# Polymer Membranes for Separation of $CO_2$ - An Overview

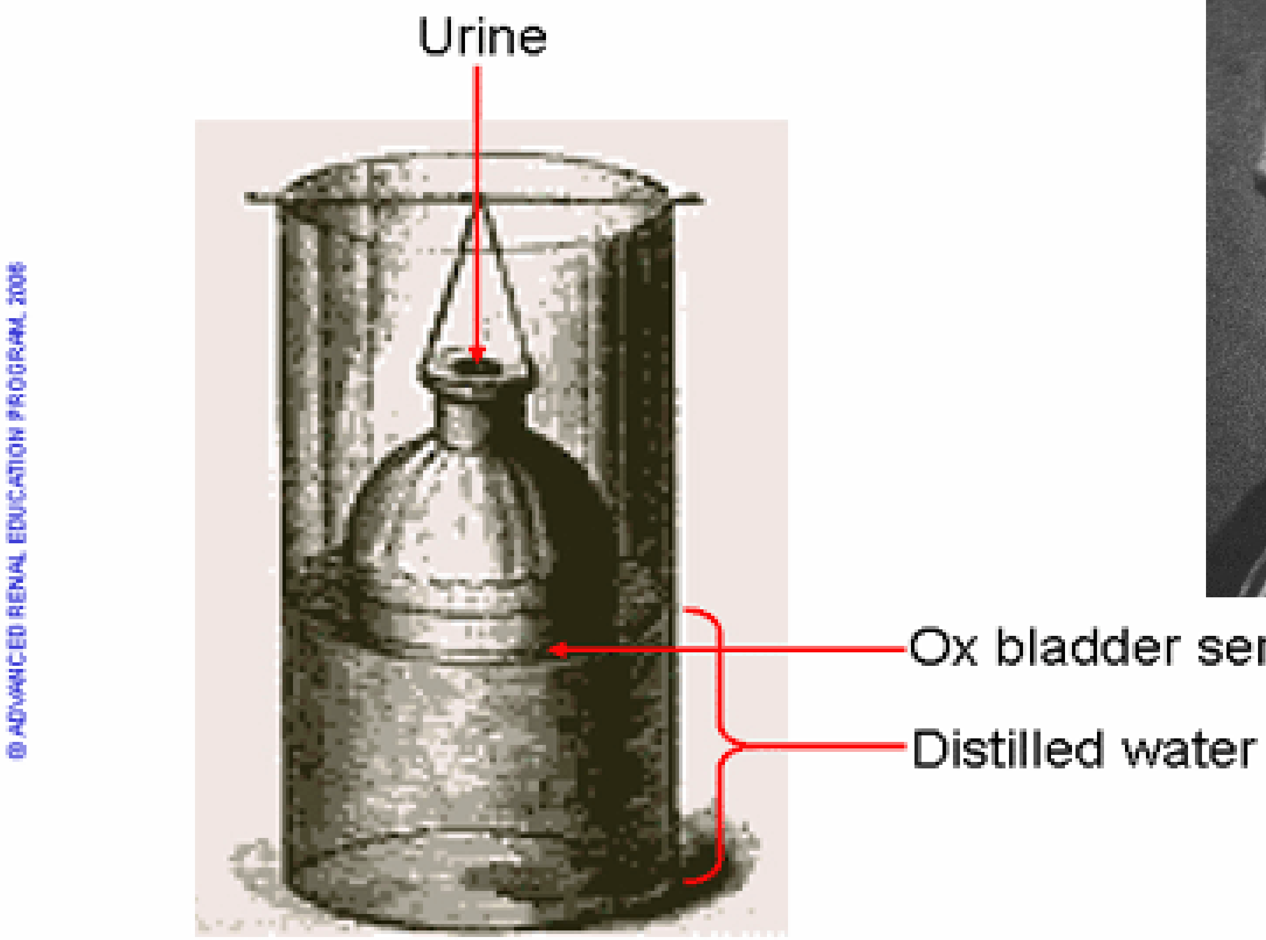
Volker Abetz, Torsten Brinkmann, Sergey Shishatskiy, Jan Wind

21.06.2011 / Frankfurt

**2nd International Conference on Energy Process Engineering**
**Efficient Carbon Capture for Coal Power Plants**
**June 20 - 22, 2011 in Frankfurt/Main, Germany**

Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

# Thomas Graham (1805 – 1869)
# Effusion/Diffusion Measurements 1831, 1854



Based on: Graham T. *Philos Trans R Soc Lond* 144:117-128, 1854

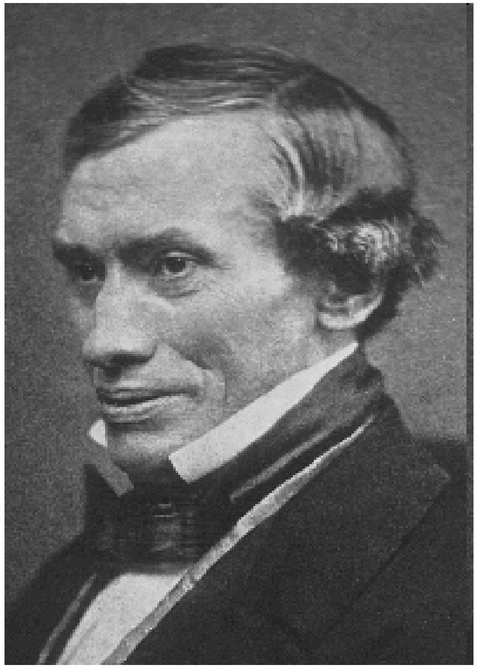
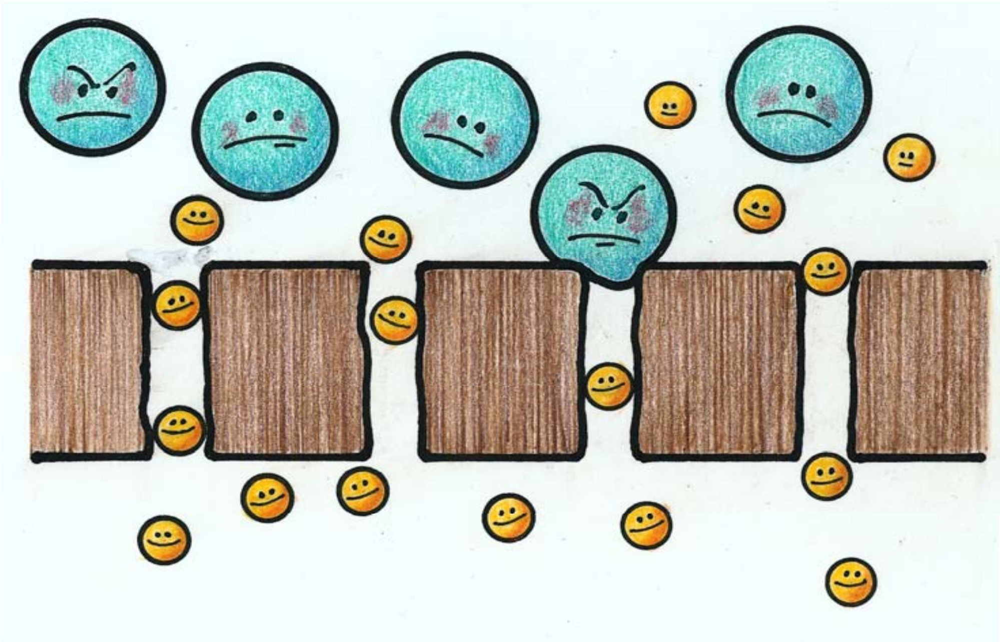


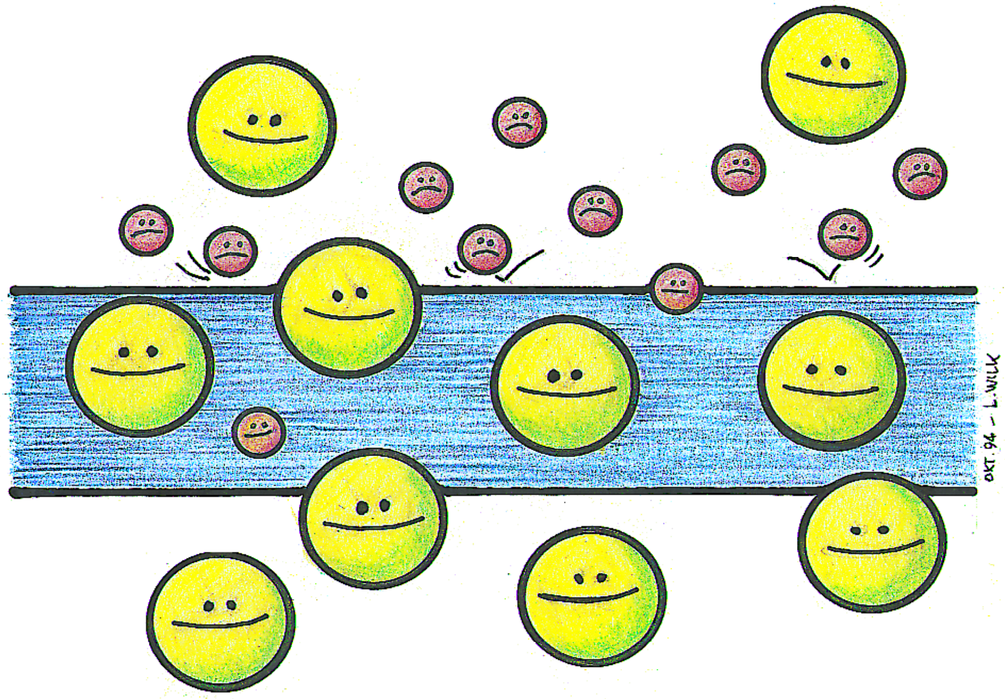
Image source: http://www.advancedrenaleducation.com

# Membranes for Separation Processes



**Porous membrane**

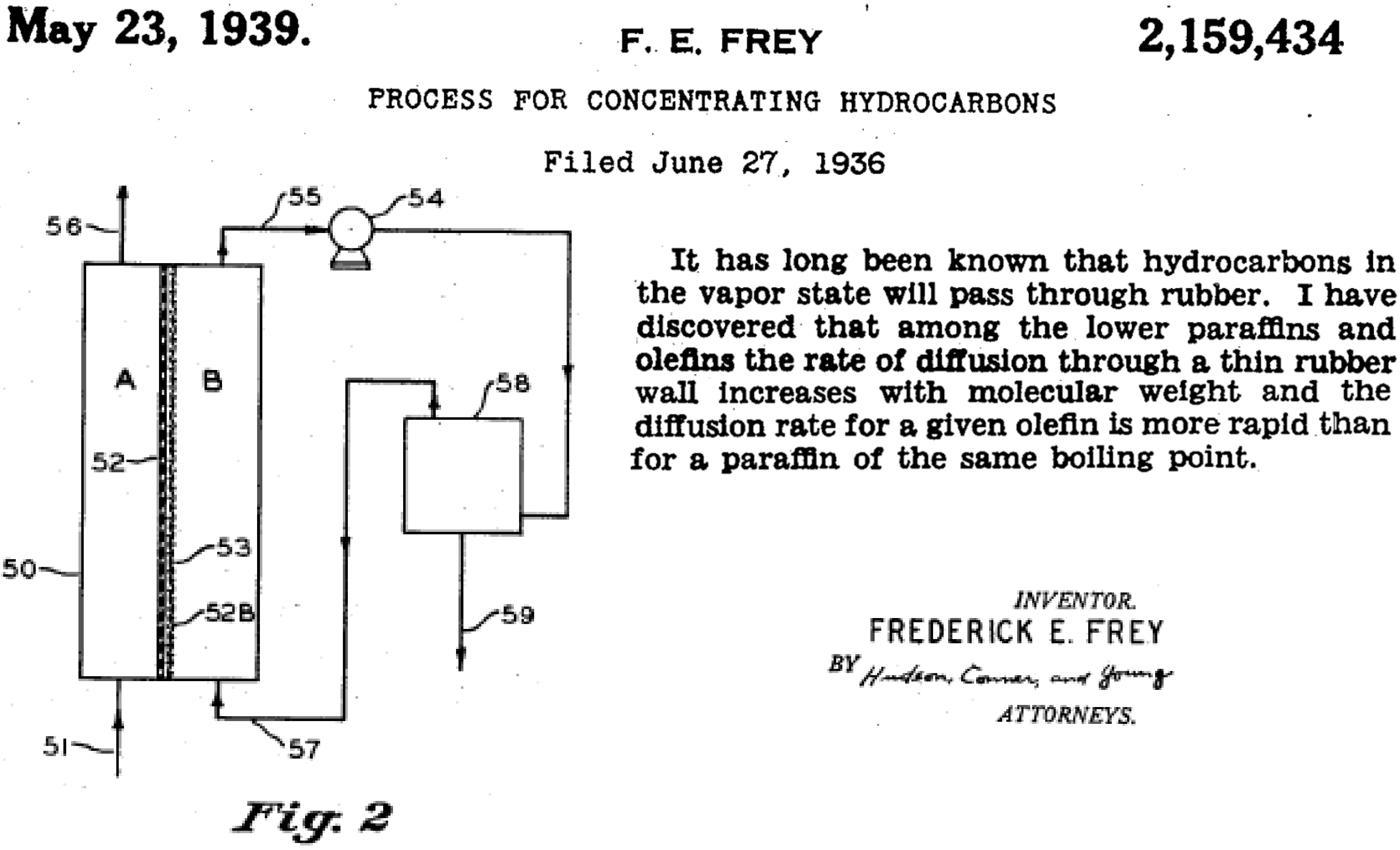
- Ultra- and microfiltration



**Solution-diffusion membrane**

- Gas and vapour permeation
- Pervaporation
- Reverse osmosis
- Nanofiltration

# First patent on membrane gas separation. 1936



**May 23, 1939.** **F. E. FREY** **2,159,434**

PROCESS FOR CONCENTRATING HYDROCARBONS

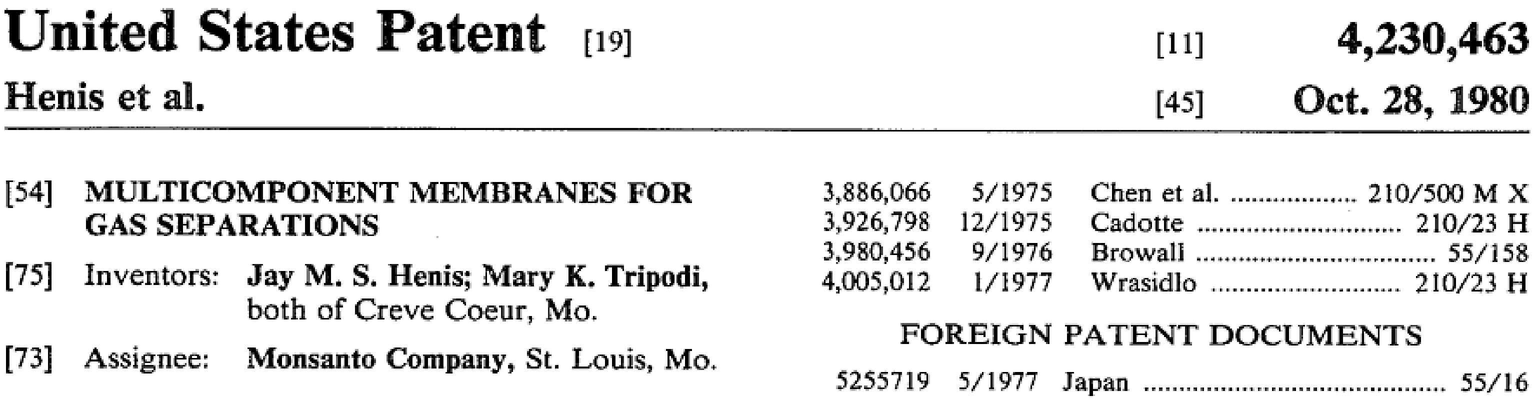
Filed June 27, 1936

*Fig. 2*

It has long been known that hydrocarbons in the vapor state will pass through rubber. I have discovered that among the lower paraffins and olefins the rate of diffusion through a thin rubber wall increases with molecular weight and the diffusion rate for a given olefin is more rapid than for a paraffin of the same boiling point.

