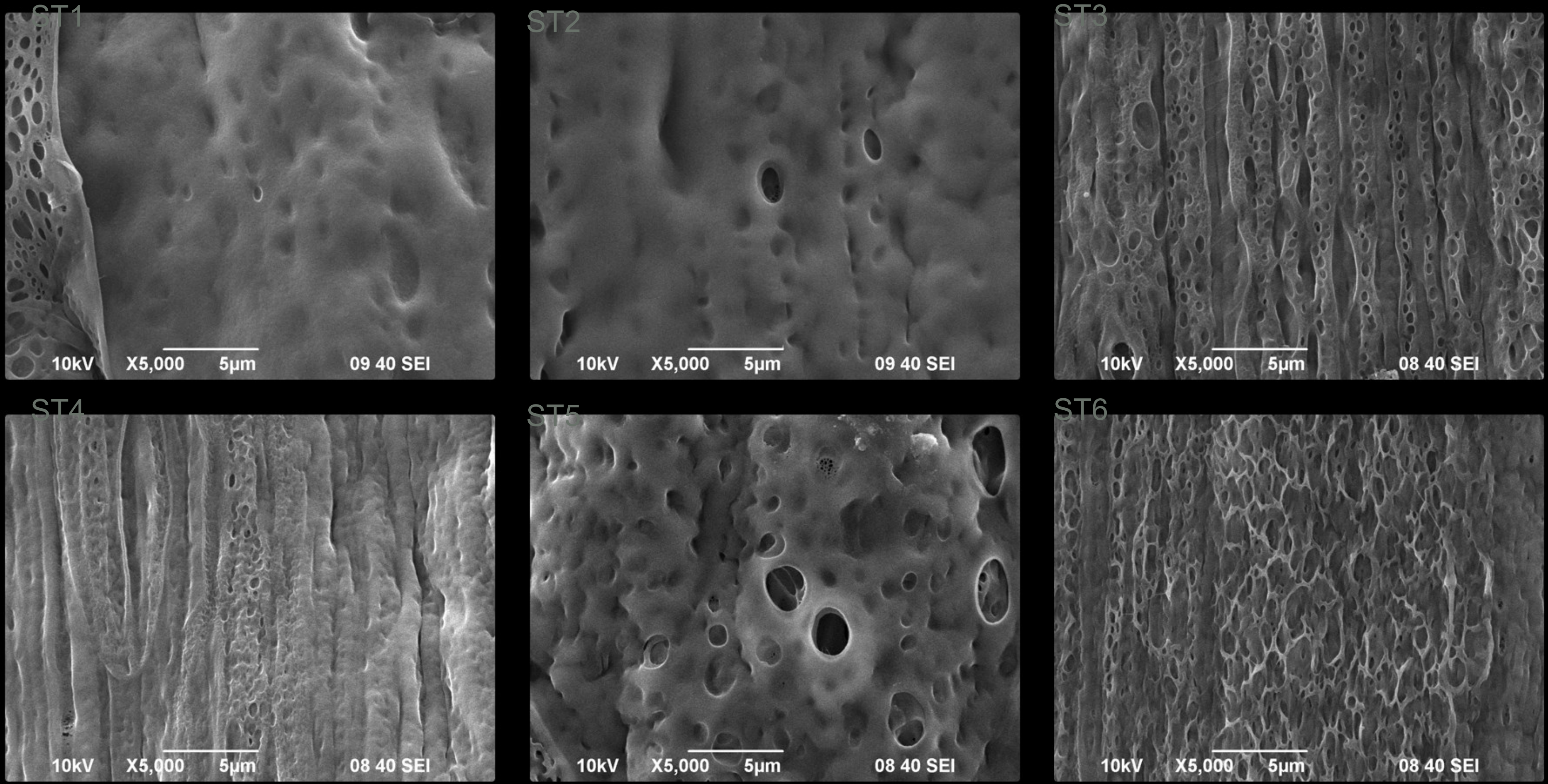



ST5




ST6





ST1
10kV X5,000 5μm 09 40 SEI
ST2
10kV X5,000 5μm 09 40 SEI
ST3
10kV X5,000 5μm 08 40 SEI
ST4
10kV X5,000 5μm 08 40 SEI
ST5
10kV X5,000 5μm 08 40 SEI
ST6
10kV X5,000 5μm 08 40 SEI

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# Dual layer Hollow fiber spinning

# Mechanical properties: elongation

| | Ultimate strength (Mpa) | ± | Elongation at brake (%) | ± |
|---|---|---|---|---|
| ST1 | 7,38 | 0,173 | 874% | 27% |
| ST3 | 7,19 | 0,226 | 791% | 10% |
| ST4 | 11,44 | 0,182 | 584% | 9% |
| ST5 | 4,92 | 0,114 | 664% | 5% |
| ST6 | 9,46 | 0,444 | 627% | 12% |

| Membranes (Materials) | Young's Modulus (MPa) | Elongation at Break (%) | Ultimate Strength (MPa) | Porosity (%) |
|---|---|---|---|---|
| U305 (Ultem@ 1000 (PEI)) | 132 | 44 | 58.5 | 55.9 |
| M264 (Matrimid@ 5218 (PI)) | 121 | 29 | 54.8 | 58.4 |
| PES28 (Ultrason E6020P (PES)) | 72 | 85 | 5.2 | 46.1 |

