"State of the art and New Trends on Polymeric Membrane Fabrication "

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27-28 January 2025 – Winter School on Membranes and Membrane Reactors Cube 1 - Eindhoven

Outline

- Brief introduction to CNR-ITM
- Introduction to Polymeric Membrane Fabrication and Green Chemistry
- Overview of non-toxic solvents and bio-Polymers in membranes
- Specific case studies using different Sustainable Solvents for membrane fabrication
- Conclusions

The Institute on Membrane Technology (CNR-ITM) is a structure created in 1993 by the Italian National Research Council (CNR – Consiglio Nazionale delle Ricerche) for the development, at national and international level, of membrane science and technology.

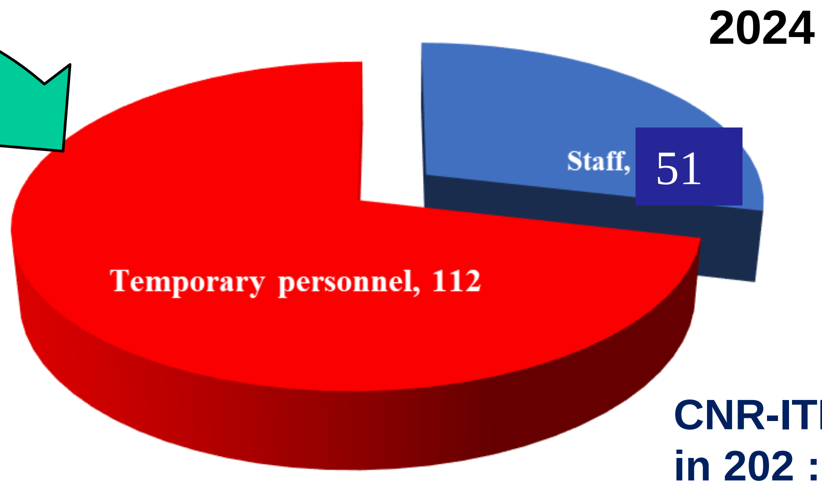
CNR-ITM is part of the Department of Chemical Science and Materials Technologies (DSCTM), Rome .

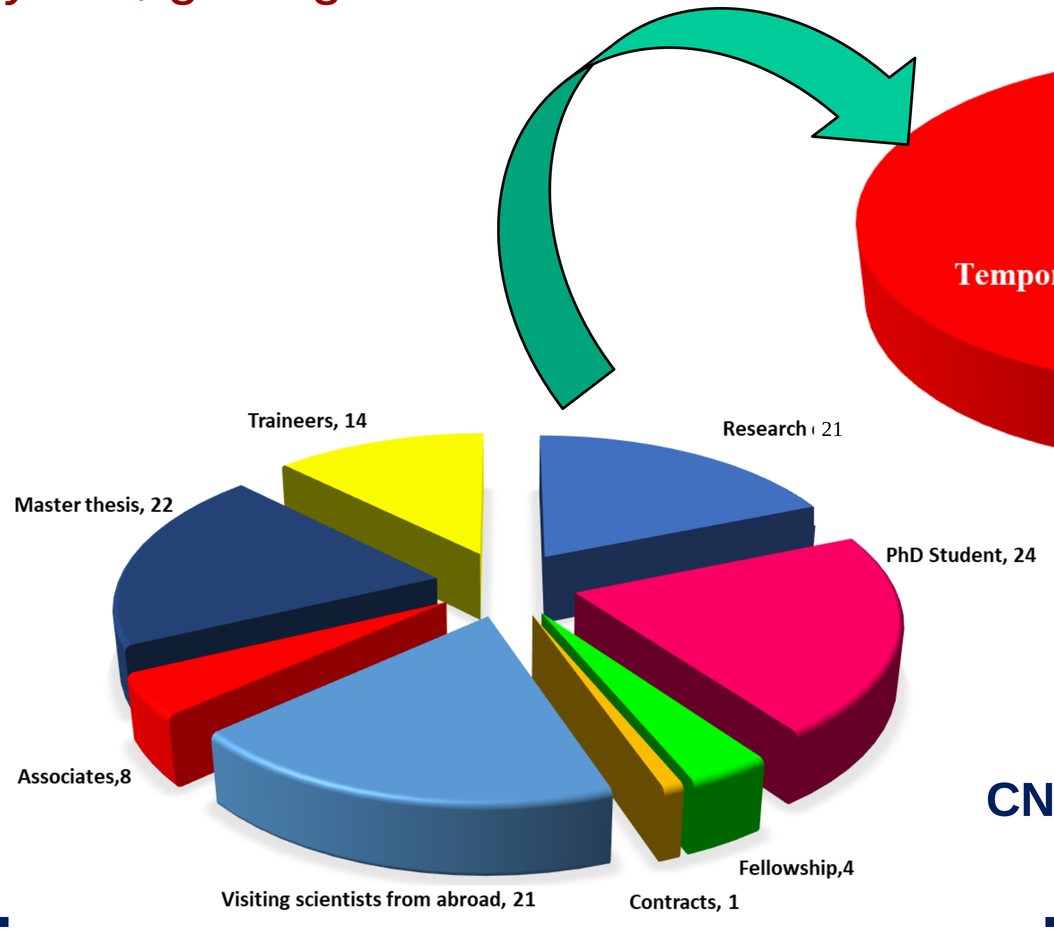
Headquarter in Rende (CS)
Section at University of Padua

Istituto per la Tecnologia delle Membrane
Consiglio Nazionale delle Ricerche

Personnel 2024-2025

ITM is a multidisciplinary Institute based on backgrounds in chemical engineering, process engineering, chemistry, biological science, food science, material science, physics, geologist





CNR-ITM Permanent staff in 202 :

- **41 Researchers (permanent staff + 4 termporary staff (TD))**
- **2 Technologist (permanent staff)**
- **8 Administrative/technical staff**