*INVENTOR.*
FREDERICK E. FREY
*BY* Hudson, Conner, and Young
*ATTORNEYS.*

# Henis, Tripodi. Multicomponent Membranes – Starting Point for Thin Film Composite Membranes



**United States Patent** [19]
**Henis et al.**

[11] **4,230,463**
[45] **Oct. 28, 1980**

[54] **MULTICOMPONENT MEMBRANES FOR GAS SEPARATIONS**

[75] Inventors: **Jay M. S. Henis; Mary K. Tripodi,** both of Creve Coeur, Mo.

[73] Assignee: **Monsanto Company,** St. Louis, Mo.

| | | | |
|---|---|---|---|
| 3,886,066 | 5/1975 | Chen et al. | 210/500 M X |
| 3,926,798 | 12/1975 | Cadotte | 210/23 H |
| 3,980,456 | 9/1976 | Browall | 55/158 |
| 4,005,012 | 1/1977 | Wrasidlo | 210/23 H |

FOREIGN PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| 5255719 | 5/1977 | Japan | 55/16 |

FIG. 6

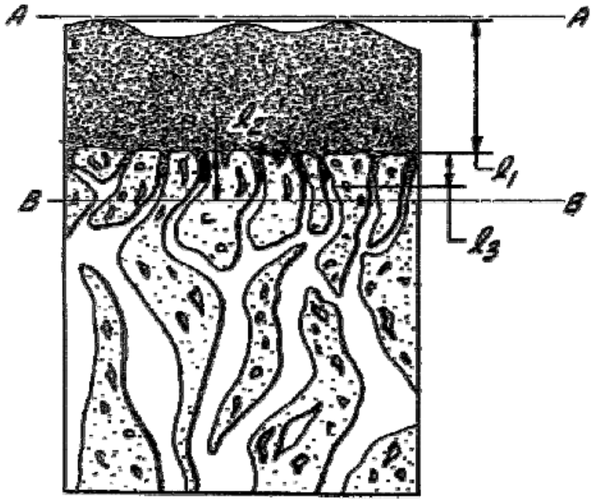
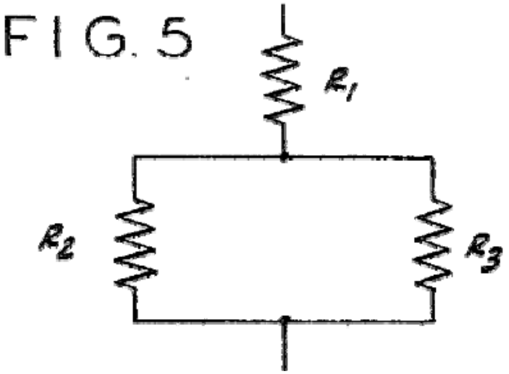


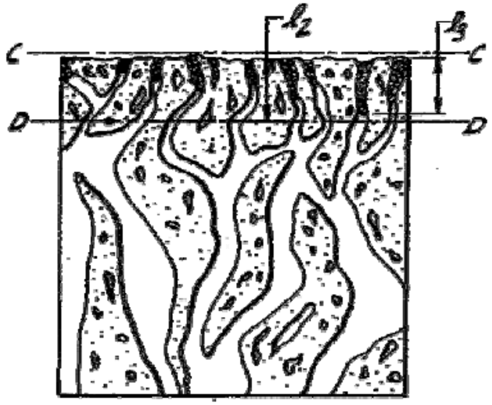
FIG. 5



$$R_i = \frac{l_i}{P_i}$$

$$R_T = R_1 + \frac{R_2 R_3}{R_2 + R_3}$$

FIG. 7



1998. $CO_2/N_2$ field tests of membrane separation units. Kvaerner

2004-2005. CSS problem acknowledged, first projects on $CO_2/N_2$ separation

2007. HGF Allianz MEMBRAIN “Gas separation membranes for zero-emission fossil power plants”

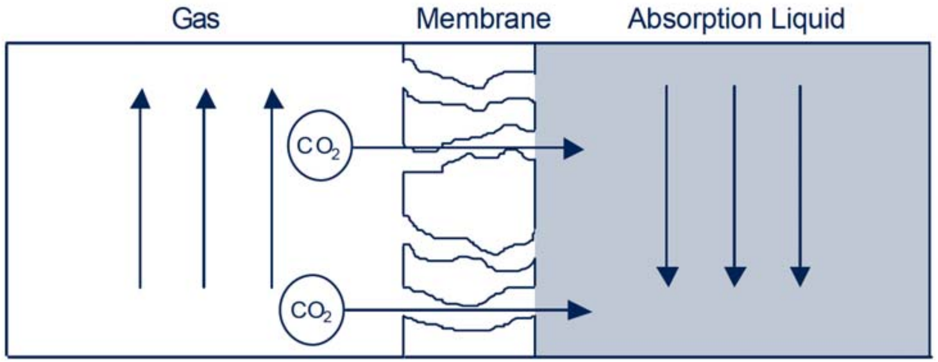
2008-2010. PEO based membranes for $CO_2$ separation developed in pilot scale. MTR, GKSS.

# Kvaerner 1995 - 1998:
# First Field Tests of $CO_2/N_2$ Membrane Separation Unit

In **1991**, the Norwegian government introduced a carbon tax in the Northern Sea of approximately 50 US dollars per ton of $CO_2$ emitted to the atmosphere.

Kvaerner initiated a discussion with oil producers in **1992**, in **1995** performance testing at TNO, GKSS, Gore, **1998** – pilot testing and scale-up.

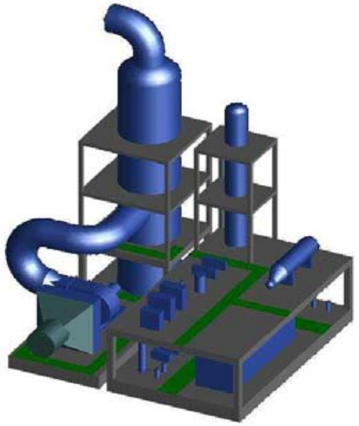
Membrane Contactor



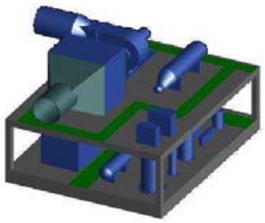
- Capital cost reduction of by 35 to 40%;
- Operating costs savings of between 38% and 42%;
- Dry equipment weight reduction of 32% to 37%;
- Operating equipment weight reduction of 34% to 40%;
- Total operating weight reduction of  44% to 50%;
- Footprint requirement reduced by 40%.

**Size comparison:**

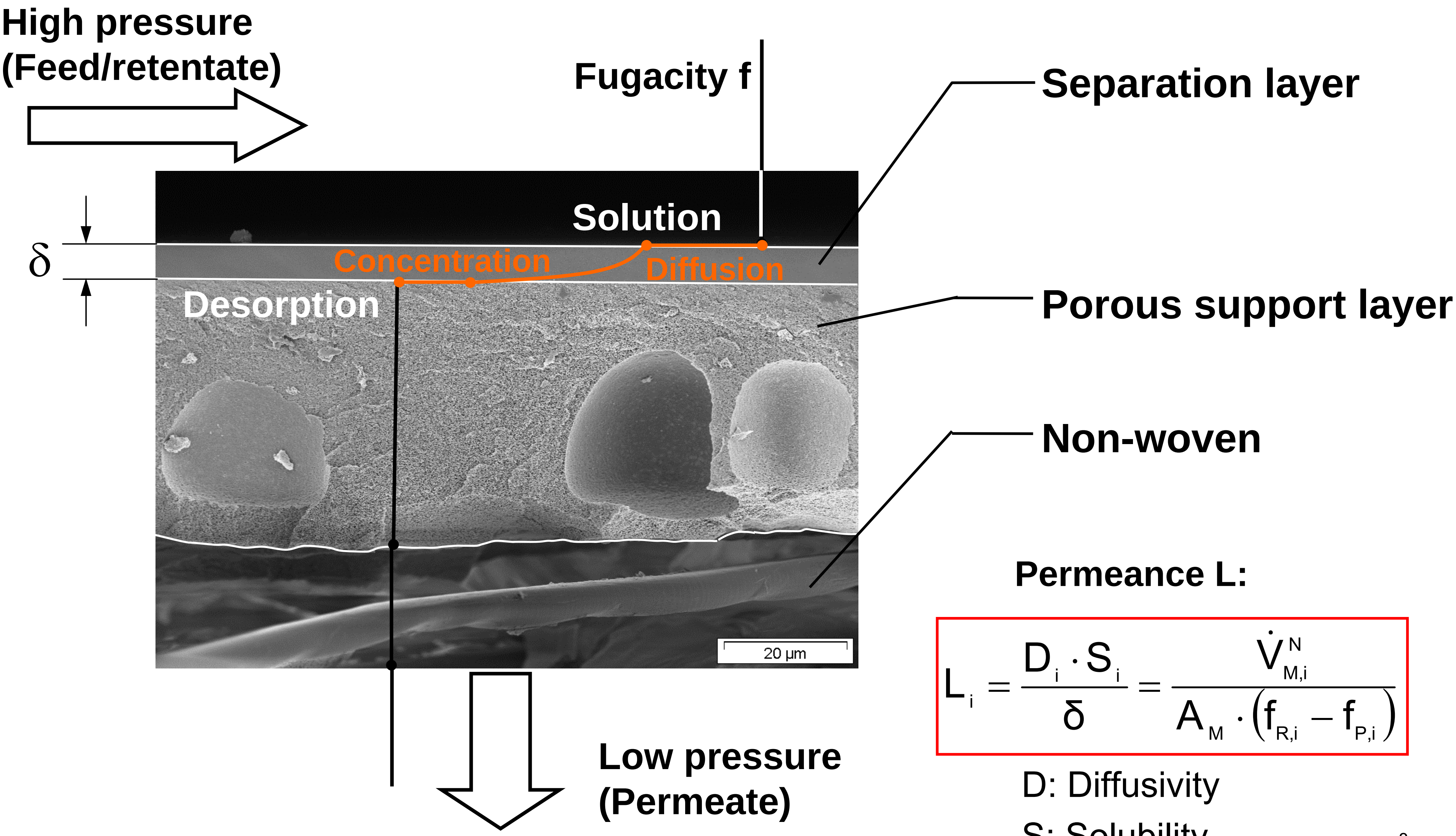
Conventional Process



Membrane Process



# Gas Permeation:
# Solution-Diffusion Mechanism



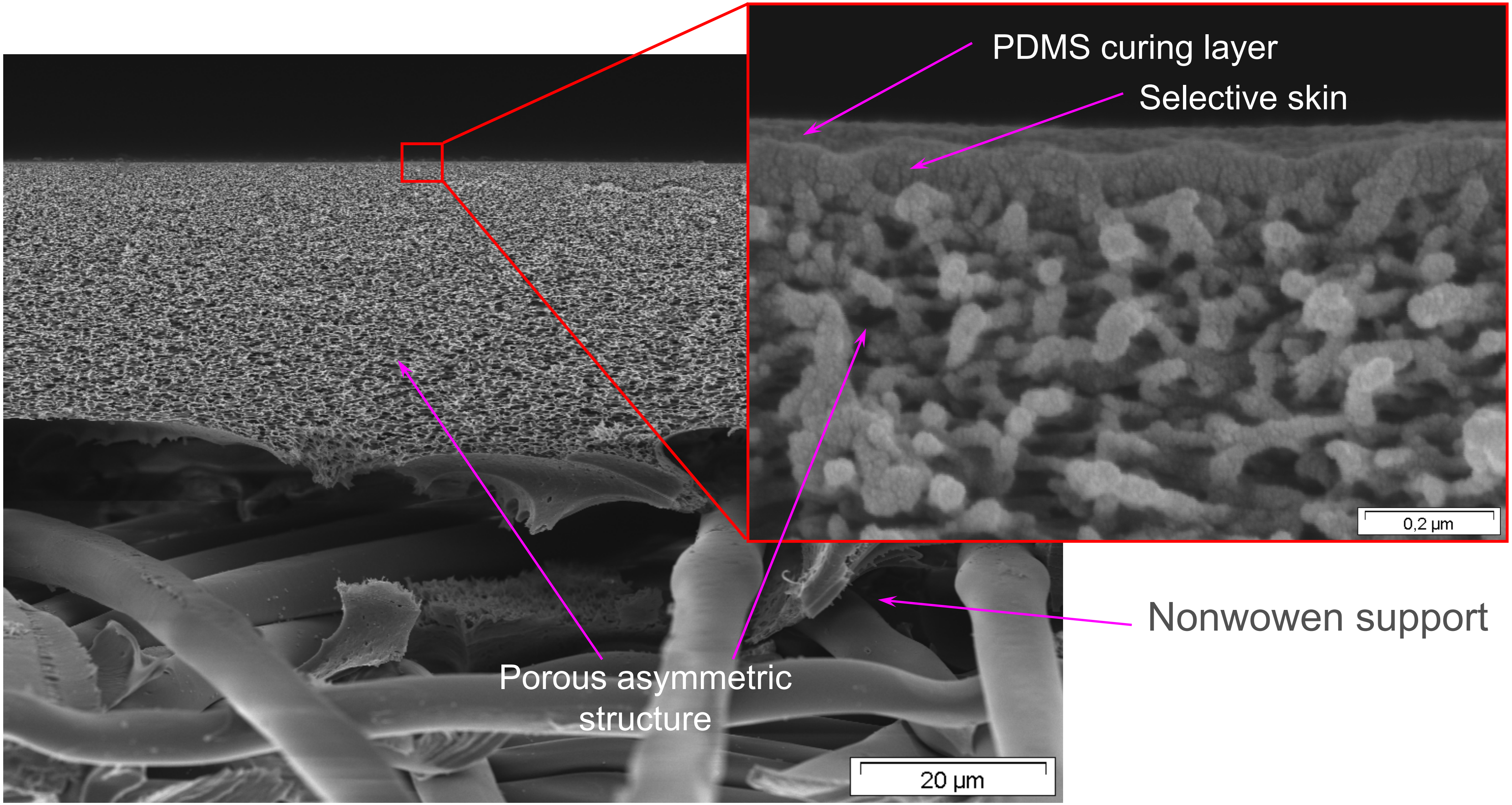
**Permeance L:**

$$L_i = \frac{D_i \cdot S_i}{\delta} = \frac{\dot{V}^N_{M,i}}{A_M \cdot \left(f_{R,i} - f_{P,i}\right)}$$