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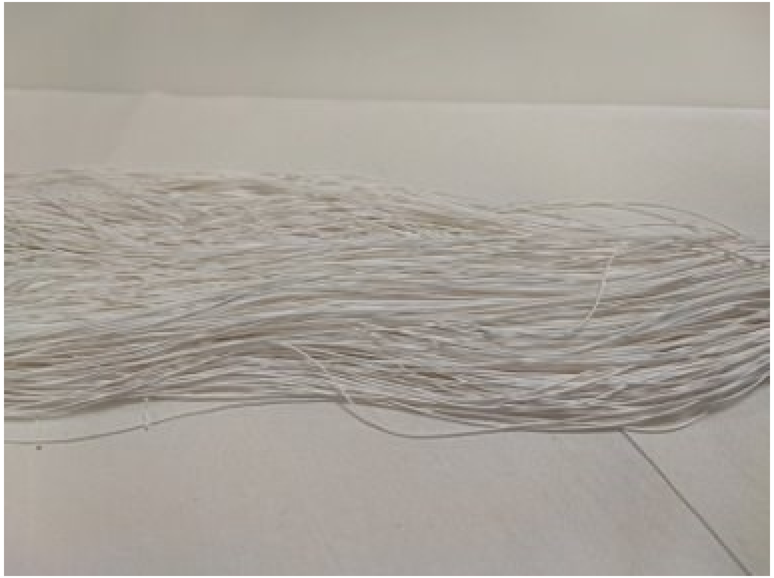
# Conclusions

More optimization:
- Increase surface porosity
- Eliminate the macrovoids
- Densify the inner layer

Scale up: successful



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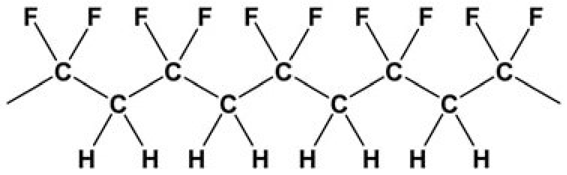
# Eskerrik asko zuen arretagatik!

# Thank you for your attention!

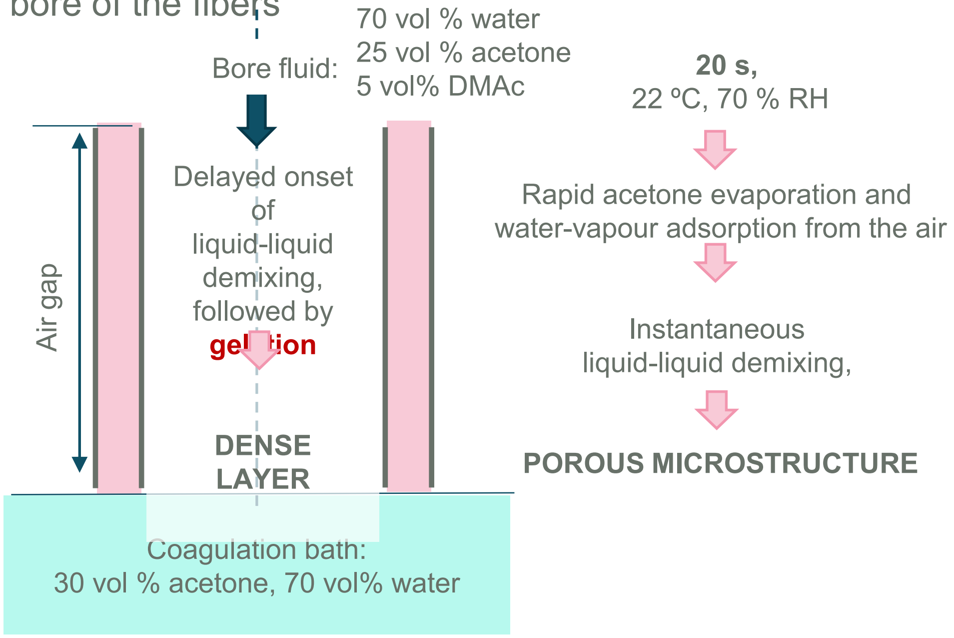
# Prototype B – Polymer spinning

**Literature background**: Procedure for casting integral asymmetric PVDF pervaporation hollow fiber membranes with a dense layer on the inside bore of the fibers




| Xc | Tm (°C) | Tc (°C) |
|---|---|---|
| 50,7 | 168,3 | 142,1 |

**Polymer dope composition:**
25 wt% PVDF
30 wt% DMAc
45 wt% Acetone




K. Jian, P.N. Pintauro, Asymmetric PVDF hollow-fiber membranes for organic/water pervaporation separations, Journal of Membrane Science, Volume 135, Issue 1, 1997, Pages 41-53