CNR-ITM Temporary personnel 2022 *(>110 researchers)*

Visiting scientists from abroad : > 20

Istituto per la Tecnologia delle Membrane
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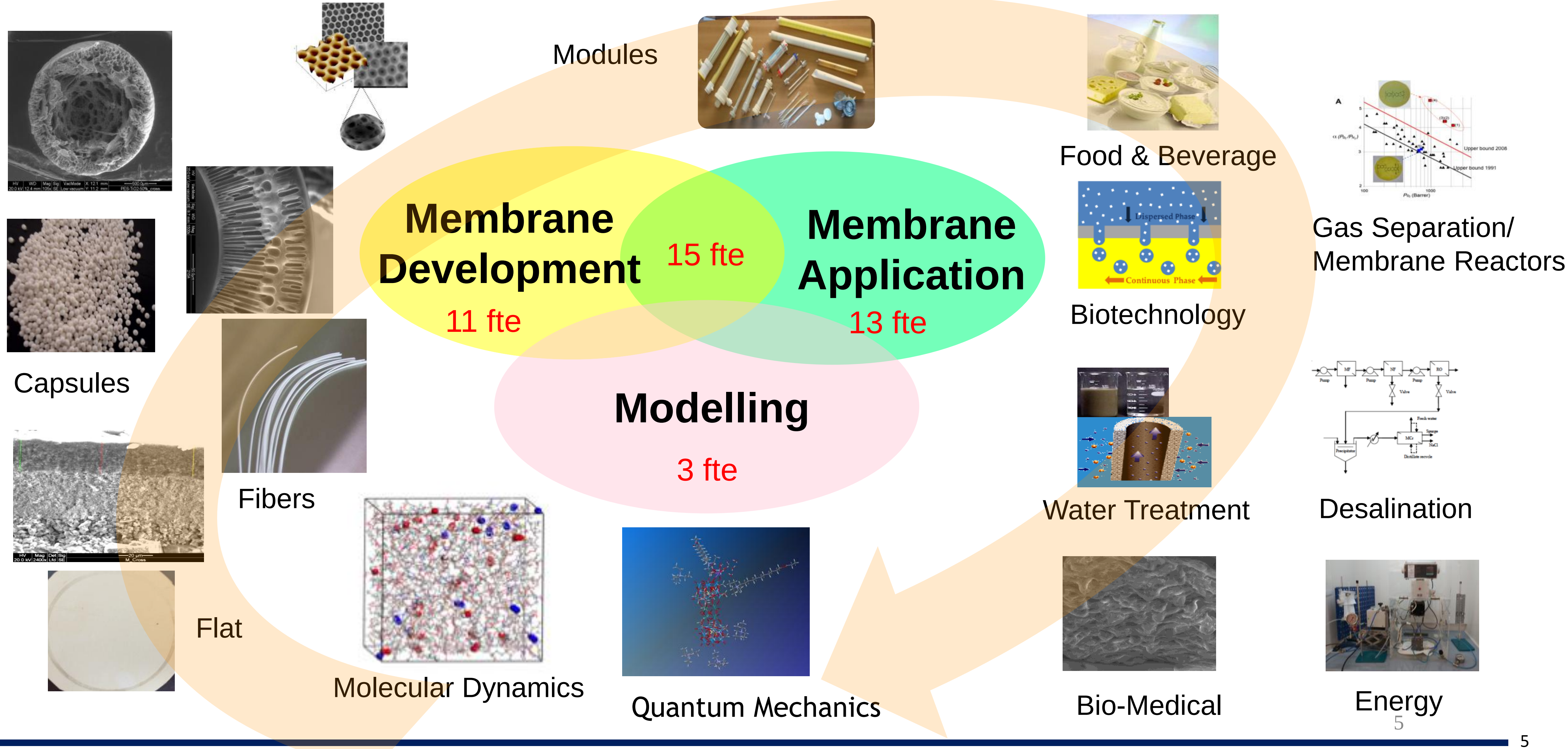
Research Activities at ITM

From TRL 1 to TRL 6



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CNR

Outreach and Communication Activities

Institute on Membrane Technology
National Research Council of Italy

ITM NEWSLETTERS

ITM INTERNATIONAL MEMBRANE WEBINARS 2022

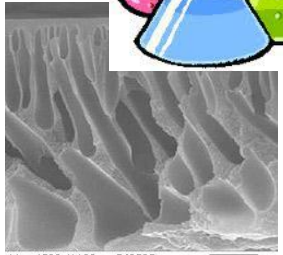
A series of lectures
given by academic and industrial
top-players of the membrane community

December 2023

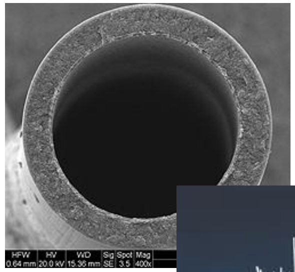
December 2024

https://www.itm.cnr.it/it/cnr-itm_newsletter_jan-june_2024

https://doi.org/10.48263/ASM2021 http://www.doi.org/10.48263/MOME1.2020



Polymeric Membrane Fabrication



The "heart" any membrane separation process is the **membrane** itself

Membranes are very different in their:

- *Material*
- *Structure*
- *Function*
- *Transport properties*
- *Transport mechanism*

As different are membrane types as diverse are the methods for making them:

- Sintering techniques (Inorganic and Polymeric)
- Irradiation and track-etching (symmetric membranes)
- Phase inversion (asymmetric membranes)
- Dip Coating, interfacial polymerization, plasma polymerization (Composite membranes)
- Electrospinning
- Layer by Layer
- Electro-spinning
- 3D printing