D: Diffusivity

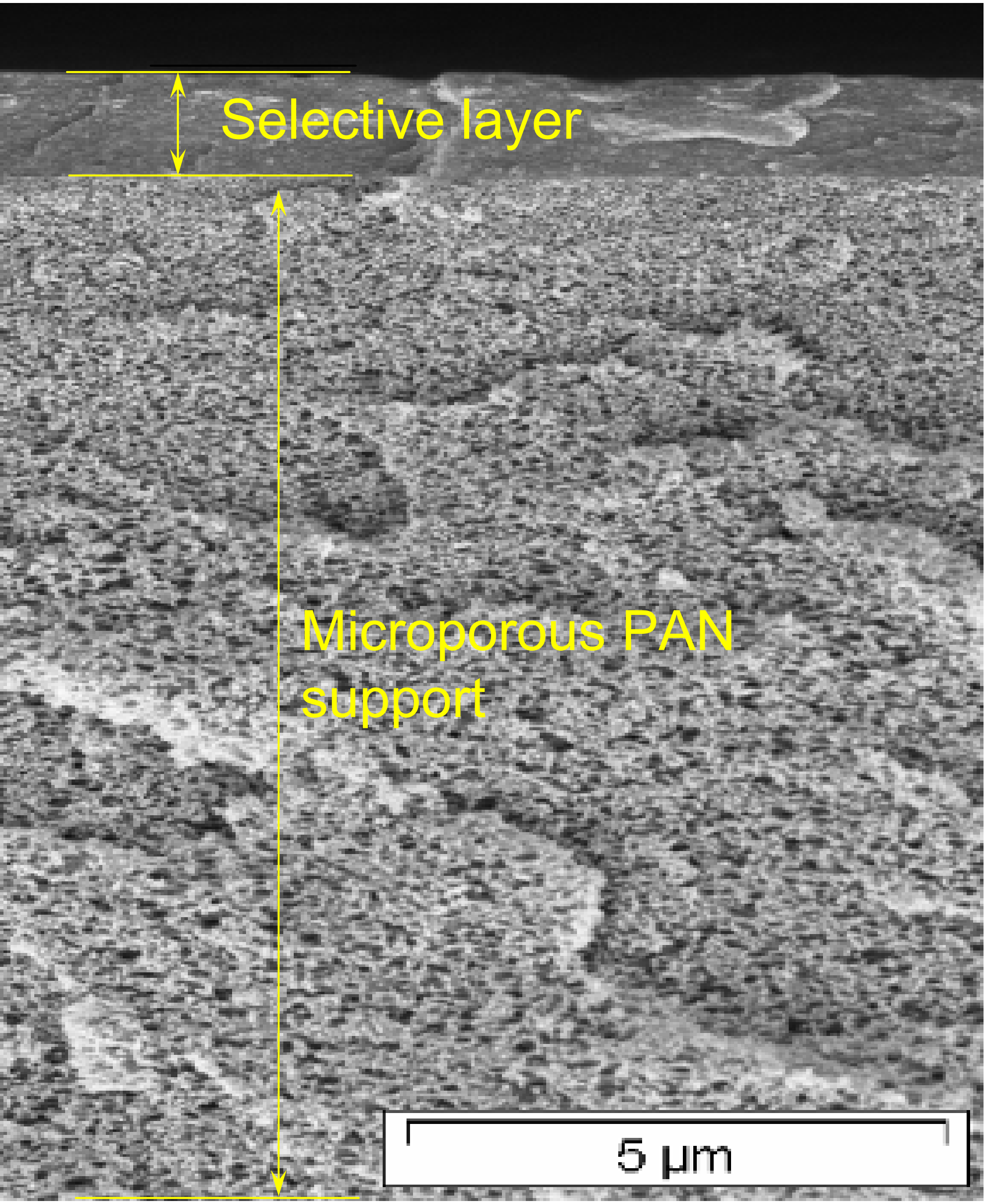
S: Solubility

# Asymmetric Gas Separation Membrane (on Nonwoven Support)

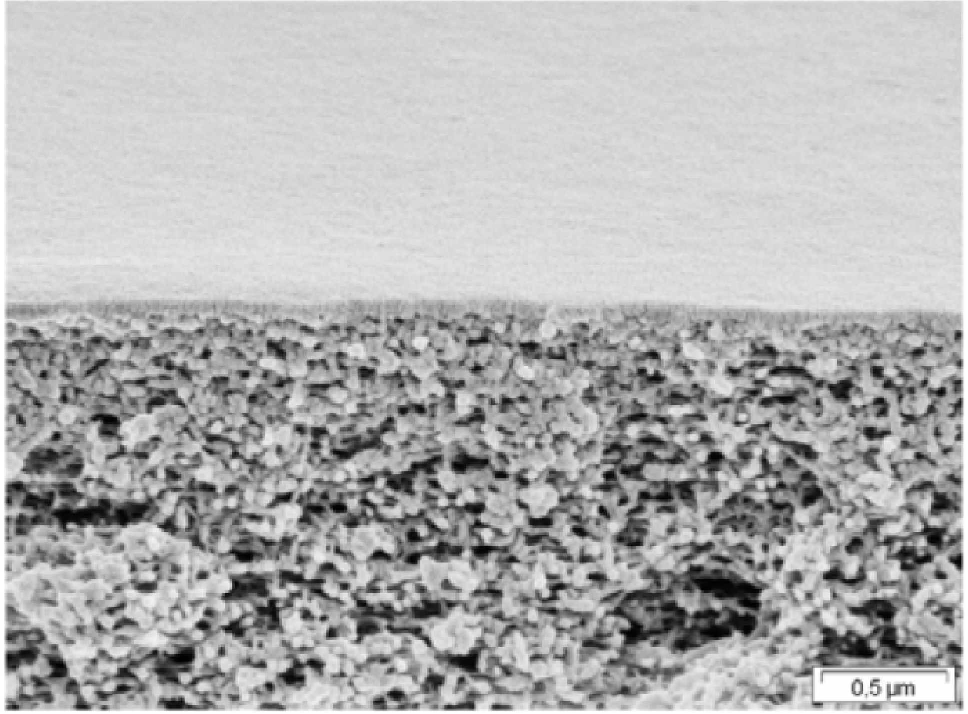


S. Shishatskiy et. al., Adv. Eng. Mat., 8 (2006), 390

# Thin Film Composite Membrane (TFCM)



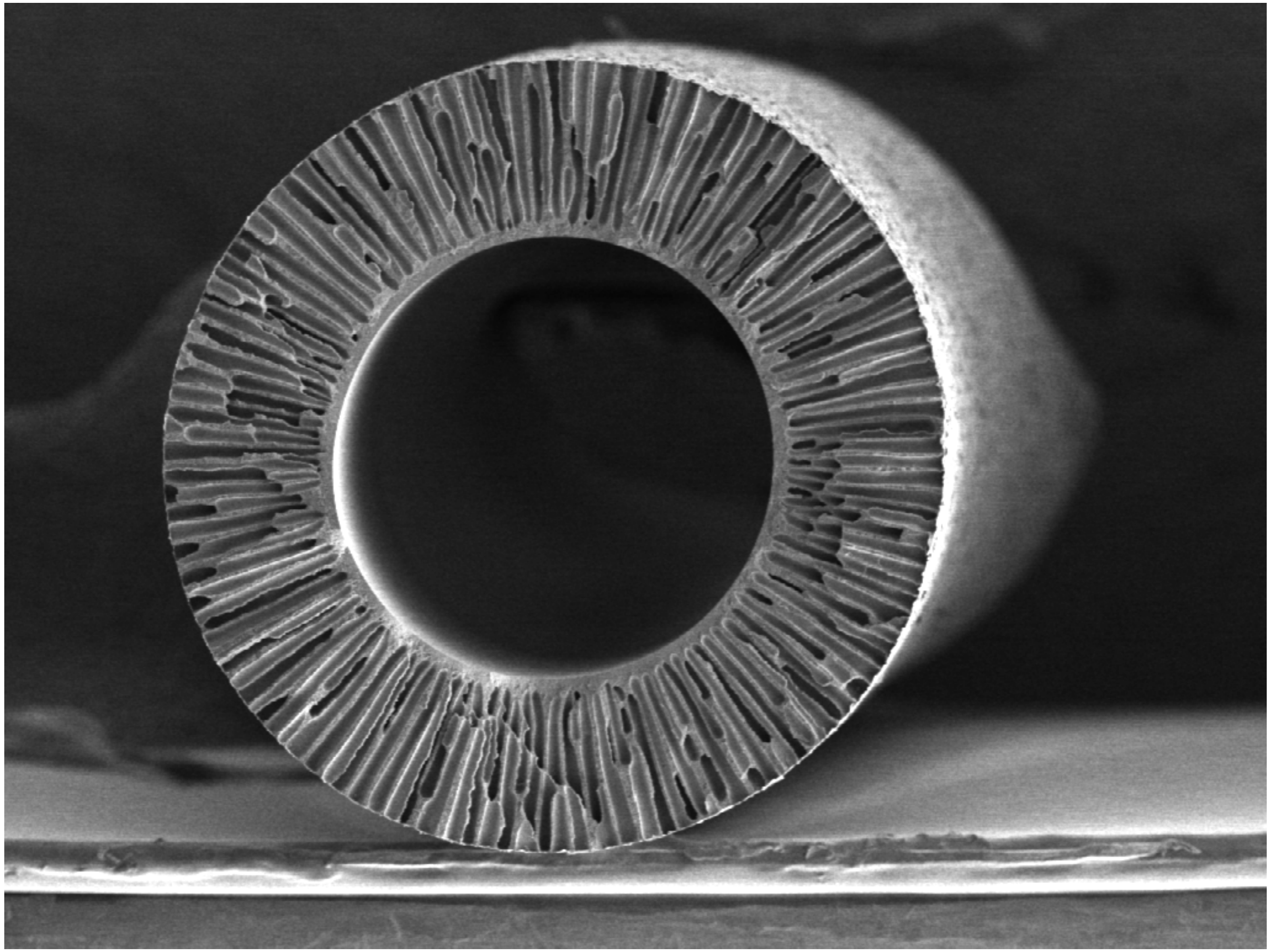
S.Shishatskiy et. al., Euromembrane 2009, Sept. 6-10, 2009, Montpellier



| Thickness (nm) | $CO_2$ ($m^3\ m^{-2}\ h^{-1}\ bar^{-1}$) | $CO_2/N_2$ |
|---|---|---|
| 170 | $0.84 \pm 0.3$ | 79.4 |
| 125 | $3.60 \pm 0.4$ | 57.9 |
| 45 | $4.80 \pm 0.6$ | 59.9 |

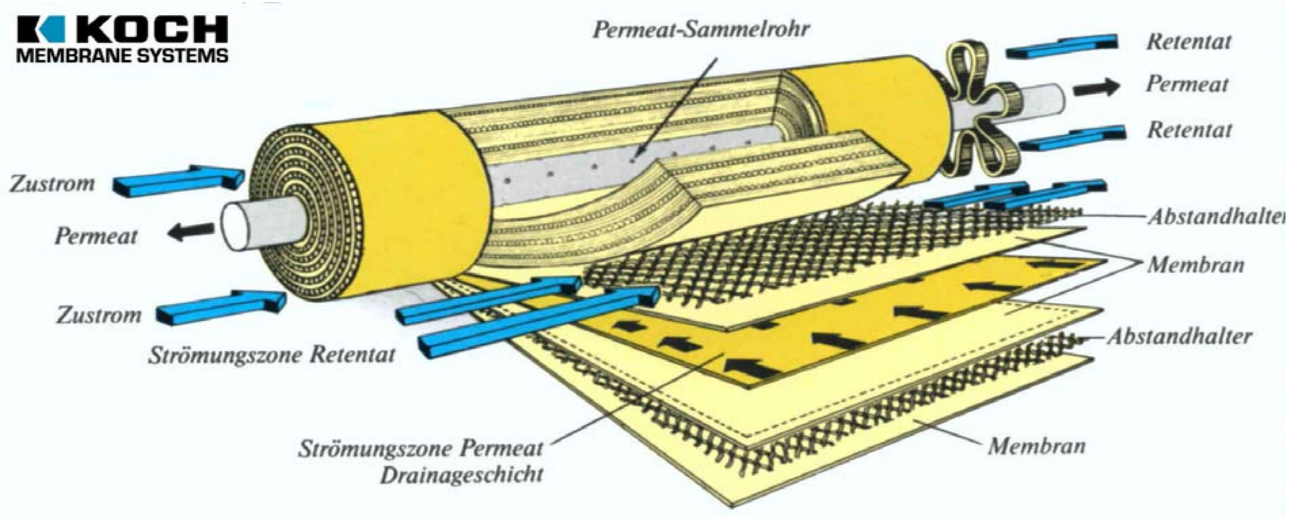
W. Yave et al., Nanotechnology, 21 (2010) 395301