Membrane structure and Membrane Application

Membrane material

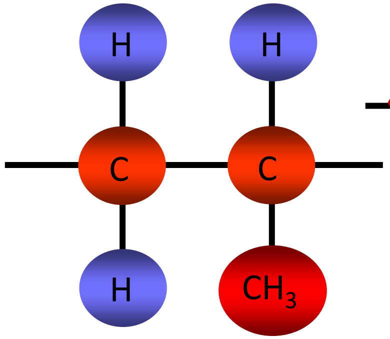
The selection of the material influences the choice of the preparation technique and depends on the application

Gas separation and pervaporation ↕ Membrane material

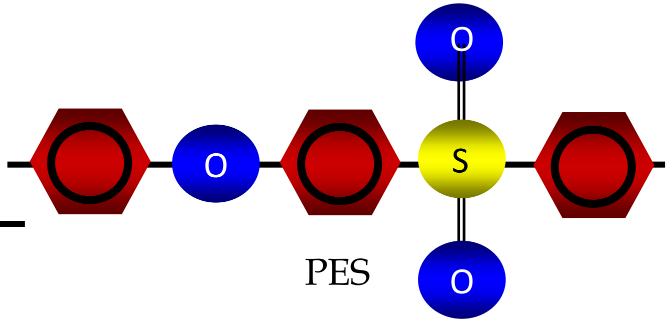
Micro- and Ultrafiltration ↕ Membrane structure

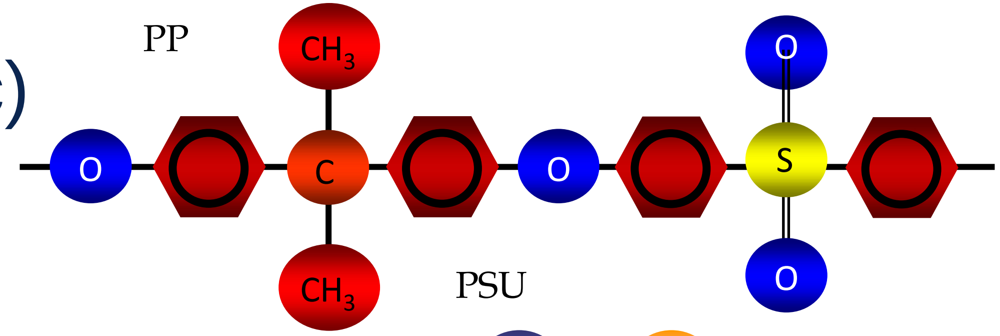
Some of the most frequently used polymers (1):

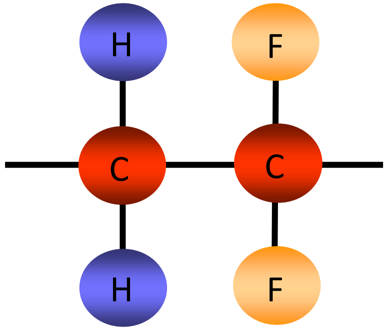
- Polypropylene (hydrophobic)
- Polysulfone (hydrophobic)
- Polyethersulfone (hydrophobic)
- Polyamide (hydrophilic)
- Polyacrilonitrile (hydrophilic)
- Polyvinilidene fluoride (hydrophobic)



PP







PVDF

Some of the most frequently used polymers (2):

By adding additives to the polymer matrix, it is possible to change its hydrophobic/hydrophilic character.

Polyethersulfone + PVP → hydrophilic

Polyvinilydene fluoride + PTFE particles → more hydrophobic

Membrane Preparation by Phase inversion

This technique is the most versatile preparation method.

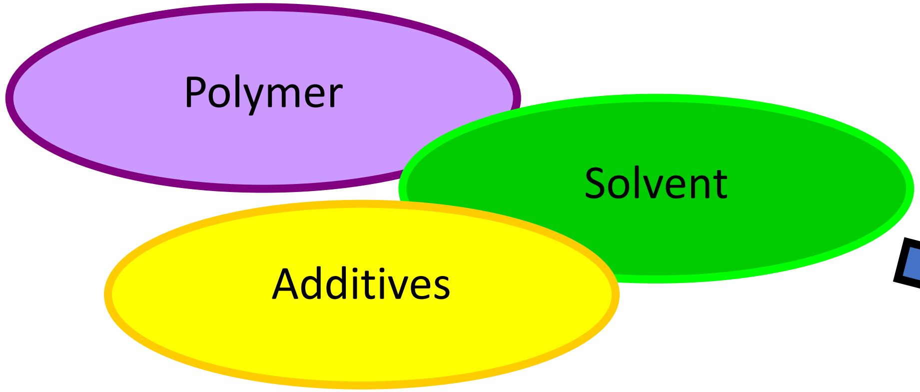
Membranes with different morphology (porous or dense), structures (asymmetric or symmetric) and function can be prepared.

A homogeneous system, consisting of the polymer dissolved in an appropriate solvent, in a single phase (liquid), is transformed, through a process of separation/solidification, in a two phase system:

- a polymer rich phase, solid, which will form the membrane itself;
- a polymer lean phase, liquid, which will form the membrane pores.

Dope or polymer solution preparation

1) Preparation of the polymeric dope



Membrane Fabrication

Most of the membranes are produced by Phase Inversion Technique

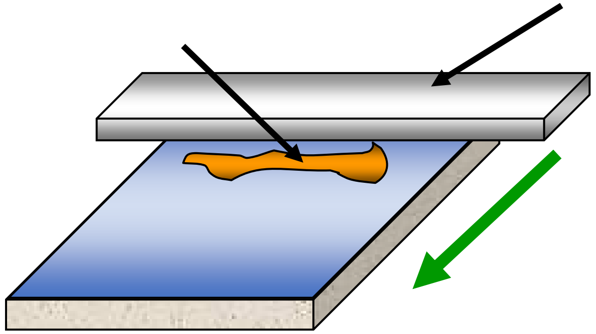
1. Dope or polymer solution preparation

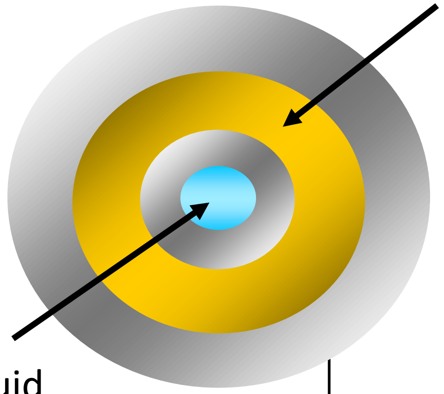
Polymer

Solvent

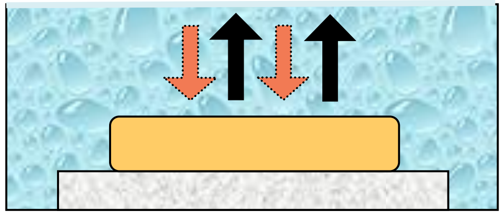
Additives

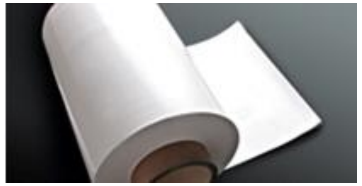
2. Membrane Formation





3) Coagulation





FLAT or HOLLOW FIBER

Membrane Preparation by Phase Inversion

There are several techniques of preparation of membranes by phase inversion, which are listed below:

EIPS = Evaporation induced phase separation
VIPS = Vapor induced phase separation
TIPS = Temperature induced phase separation
NIPS/DIPS = Non-Solvent induced or Diffusion induced phase separation

The only thermodynamic presumption for all procedures is that the system must have a miscibility gap over a defined concentration/temperature range

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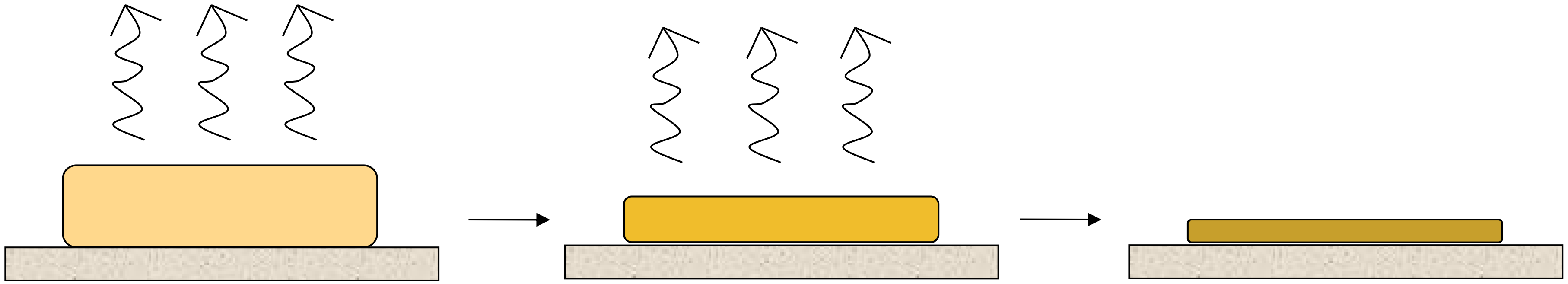

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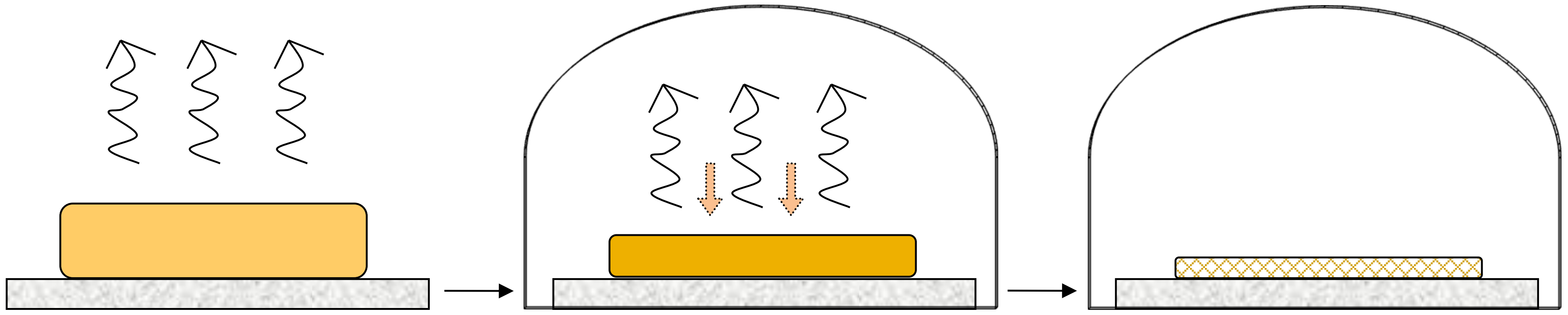