# Hollow Fiber Membrane:
# Integral Asymmetric and/or TFCM

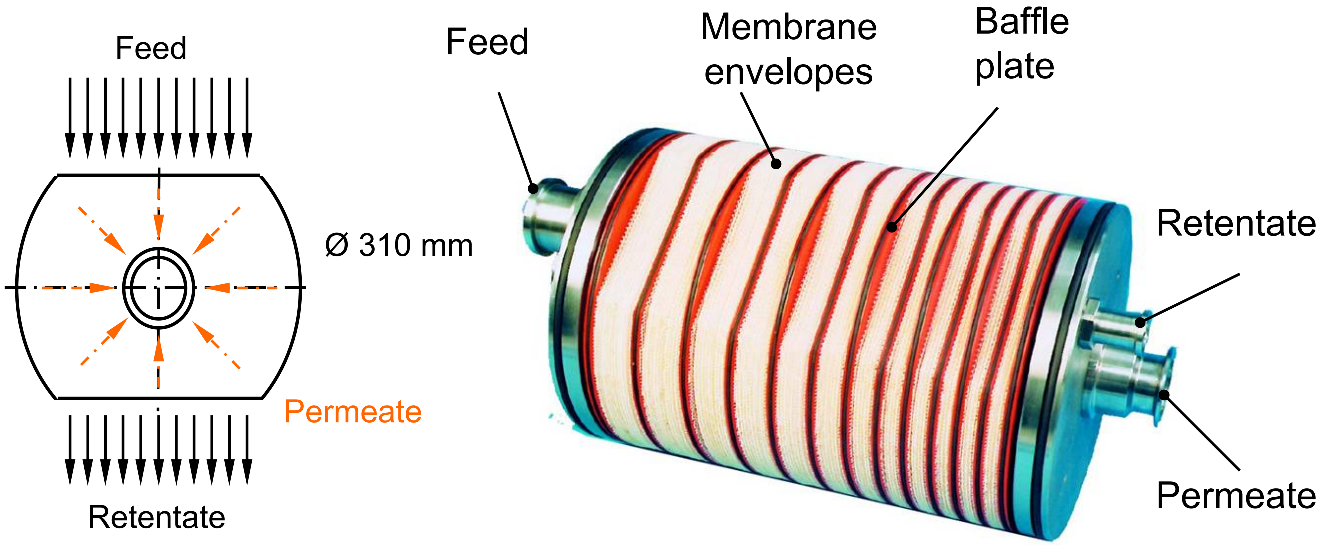


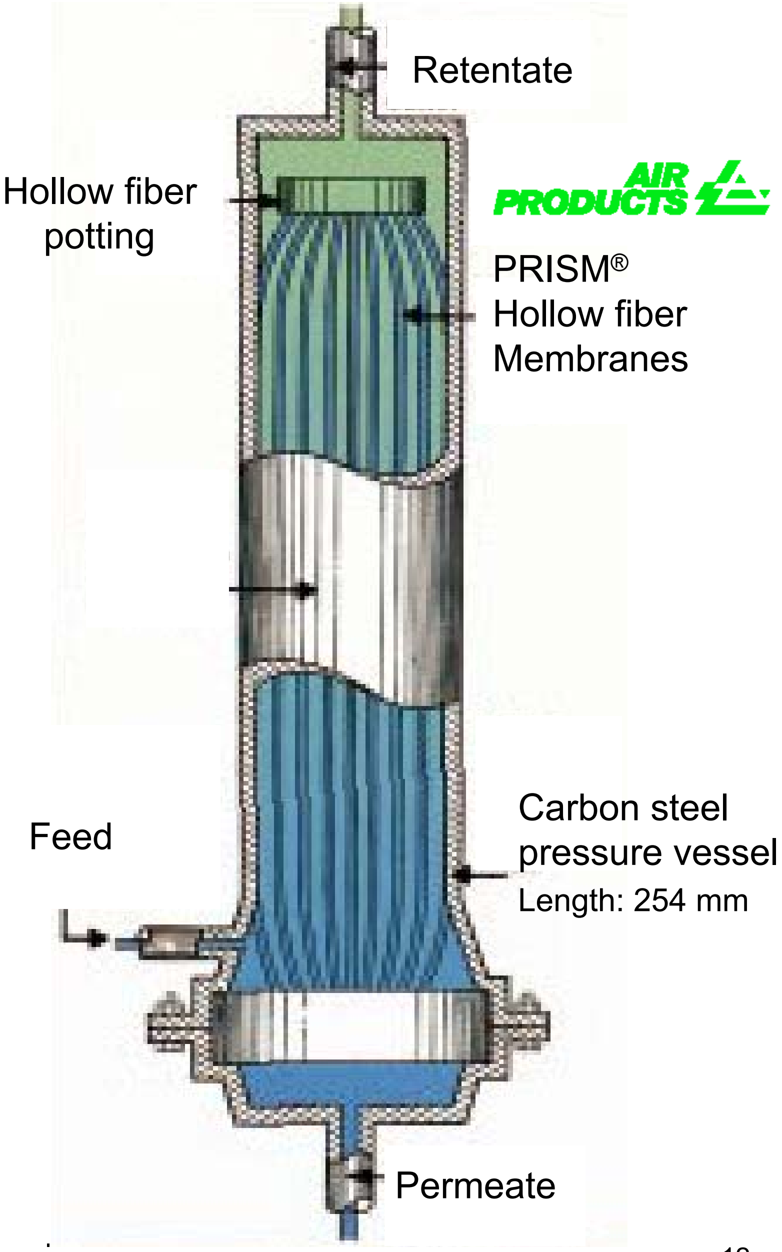
Courtesy of HZG

# Variation of Membrane Module Design

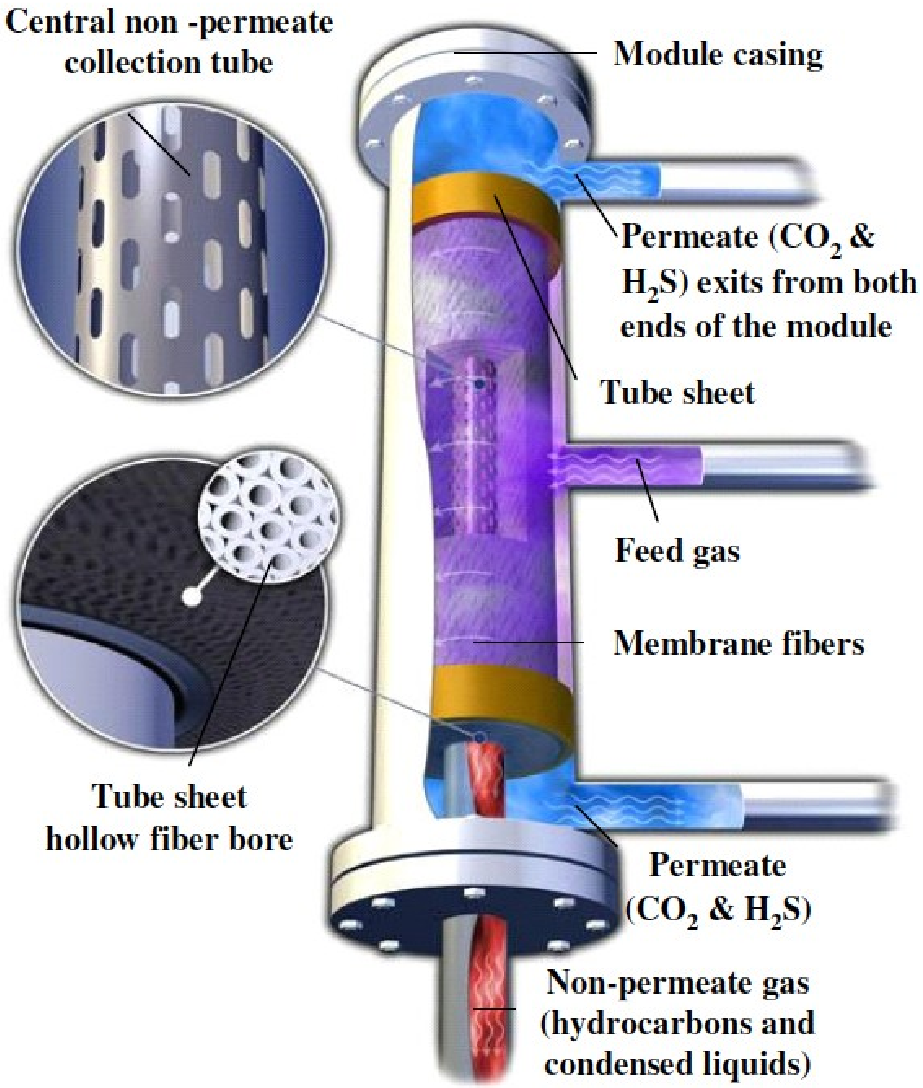


## HZG Envelope Type Module





# Membrane Module Is Not A Small Toy!
# CYNARA® Cellulose Acetate Hollow Fiber Modules

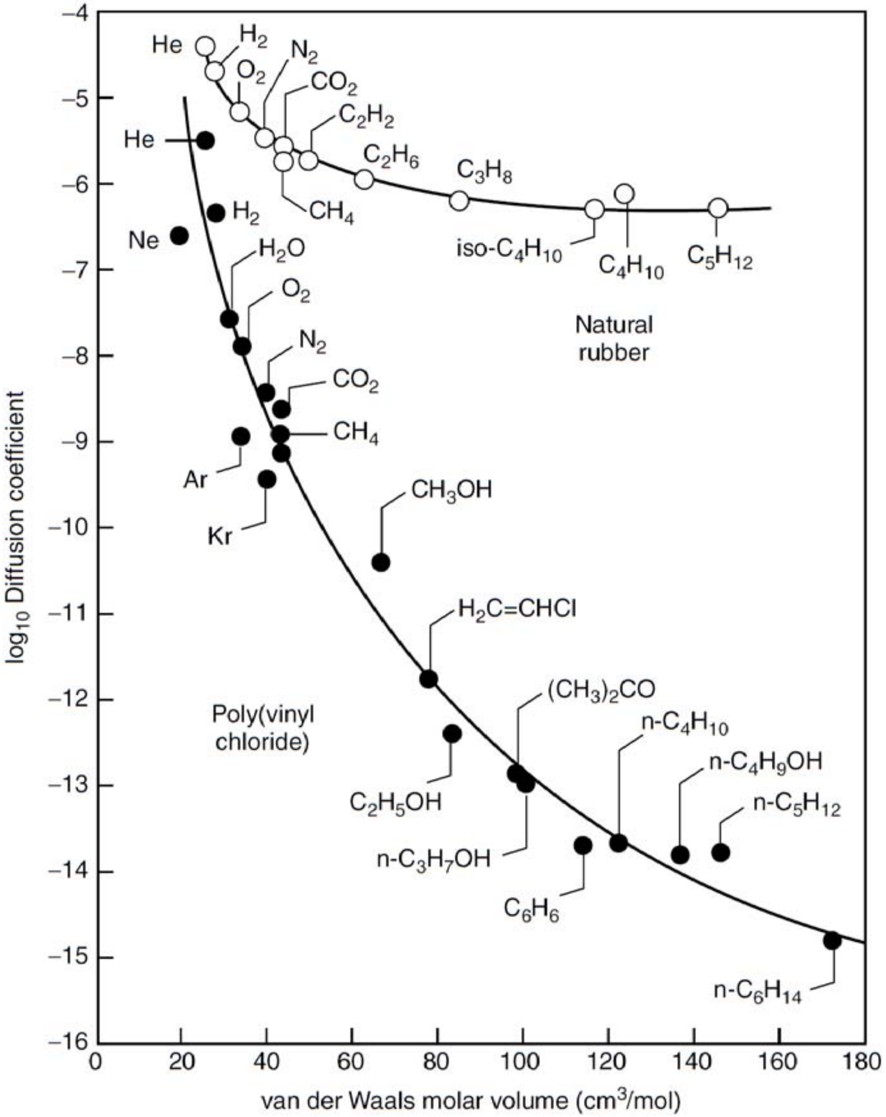


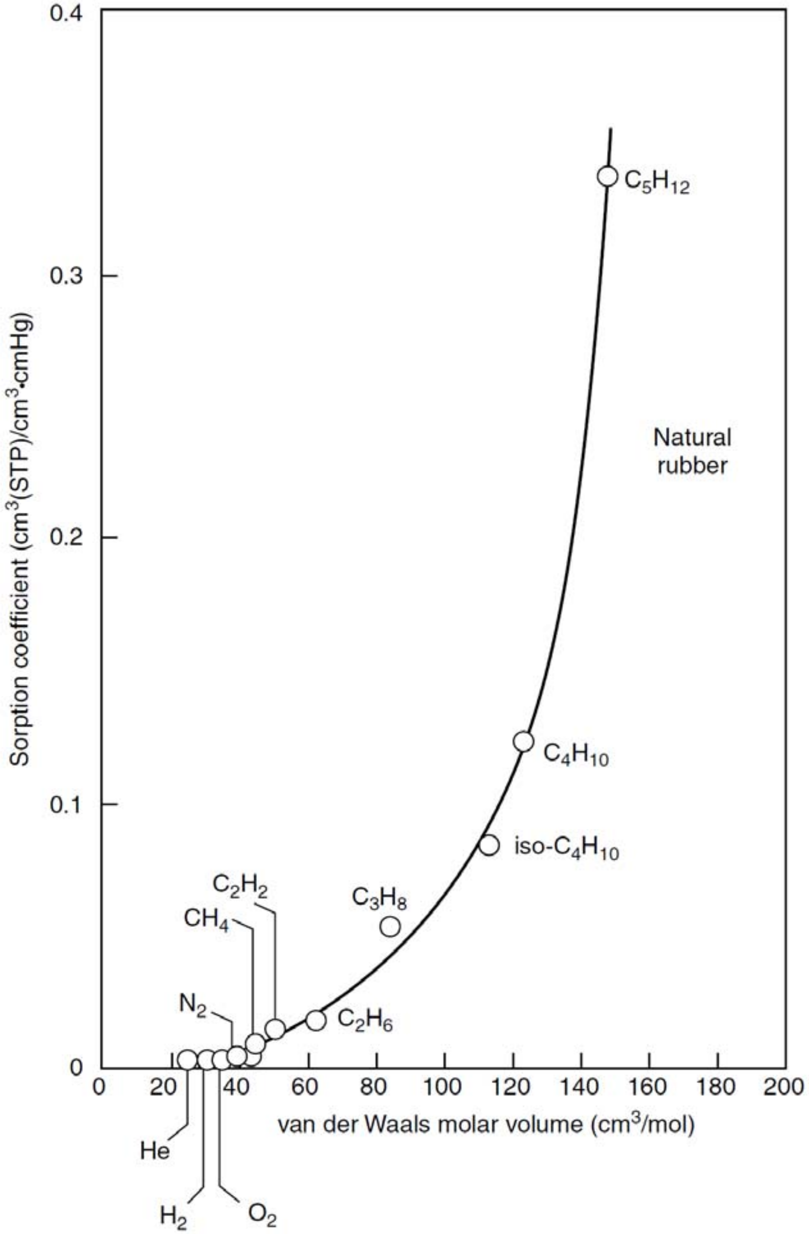
NATCO CYNARA® : http://natcogroup.com/products-cynara-membranes