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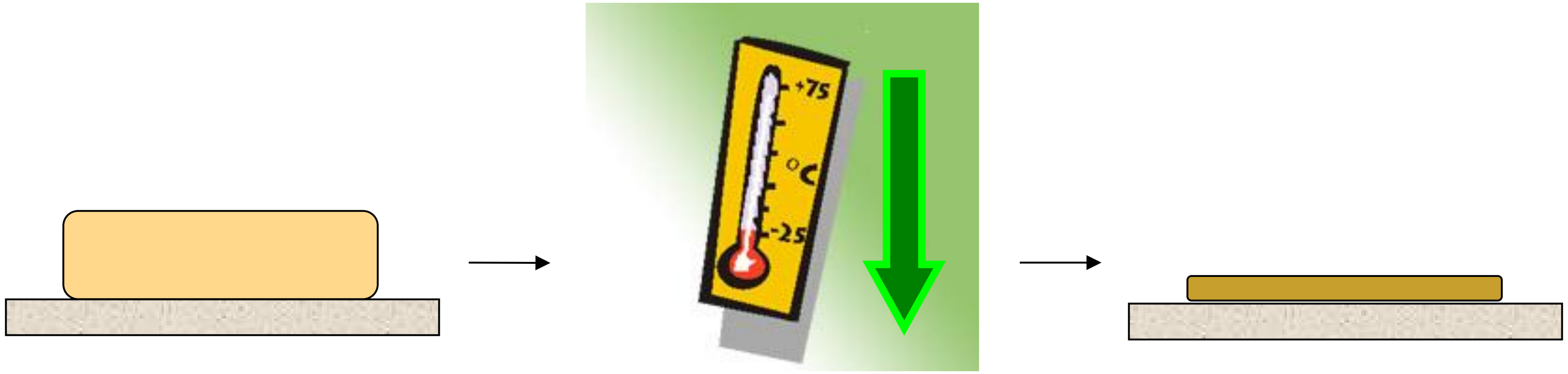

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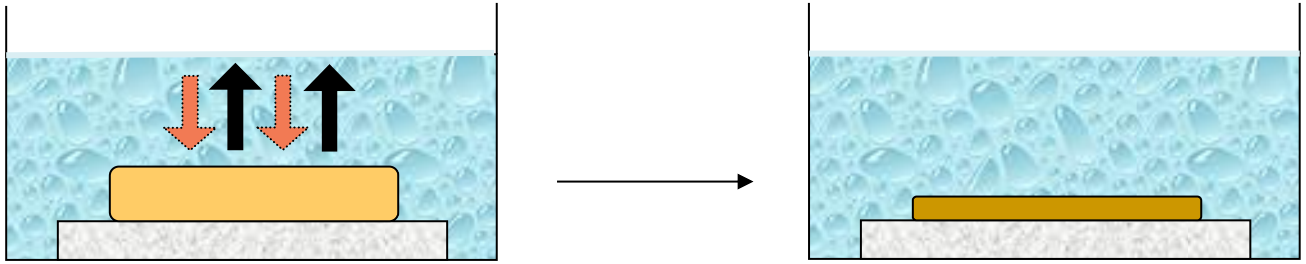


The only thermodynamic presumption for all procedures is that the system must have a miscibility gap over a defined concentration/temperature range

Membrane Fabrication by Phase Inversion

The structure (asymmetric or symmetric, porous or dense) of the prepared membrane will depend on different factors:

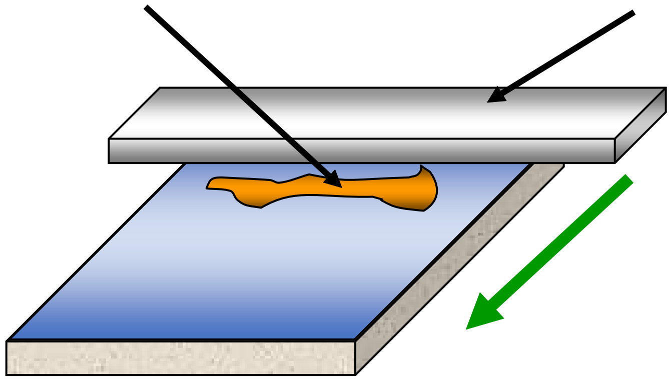
- choice of the polymer;
- choice of solvent and non solvent;
- composition of the casting solution;
- temperature of the casting solution and the coagulation bath;
- evaporation time.

Membrane Preparation by Phase Inversion

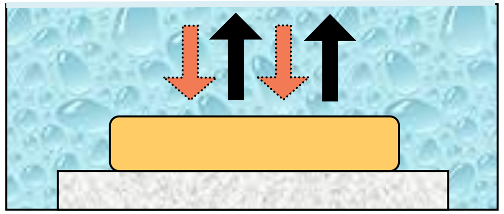
The practical membrane preparation by diffusion induced phase inversion

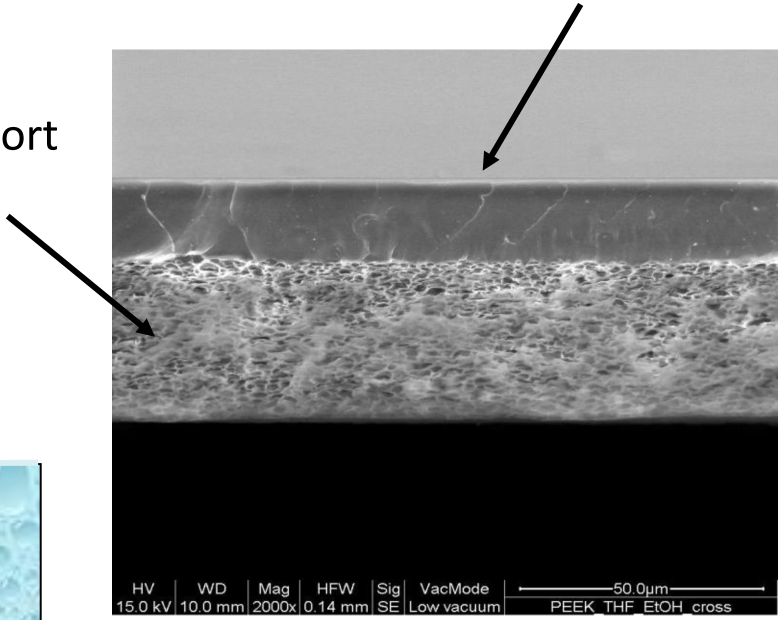
Flat sheet membranes

2) Casting



3) Coagulation





4) membrane

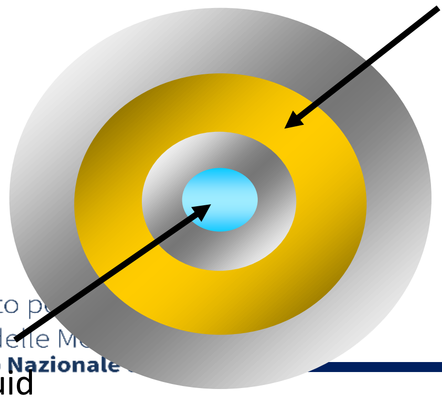
Membrane Preparation by Phase Inversion

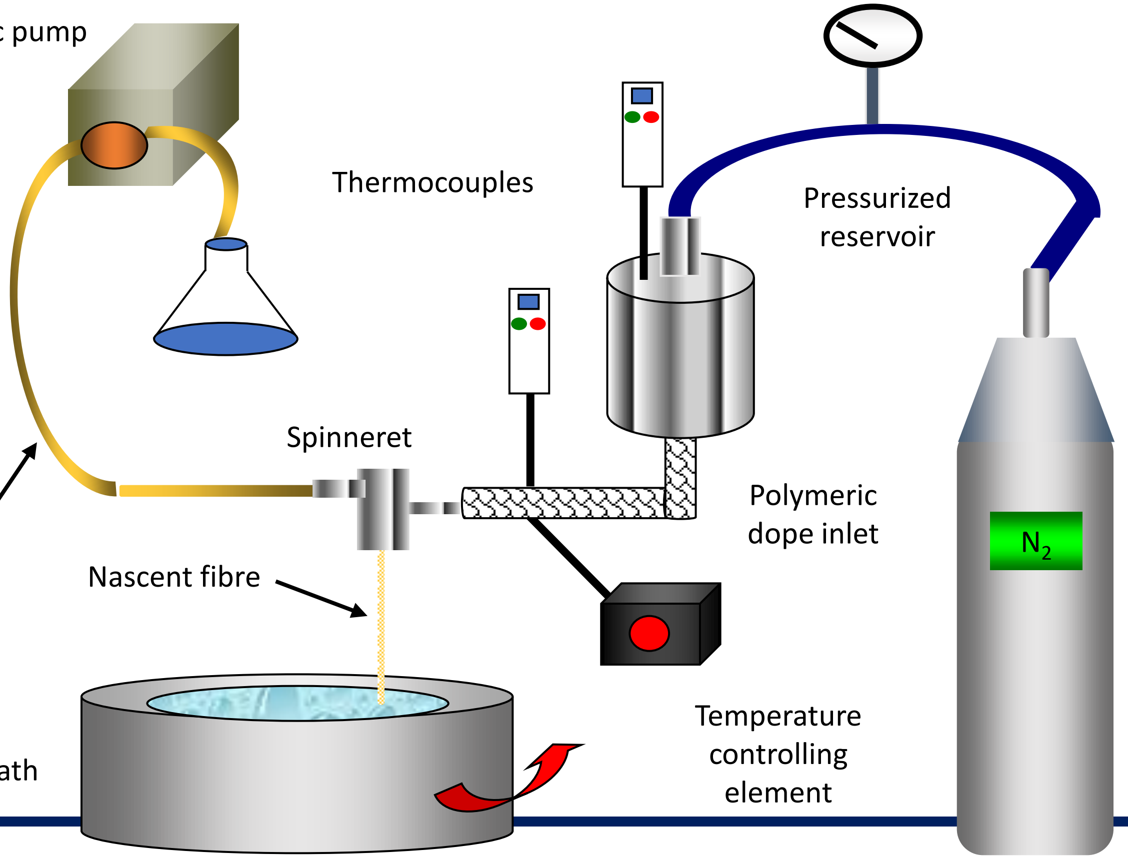
The practical membrane preparation by diffusion induced phase inversion