# Large Surface Area Needed?

Ashkelon Desalination Plant,
40,000 membrane modules, 165,000 m$^3$/day

# Gas Diffusion and Sorption in Polymers Depend on Molecular Nature and Size

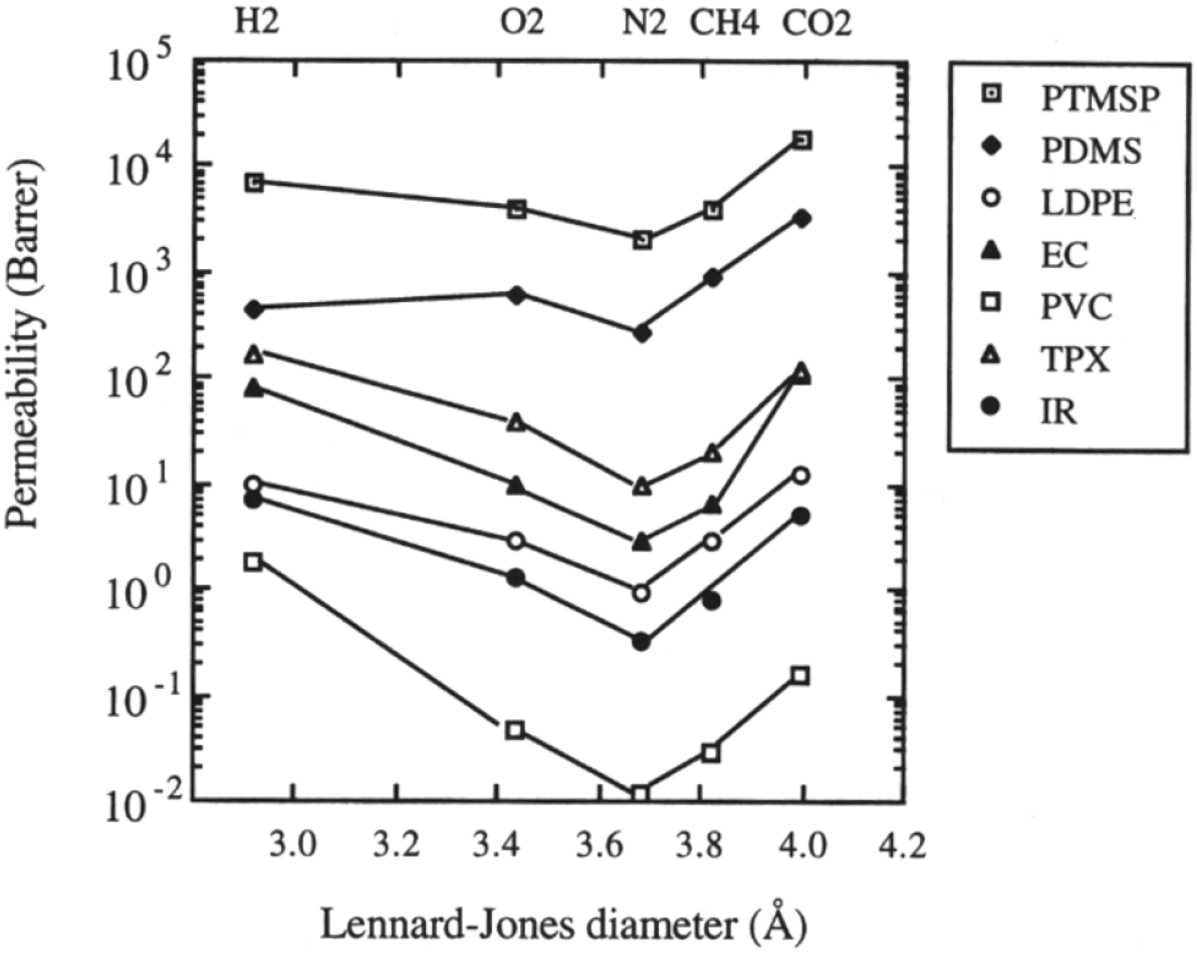


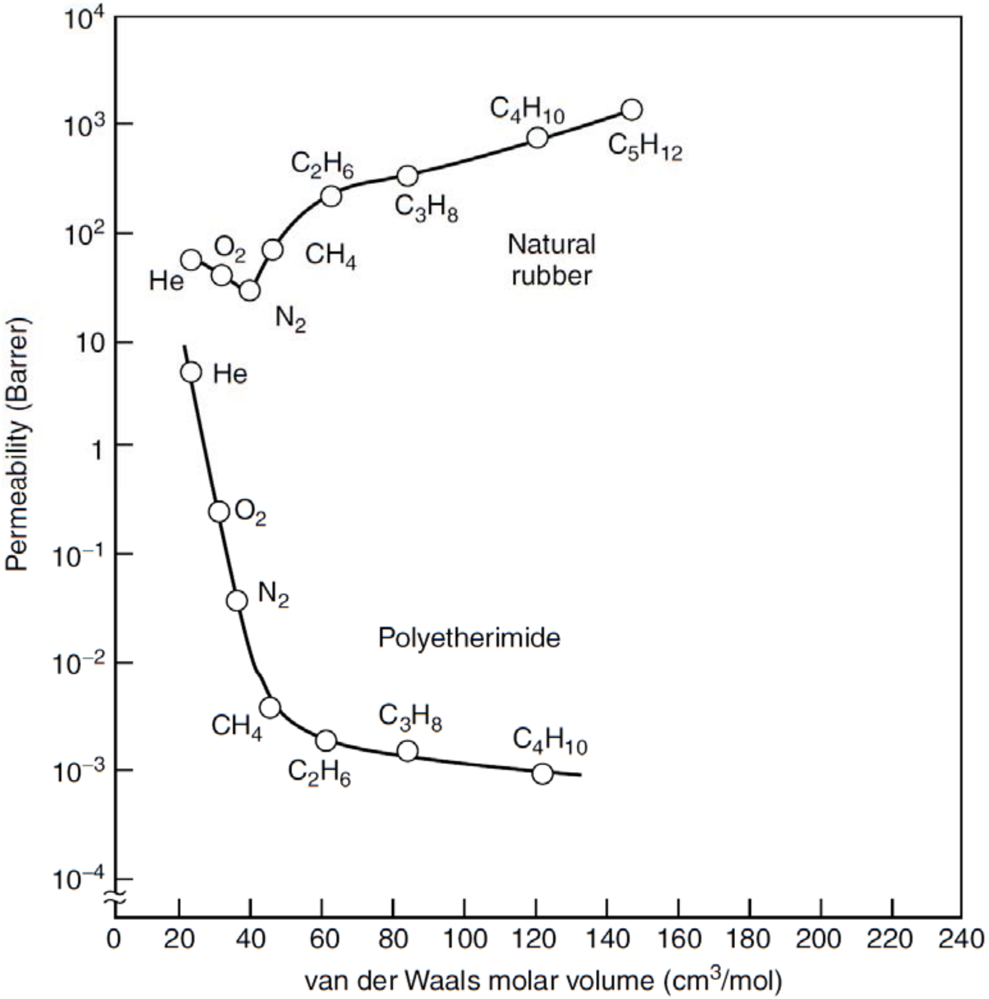


F. Gruen, *Experimenta* **3**, 490 (1947)

G.J. van Amerongen, *J. Appl. Phys.* **17**, 972 (1946)

# Superposition of Diffusion and Solubility Leads to V-shaped Permeability Dependence on Molecular Size

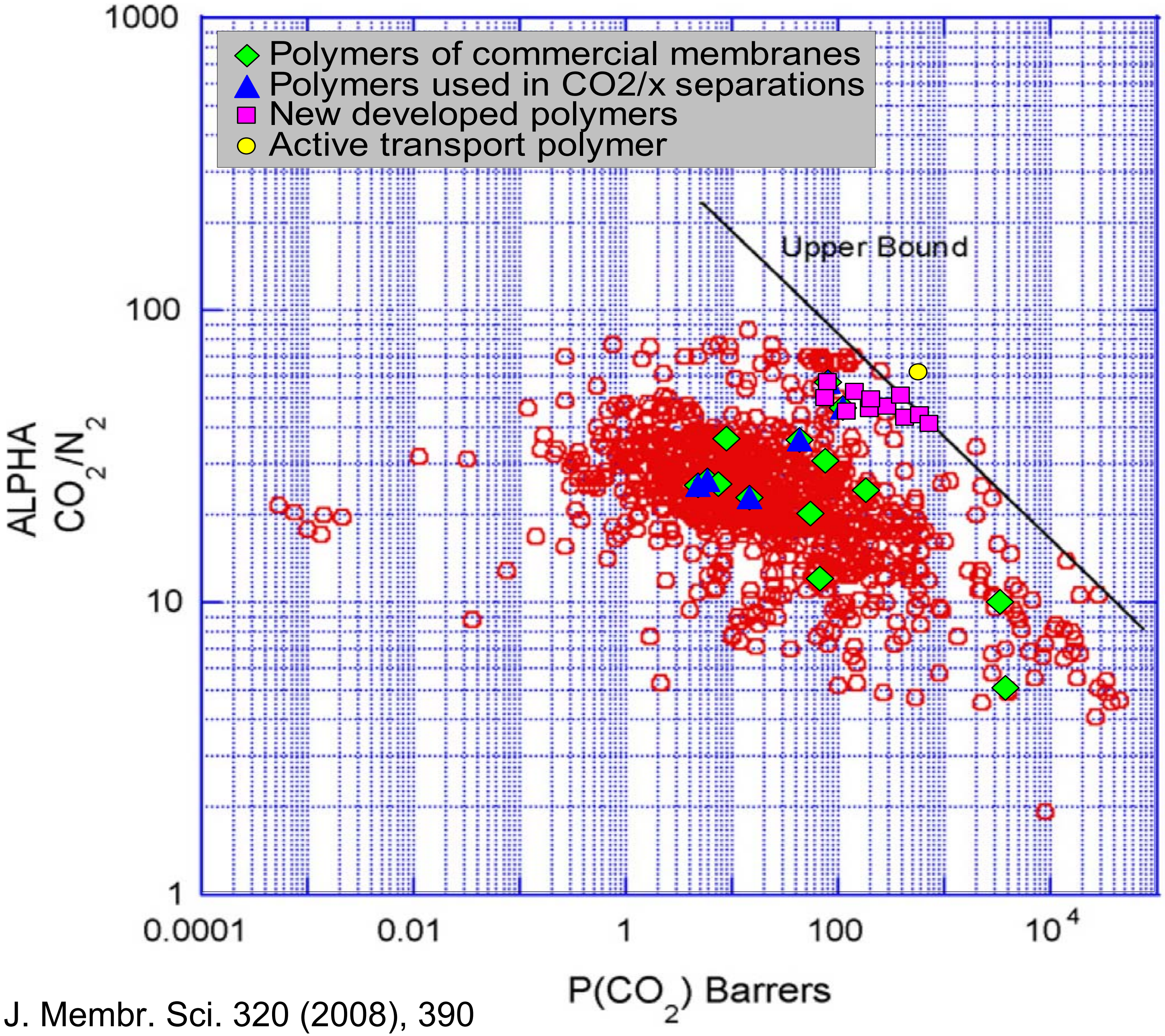




http://people.pwf.cam.ac.uk/jae1001/CUS/teaching/materials/M6_Lecture_6.pdf

R.D. Behling et al., AIChE Symposium Series Number 272, Vol. 85, p. 68 (1989)

# $CO_2/N_2$
# Industrially Used Polymers on Robeson Plot



L. M. Robeson, J. Membr. Sci. 320 (2008), 390

# Polymers of Industrial Gas Separation Membranes

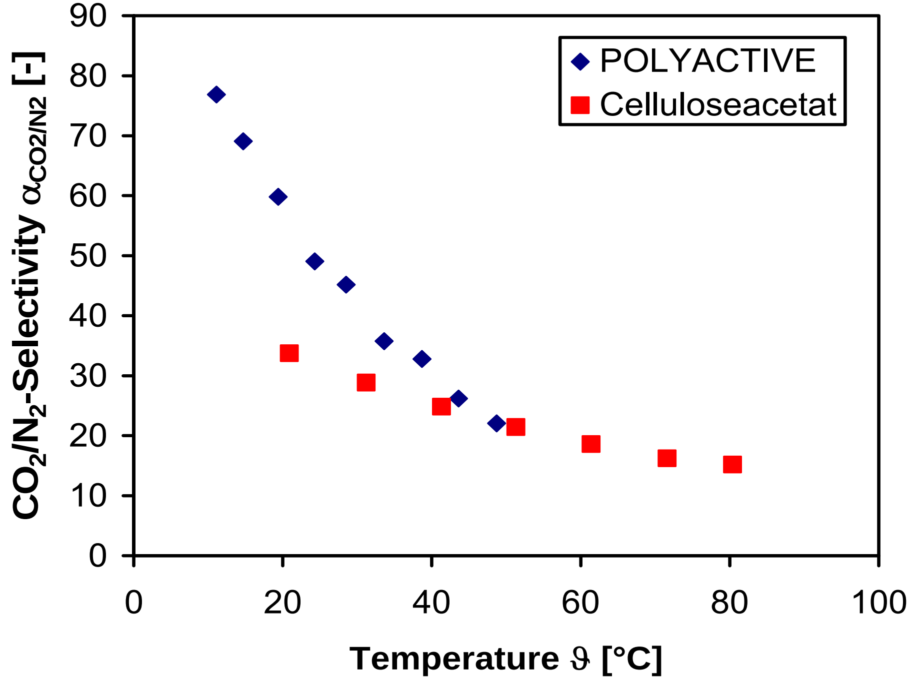
| **Polymer** | **P($CO_2$)*** | **$CO_2/N_2$** | **$CO_2/CH_4$** | **$CO_2/H_2$** |
|---|---|---|---|---|
| Polysulphone | 4.92 | 24.6 | 23.4 | - |
| Cellulose Acetate | 5.96 | 25.8 | 29.1 | 0.4 |
| Polycarbonate | 7.5 | 25 | 23.4 | 0.62 |
| Matrimid | 8.9 | 35.6 | 40.5 | 0.37 |
| Ethyl Cellulose | 14.7 | 22.4 | 10.4 | 1.9 |
| Polyimide | 44 | 35.2 | 30.3 | - |
| Poly(phenylene oxide) | 56.8 | 19.9 | 25.8 | 0.67 |
| Poly(4-methyl pentene-1) | 69.5 | 11.8 | - | 0.68 |
| Poly(phenylene oxide) brominated | 78 | 30 | 15.6 | - |
| PEBAX | 82.1 | 55.5 | 15.6 | 9.9 |
| Polyactive | 115 | 45.6 | 17 | 10.2 |
| Poly(vinyl trimethyl silane) | 190 | 23.8 | 14.6 | 0.95 |
| Poly(dimethyl siloxane) | 3489 | 9.9 | 3.5 | 4.9 |
| Teflon AF | 3900 | 5 | 6.5 | 1.2 |

Highlighted polymers are used in $CO_2$/x separation processes

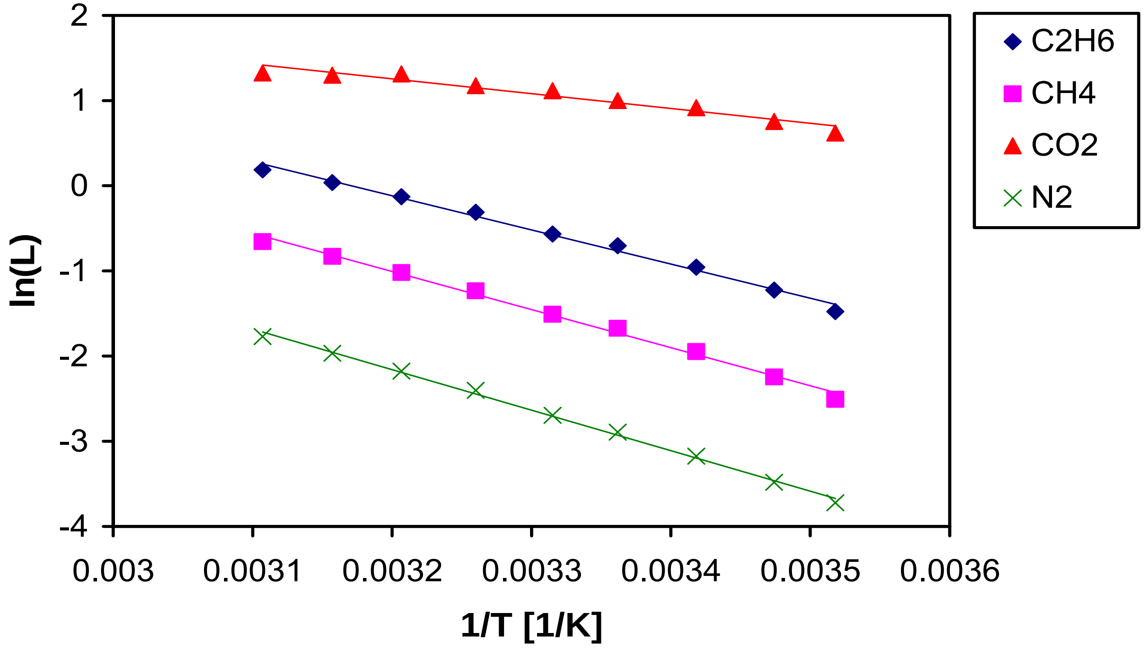
* Permeability in Barrer: 1Barrer = $1 \cdot 10^{-10}$ $cm^3$(STP) cm $cm^{-2}$ $s^{-1}$ $cmHg^{-1}$

# Membrane Parameters Depend on Application Conditions

Temperature dependency of selectivities



Temperature dependency of permeances: POLYACTIVE®



Pure gas selectivities at 20°C

| | Celluloseacetate | POLYACTIVE® |
|---|---|---|
| **$CO_2/N_2$** | **33.74** | **60.73** |
| **$CO_2/CH_4$** | **26.02** | **17.53** |
| **$CO_2/H_2$** | **0.70** | **10.33** |
| **$CO_2/C_2H_4$** | **15.66** | **4.07** |