Hollow fiber membranes

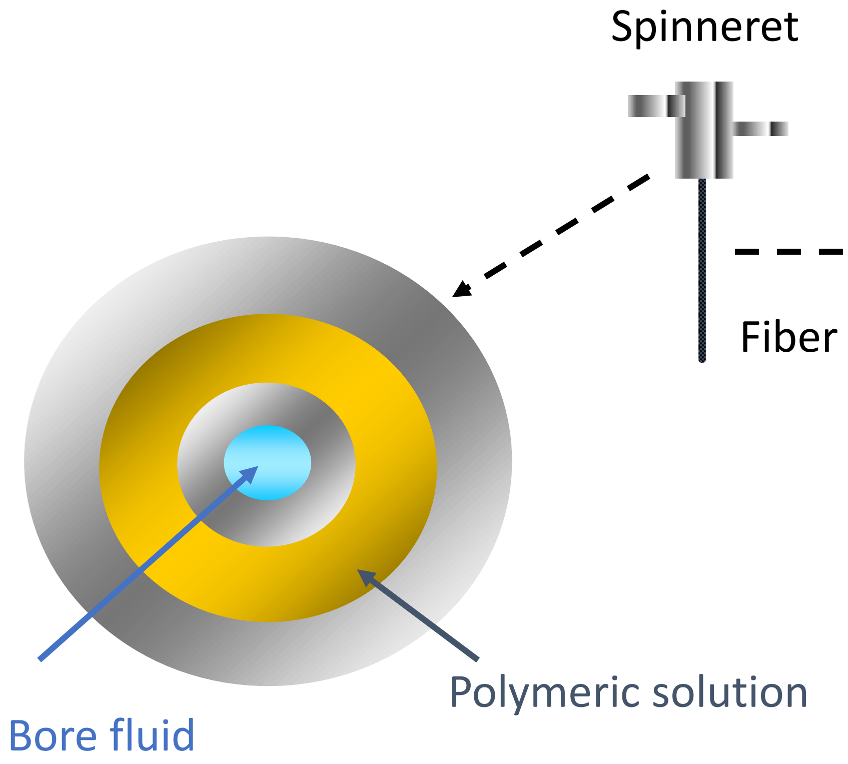
2) Hollow fibers spinning

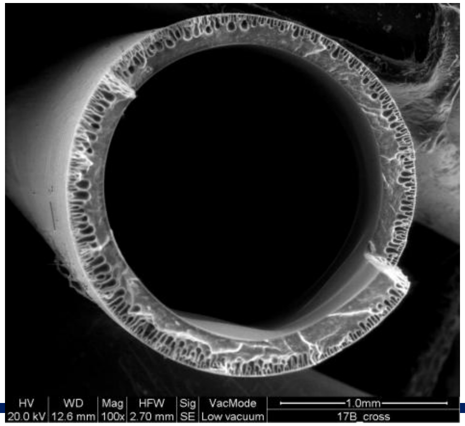
- Wet spinning
- Dry/wet spinning

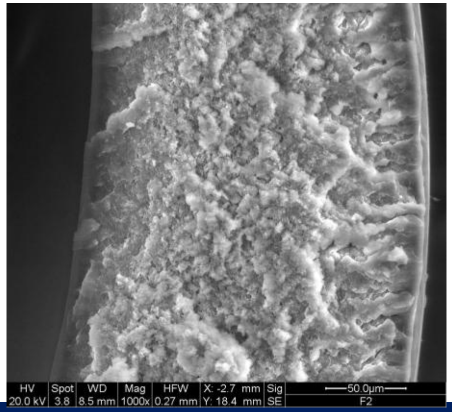




Preparation of HF membranes



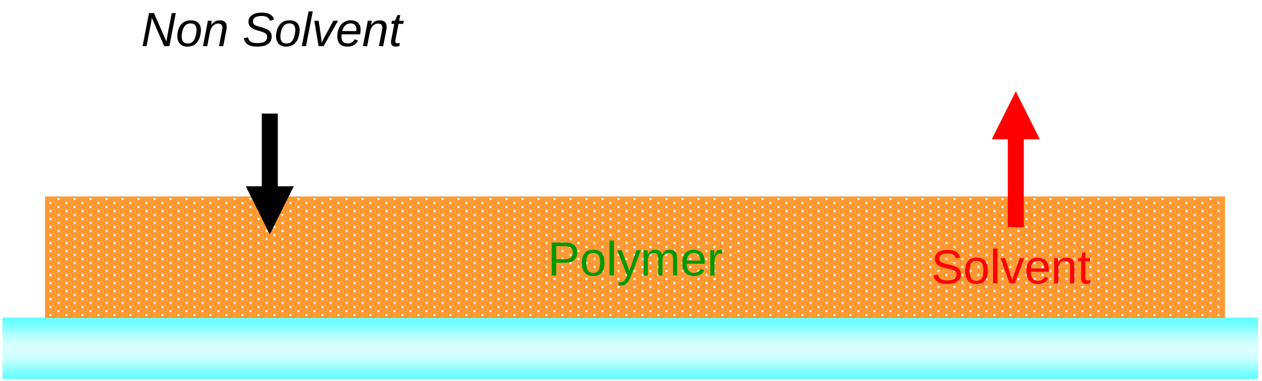




Mechanism of membrane preparation in NIPS

The process of phase inversion depends on a number of <u>*kinetic factors*</u> and <u>*thermodynamic*</u>, which determine the membrane morphology.

Of fundamental importance is the exchange rate of solvent and nonsolvent in the cast polymeric solution. Depending on these exchange rates, membranes with symmetric or asymmetric structures (porous or dense) are formed. Based on the calculated composition paths and supported by experimental data.



A. Figoli, S. Simone, E. Drioli, Polymeric Membranes, Chapter 1. Eds. Nidal Hilal, Ahmad Fauzi Ismail, and Chris Wright, Membrane Fabrication, CRC Press, 2015 Print ISBN- 978-1-4822-1045-3

Membrane Preparation by Phase Inversion

Reuvers et al. classified membrane formation processes into two groups:

1) Delayed demixing

Membranes formed show a porous (often closed-cell, macrovoid free) substructure with a dense relatively thick skin layer

2) Instantaneous demixing

Membranes formed show a highly porous substructure (with macrovoids) and a finely porous skin layer.

Which specific process dominates is mainly determined by the solvent/nonsolvent affinity and the solvent concentration in the coagulation bath.

In particular, in the case of good solvent/nonsolvent miscibility, the latter can easily penetrate into the casting solution and create a porous structure. In this light, the good solubility of polymers in solvents having different polarities and miscibilities with nonsolvents thus allows one to obtain various membrane morphologies

Reuvers AJ, van der Berg JWA, Smolders CA. J Membr Sci, 1987;34:45.

Solubility parameters (1)

The solubility of the polymer in the solvents is determined by their chemical structure. If the polymer has a polar functional group in their structure, it will dissolve in a polar solvent because of the better solubility, caused by the similarity of the structure between solutes and solvents.

In the case of the common organic solvents, their Hildebrand solubility can be divided in three components corresponding to three interactions, as proposed by Hansen:

dispersive interactions, polar cohesive forces, which is produced by the dipole-dipole interaction, and hydrogen bonding interactions, described in equation 5.