- Arrhenius relationship:

$$\ln(L_i) = \ln(L_{\infty,i}) + \frac{E_i}{R \cdot T}$$

T. Brinkmann et al., 13th Aachener membrane colloquium, 27-28 Oct. 2010, Aachen

# Membrane Parameters Depend on Application Conditions

$CO_2$ induced polymer plasticisation

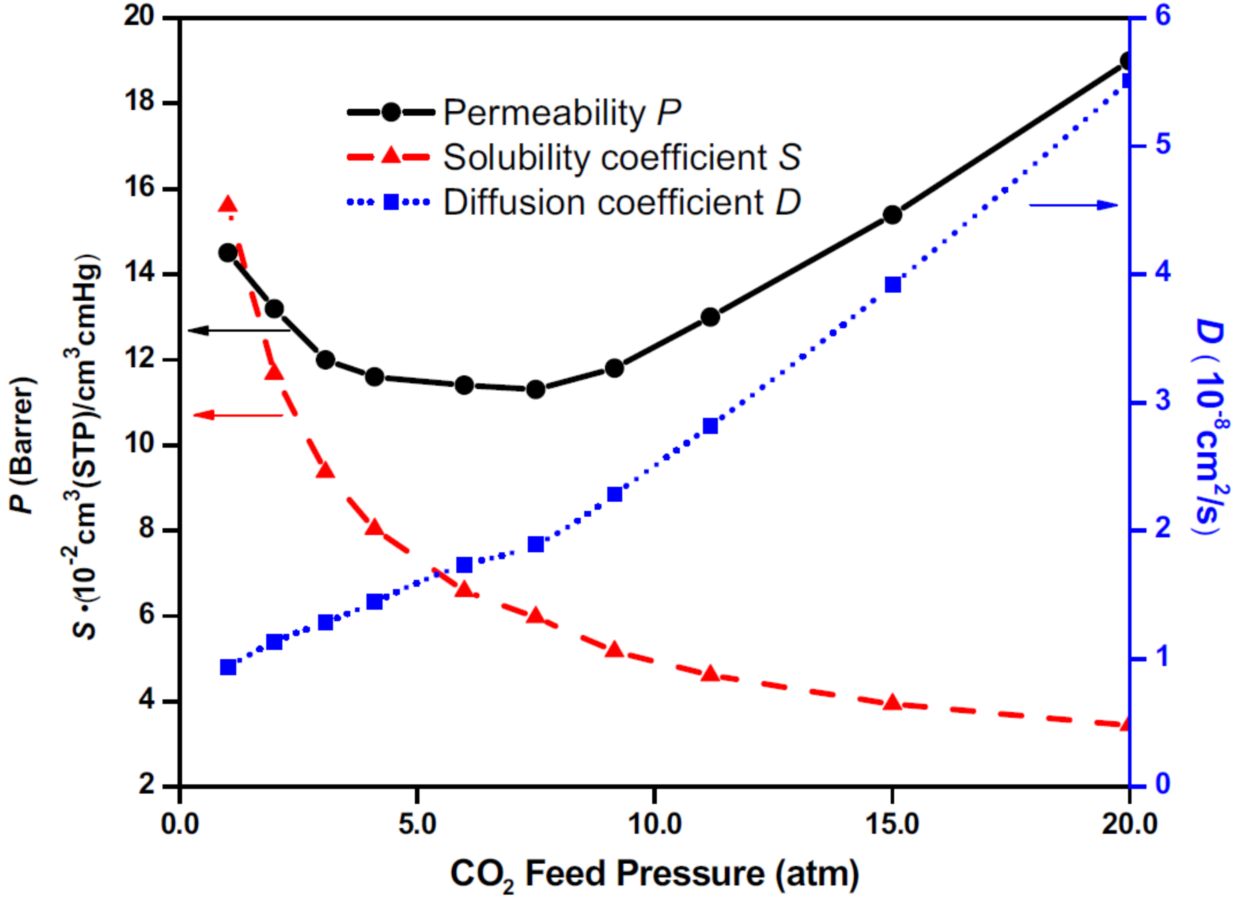
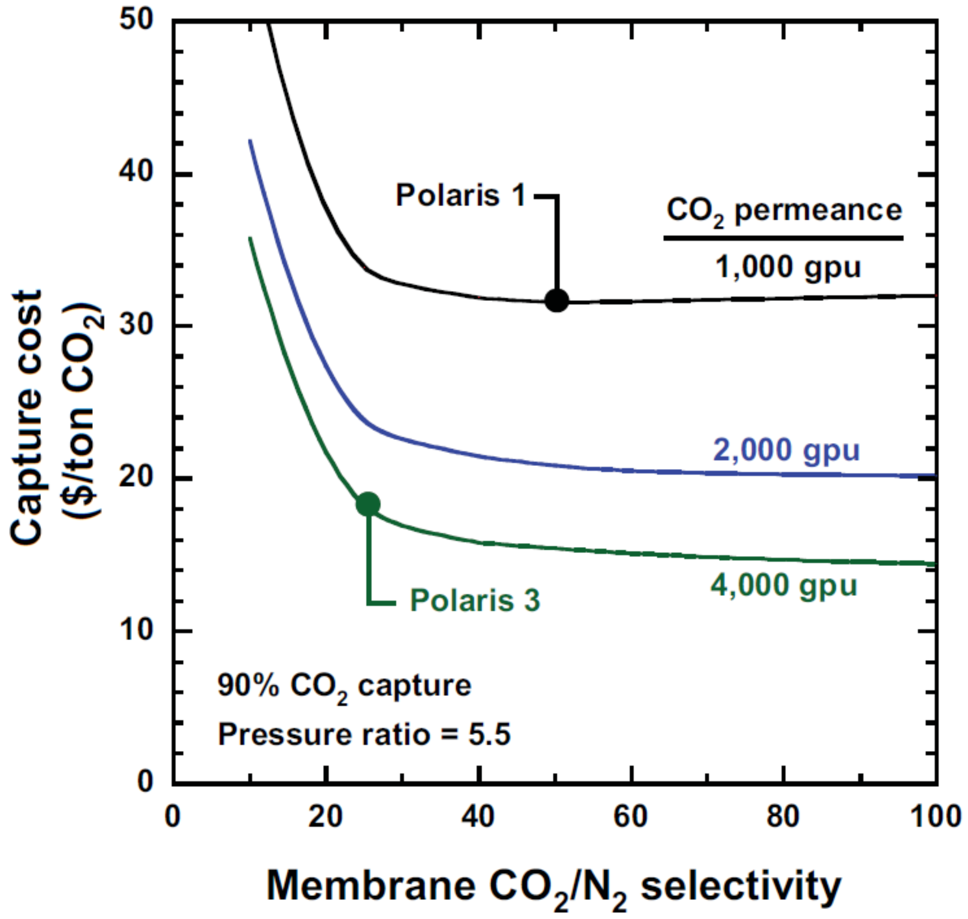


**Fig. 1.** Experimental permeability, solubility, and diffusion coefficients of $CO_2$ in 6FDA-ODA polyimide membrane at 35 °C.

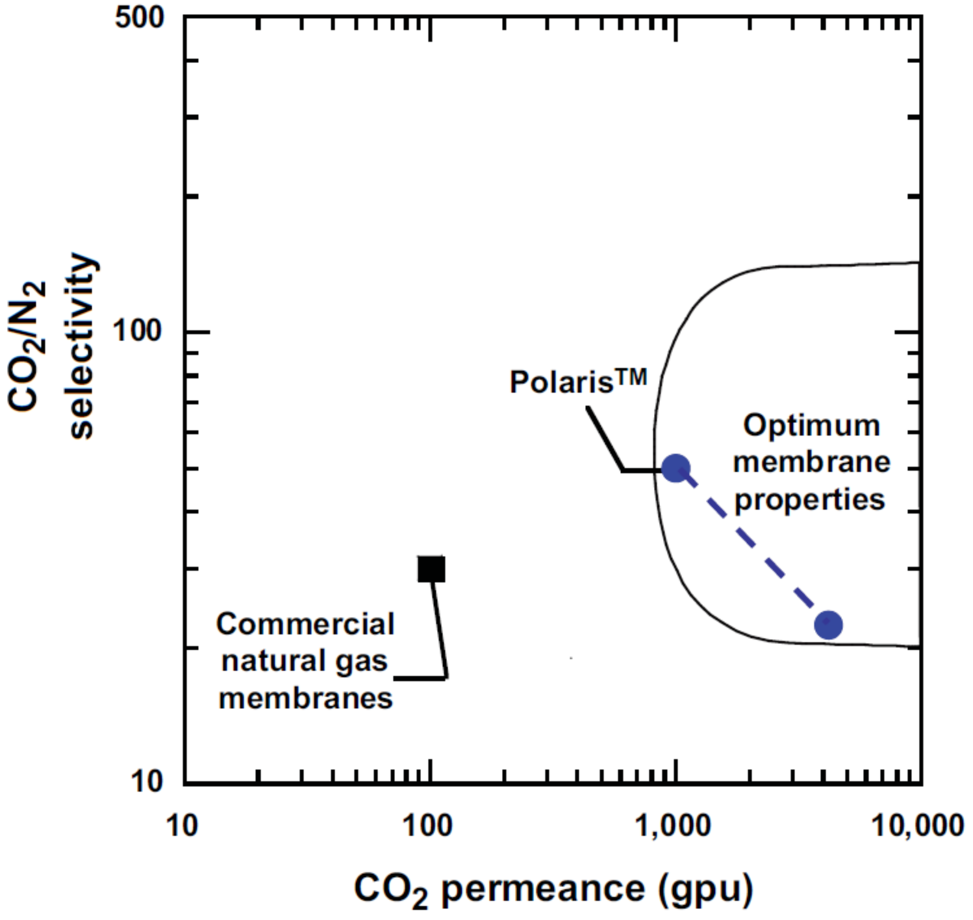
L. Zhang et al, Polymer 51 (2010) 4439-4447

# Higher $CO_2$ Permeance Reduces Cost More than Higher Selectivity

Baseline amine capture cost is >$80/ton $CO_2$



High permeance and modest selectivity is needed



R.W. Baker, XXVI EMS summer school, Sept. 29 – Oct. 2, 2009, Geesthacht/Ratzeburg

# Main $CO_2$ Related Research Activities

**Applications**

$CO_2/CH_4$
- Natural gas
- Associated gas
- Biogas

$CO_2/N_2$
- Carbon sequestration and storage
- Biogas

$CO_2/H_2$
- Syngas
- Biogas
- Fuel cells

**Materials**

Pure polymers:
- Polyimides
- PEO based
- High free volume polymers (PIMs, polyacetylenes...)

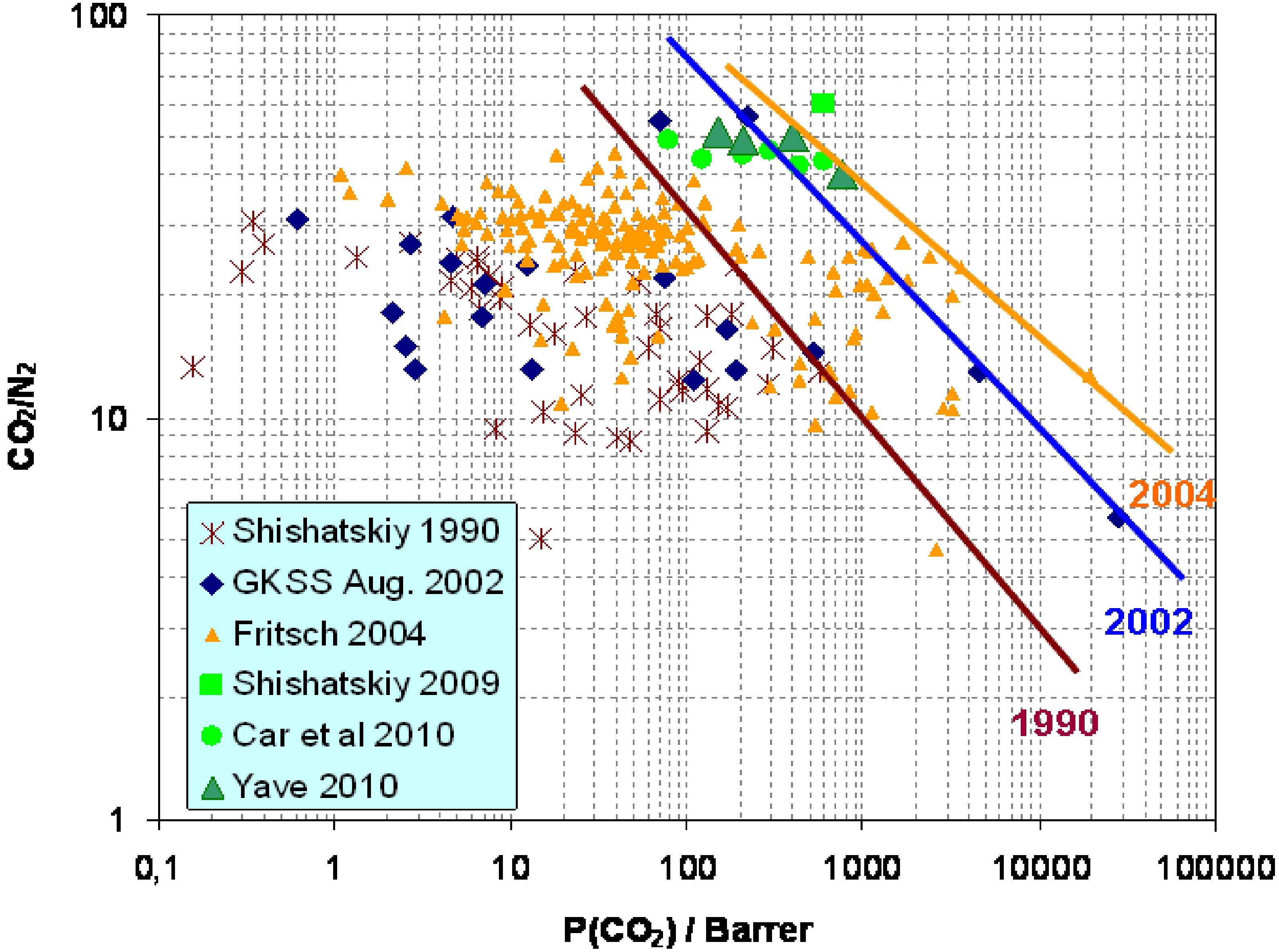
Activated transport
- Amines
- Organic acids
- Ionic liquids

Mixed matrix and hybrid materials
- Permeable fillers as zeolites, MOFs, ZIFs, CMS
- Impermeable nano-particles ($SiO_2$, $TiO_2$ etc.)

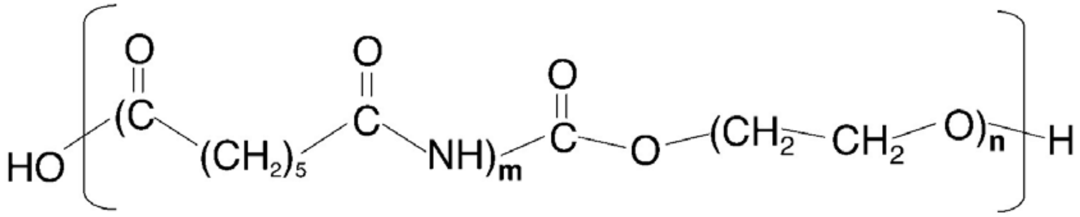
**ICOM-2011**: 3 Sessions for "$CO_2$ Capture"; 36 oral presentations with key words:

- Flue gas
- Biogas
- Polybenzimidazole
- Polyethylene oxide
- Sulfonated PEEK
- PIMs
- Copolyimide
- Thermally rearranged polymer
- Partially pyrolized membranes
- Hybrid membrane
- Mixed matrix
- MOF
- SAPO-34
- ZIF-8
- Hybrid absorber
- Contactor
- Water vapor
- $H_2S$
- Facilitated transport (amine)
- Enzyme based membranes
- Ionic liquid
- Plasticization
- LBL self-assembly
- Pd membrane
- PVAm/PVA blend

# Progress of the $CO_2/N_2$ Upper-bound During the Last 20 Years



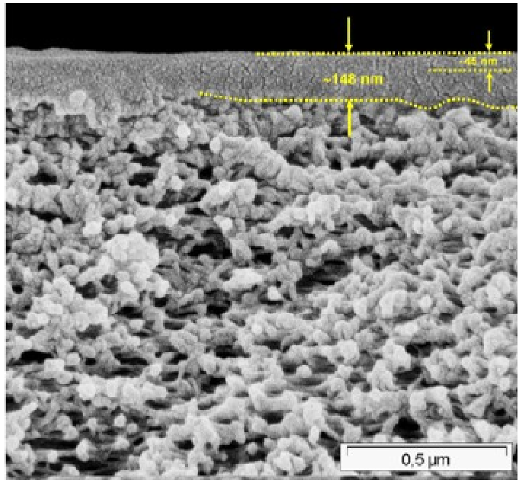
# Poly ethylene oxide (PEO)-based block copolymers



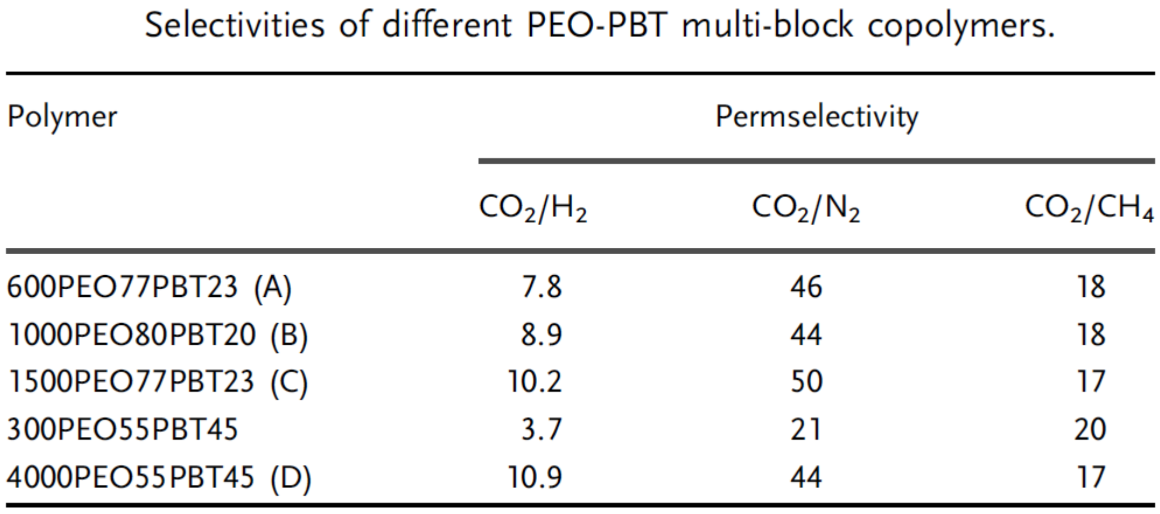
$$HO\left[\left(C(=O)-(CH_2)_5-C(=O)-NH\right)_m-C(=O)-O-\left(CH_2-CH_2-O\right)_n\right]H$$

Example:

Pebax®



- Highly-developed membranes for $CO_2$ capture
- 100 $m^2$ scale production for field tests
- <100nm thin multilayer membranes developed by MTR and HZG
- Highly ordered block segments in the focus of University of Twente
- HZG investigated smart additives on basis of polyethylene glycol (PEG) / PEG ethers
- MTR  test of spiral wound modules on flue gas of natural gas fired power plant

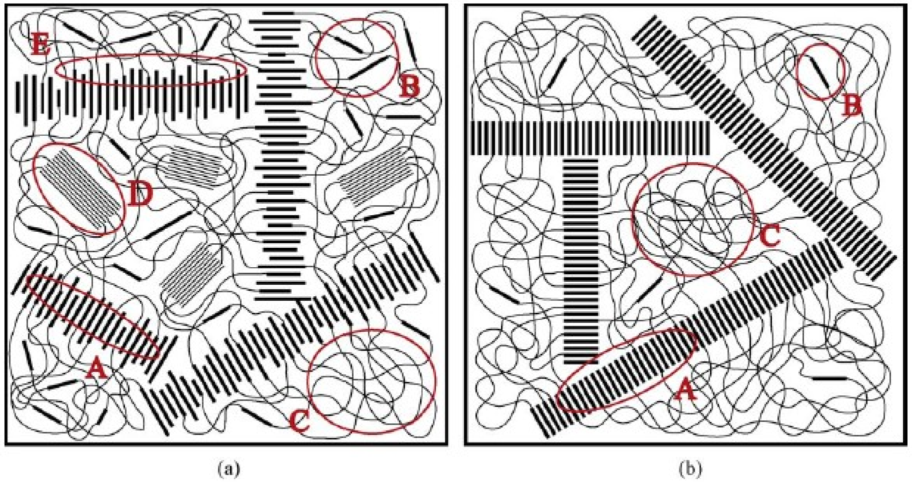


Selectivities of different PEO-PBT multi-block copolymers.

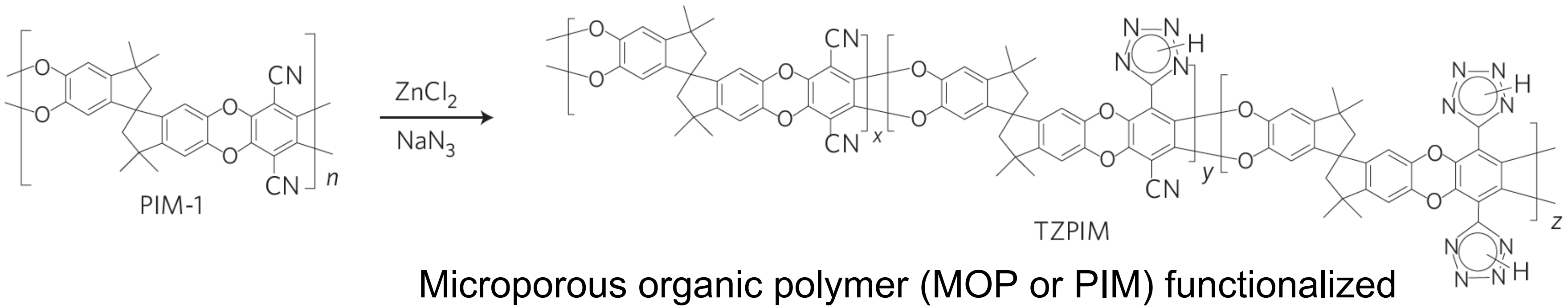
| Polymer | Permselectivity | | |
|---|---|---|---|
| | $CO_2/H_2$ | $CO_2/N_2$ | $CO_2/CH_4$ |
| 600PEO77PBT23 (A) | 7.8 | 46 | 18 |
| 1000PEO80PBT20 (B) | 8.9 | 44 | 18 |
| 1500PEO77PBT23 (C) | 10.2 | 50 | 17 |
| 300PEO55PBT45 | 3.7 | 21 | 20 |
| 4000PEO55PBT45 (D) | 10.9 | 44 | 17 |

*Adv. Funct. Mater.* **2008,** *18,* 2815–2823

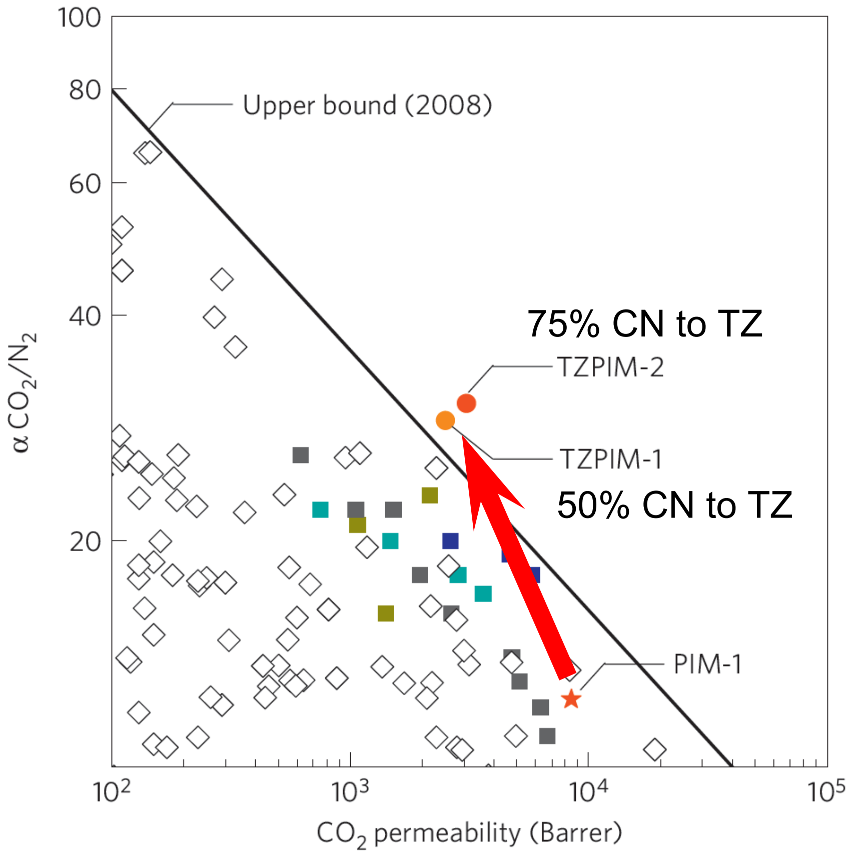
*S.R. Reijerkerk et al. / International Journal of Greenhouse Gas Control 5 (2011) 26–36*



# Polymer Nanosieve Membranes for $CO_2$-capture Applications

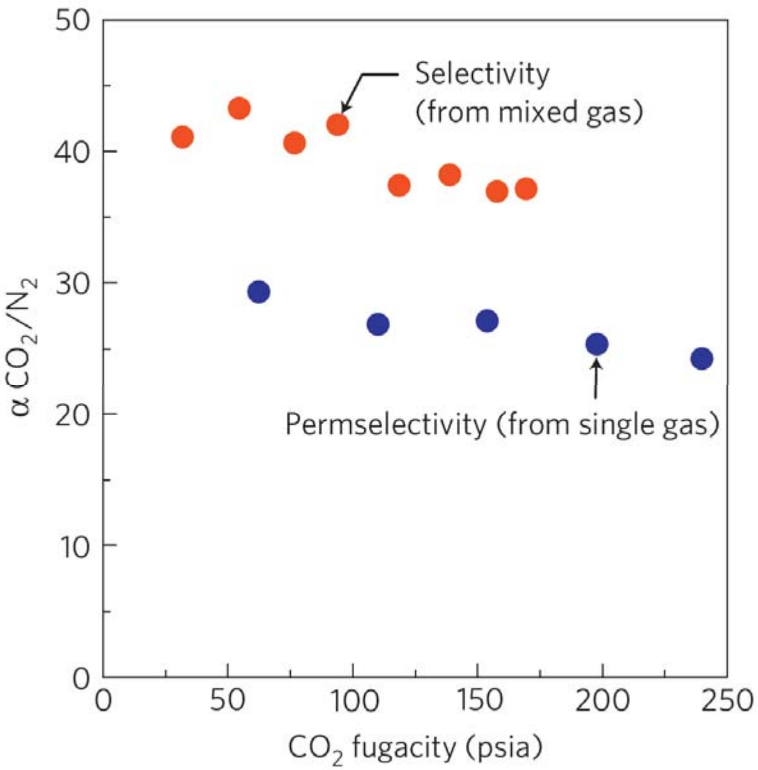


Microporous organic polymer (MOP or PIM) functionalized with $CO_2$-philic pendant tetrazole groups



75% CN to TZ

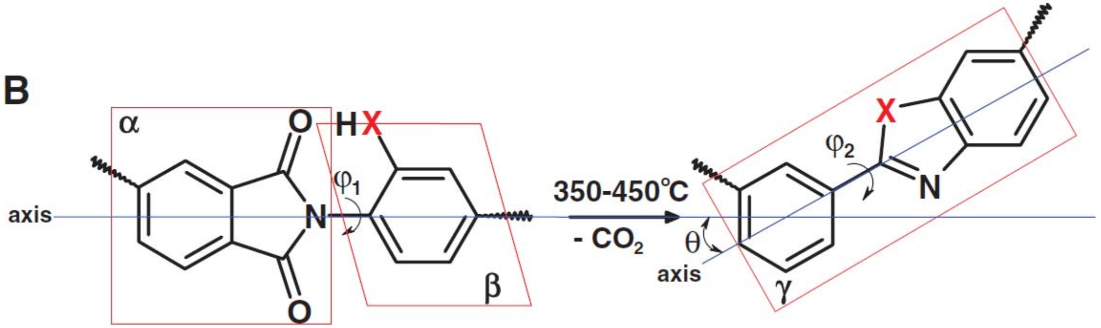
50% CN to TZ

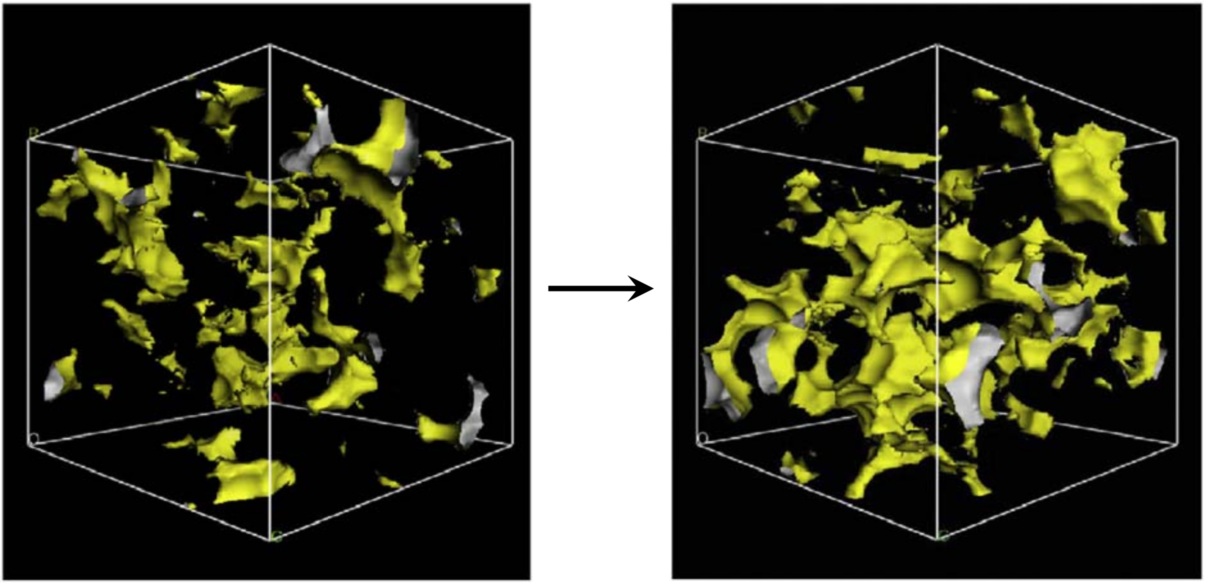


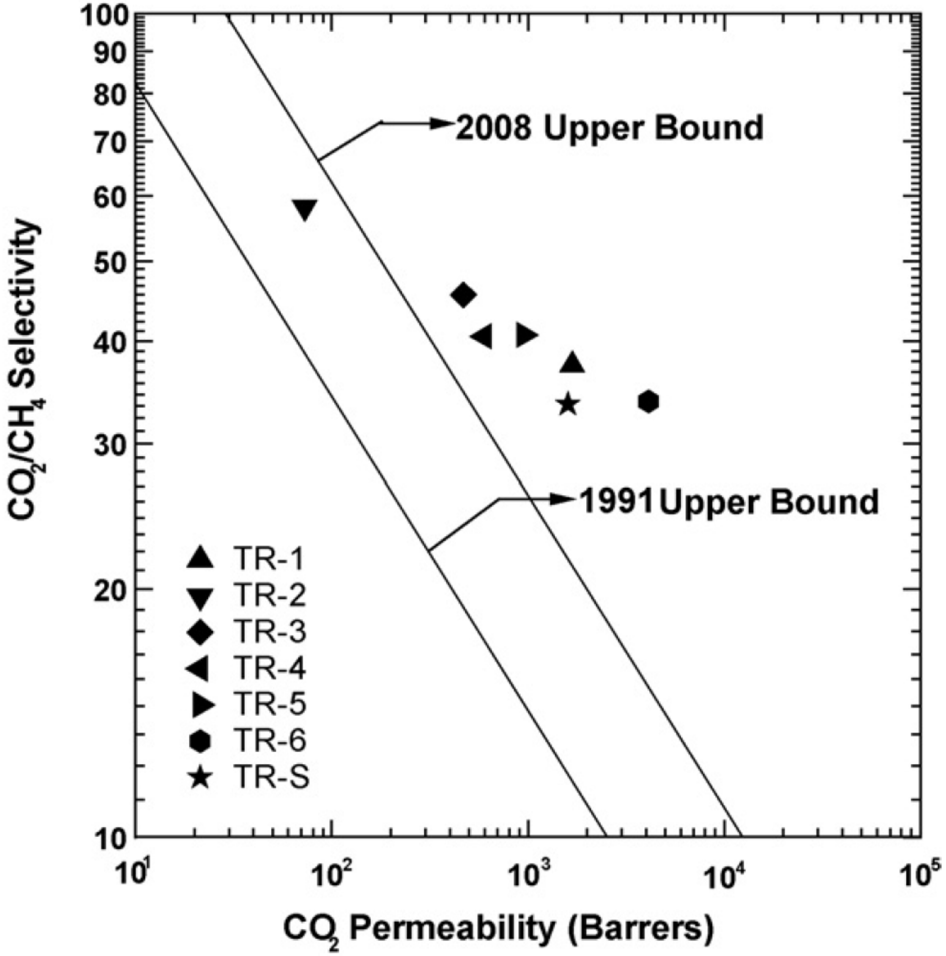
N. Du et al., Nature Materials, 10 (2011) 372

# Polymer Cavities Tuned for Fast and Selective Transport of Small Molecules

Thermally Rearranged Polymers: fine free volume tuning by temperature treatment.



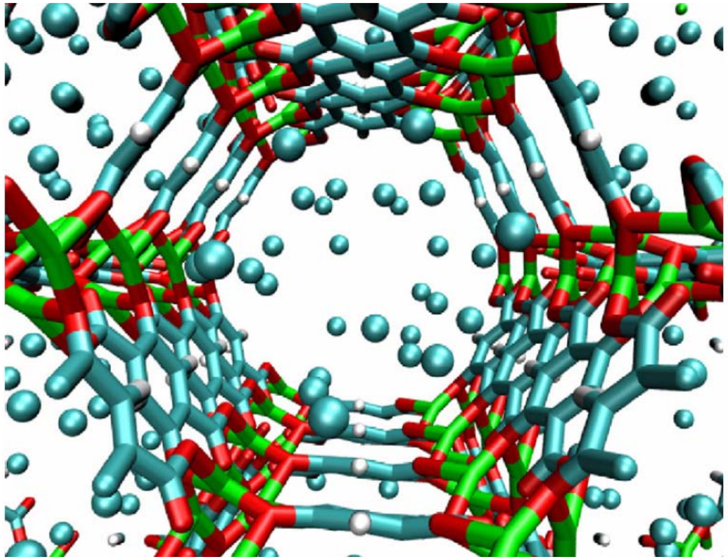




H. Park, Science, 318 (2007) 254

H. Park, J.Membr.Sci., 359 (2010) 11

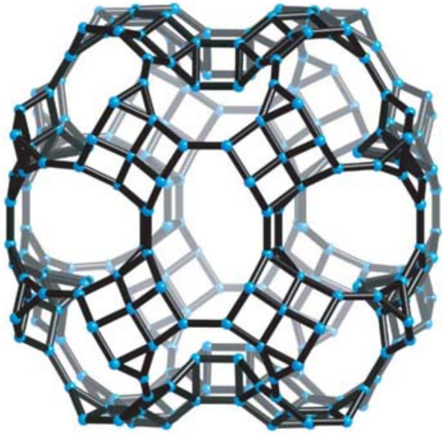
# Mixed Matrix Membranes:
# MOF, Zeolite to Improve Polymer Matrix



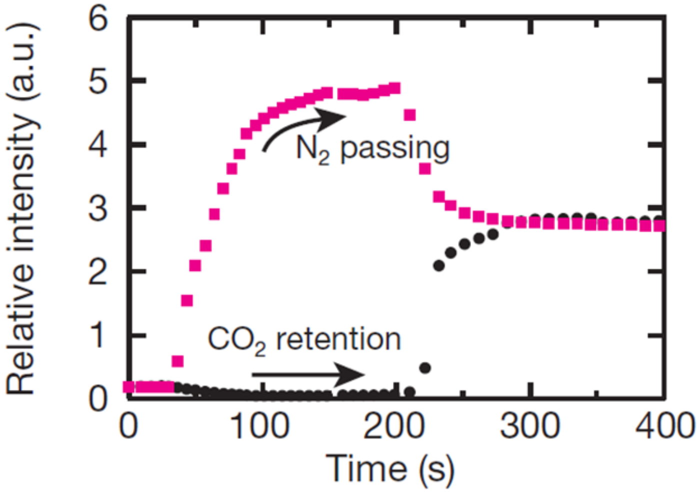
Modelling of $CO_2$ molecules in 1.1nm
1D channel of MgMOF-74

“$CO_2/N_2$ permeation selectivities with MgMOF-74 membranes at $p_{t0}$ > 1 MPa are about a factor two higher than those reported for SAPO-34 and DDR membranes.”

R.Krishna et al., J.Membr.Sci., 377(2011) 249



Ball and stick model of **moz** cage in ZIF100.



“Only $CO_2$ is retained in the pores while
$N_2$ and other gases passes through without hindrance.”

B. Wang et. al., Nature, 453 (2008) 207

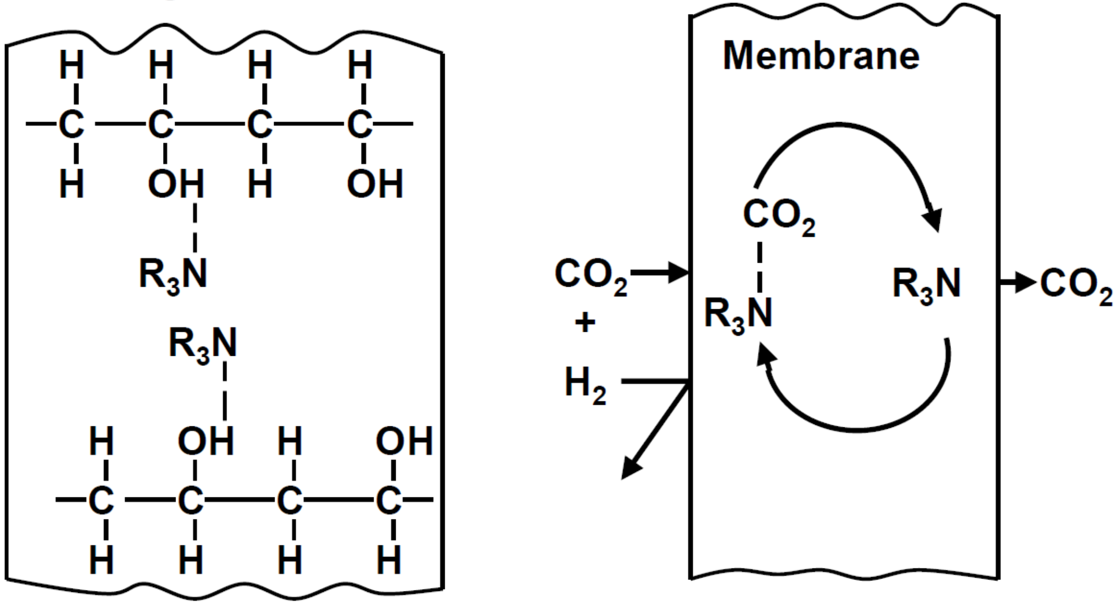
# $CO_2$ Facilitated Transport for $H_2$ Purification

- **Drive Water-Gas-Shift (WGS) Reaction to Product Side**

$$CO + H_2O \rightarrow H_2 + CO_2 \uparrow$$

**$CO_2$-Selective Membranes by Incorporating Amines in Polymer Networks … Facilitated Transport**

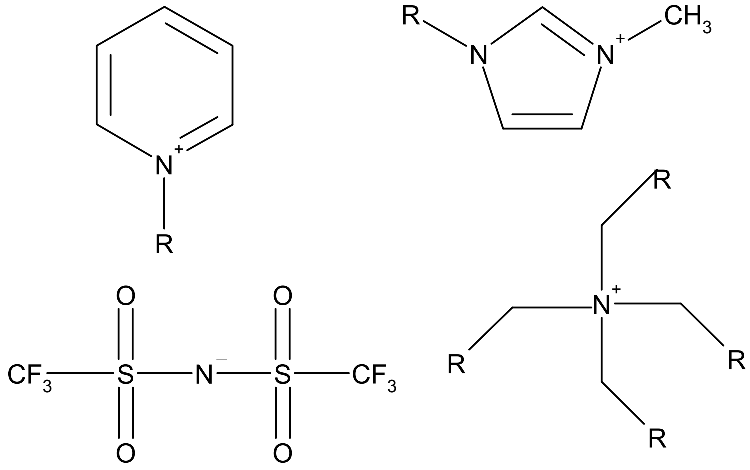
**Example: Polyvinylalcohol-Containing Amine Membrane**



J. Huang et al., in Hydrogen and Syngas Production and Purification technologies, eds. K. Li et al., AICHE, 2010

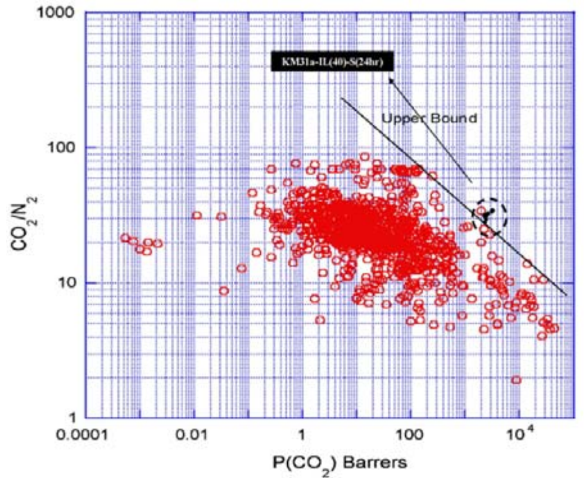
# Ionic Liquids:
# Immobilized in Membrane to Facilitate Transport

Examples of **Ionic liquids** :



**IL immobilized in porous PVDF**

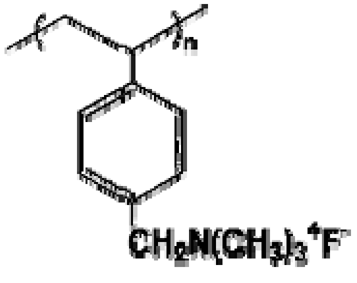
D.-H. Kim et al., J.Membr.Sci., 372 (2011) 346



**Quaternary ammonium** salts and polymers

R. Quinn et al., J.Membr.Sci., 131(1997) 49

| salt |
|---|
| $[(CH_3)_4N]F$ |
| CsF |
| KF |
| $[(C_4H_9)_4N]F$ |
| $[(C_2H_5)_4N]CH_3CO_2$ |



PVBTAF

Selectivity $CO_2/N_2$ = 610 – 970 depending on conditions

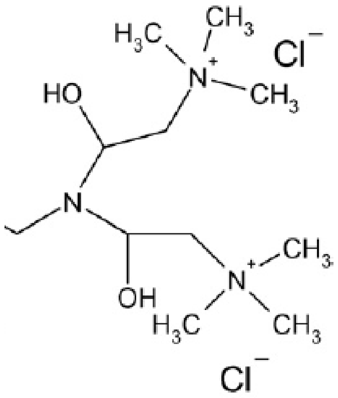
Measured for 20% $CO_2$, 63.2% $N_2$, 16.8% $O_2$, 31% humidity

Quaternary ammonium moiety with **high $CO_2$ affinity**

S.Shishatskiy et al., J.Membr.Sci., 359(2010) 44

Blended with PEBAX 50/50:

| | $P(CO_2)$ Barrer | $\alpha(CO_2/N_2)$ |
|---|---|---|
| Dry | 17.0 | 53 |
| Wet | 590 | 60 |



See also: A.Hussain, M.-B. Hägg, J.Membr.Sci., 359(2010) 140

# Conclusions

1. Membrane gas separation is industrially acknowledged technology
2. Many polymers have been tested for gas and vapor transport properties but less then 20 have found way to industrial applications.
3. Stability of the polymer processing properties, polymer price from the point of view of common membrane production (integral asymmetric hollow fiber membranes) are the main issues on the way of polymer to membrane separation units.
4. Development of thin film composite membrane (TFCM) formation technique for both flat and hollow fiber membranes opens the window of possibility for expensive polymers and hybrid materials.
5. Efforts on polymer synthesis and modification have significantly shifted the Robeson's "Upper Bound" to the side of higher permeabilities but didn't influence the upper selectivity border for $CO_2$/x gas pairs.
6. Newest research in various fields: ionic liquids, inorganic nanoparticles, carbon materials, microcrystals of zeolites, MOF's, etc., basic research on polymer chains arrangements allow one to expect a breakthrough in membrane material development.

With the hope for green and prosperous future,

# Thank you for your attention!