Solubility parameters (2)

Hansen's theory is based on three components:

δ_d - Dispersion forces
δ_p - Polar interactions
δ_h - Hydrogen bonding

the unit: $MPa^{1/2}$

"Polymers are soluble only in solvents of similar of solubility parameters δ "

Based on Hansen's theory, the Hildebrand's solubility parameter (δ) of a chemical specimen can be calculated :

$$\delta = \sqrt{\delta_d^{\,2} + \delta_p^{\,2} + \delta_h^{\,2}}$$

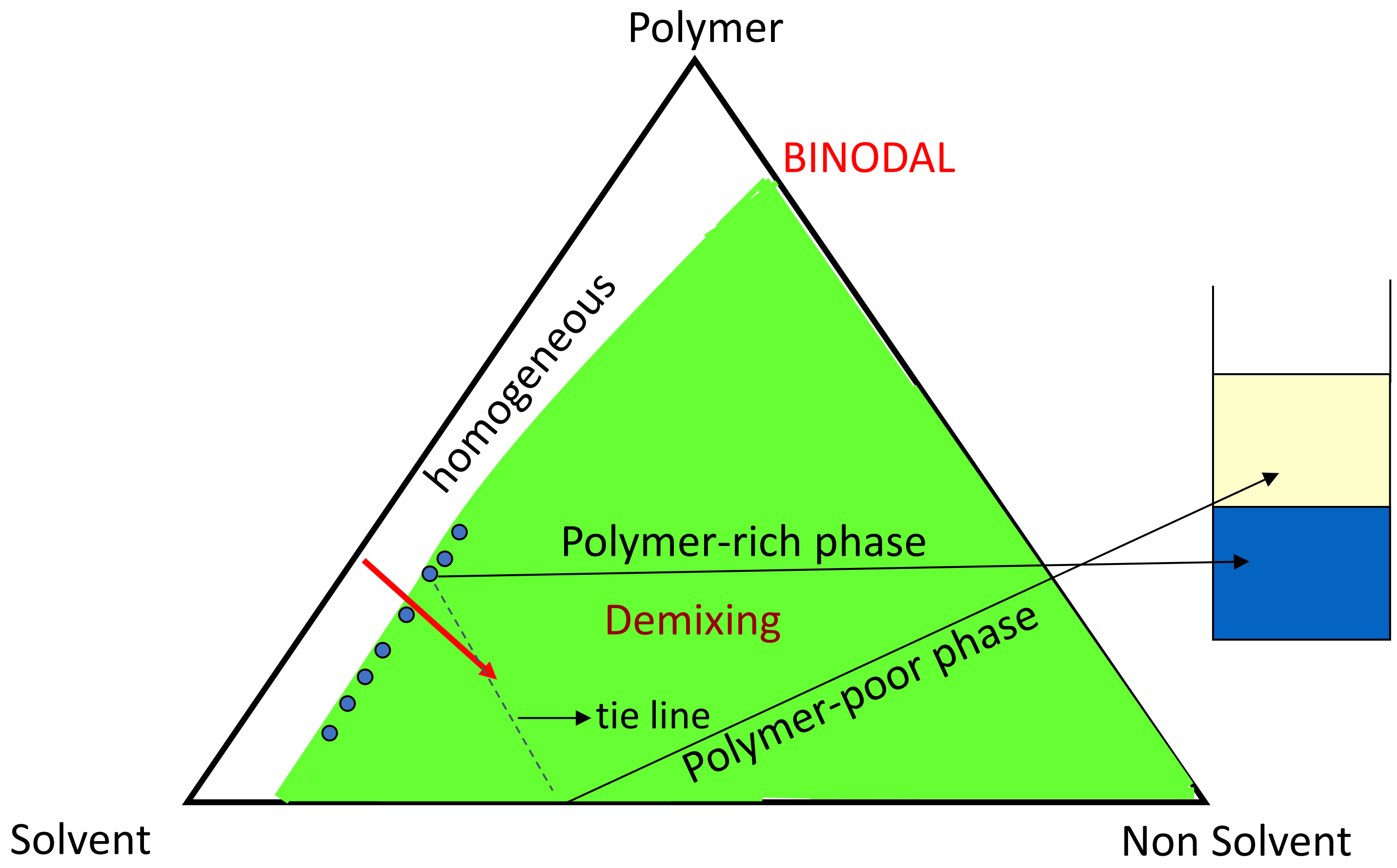
❖ C. M. Hansen, in Hansen Solubility Parameters: A User's Handbook, ed. C. Hansen, CRC Press, Boca Raton, 2° edn, 2007.
❖ Figoli A., Marino T., Simone S., Di Nicolò E., Li X.M.,He T., Tornaghid S., Drioli E. "Towards non-toxic solvents for membrane preparation: a review", Green Chemistry, 16, 4034-4059, 2014.

Hansen solubility parameters of commonly used materials for the fabrication of membranes

	δ_D	δ_P	δ_H	$\delta_{exp.}$	$\delta_{ref.}$ (Hildebrand)
Polymers					
Polyacrylonitrile (PAN)	17.9	16.7	6.3		25.2[82]
Polyethersulfone (PES)	19.6	10.8	9.2		24.2[82]
Polysulfone (PSf)	20	8	8		23[82]
Cellulose	18.7	12.5	23.4		32.5[82]
Cellulose acetate (CA)	18.6	12.7	11		25.1[82]
Cellulose triacetate (CTA)	17.2	5.7	6.0		19.1[82]
Poly(vinylidine fluoride) (PVDF)	17	12.1	10.2		23.2[82]
EXTEM^{TM}	21	10.9	10.6	26[48]	
Polyetherimide (PEI)	19.6	7.6	9.0		22.9[82]
Solvents					
Dimethyl aceteamide (DMAc)	16.8	11.5	10.2		22.7[82]
Dimethyl sulfoxide (DMSO)	18.4	16.4	10.2		26.5[82]
N-methyl-2-pyrrolidone (NMP)	18	12.3	7.2		22.9[82]
Dimethylformamide (DMF)	17.4	13.7	11.3		24.8[82]
Acetone	15.5	10.4	7		19.9[82]
Water	15.5	16	42.3		47.8[82]

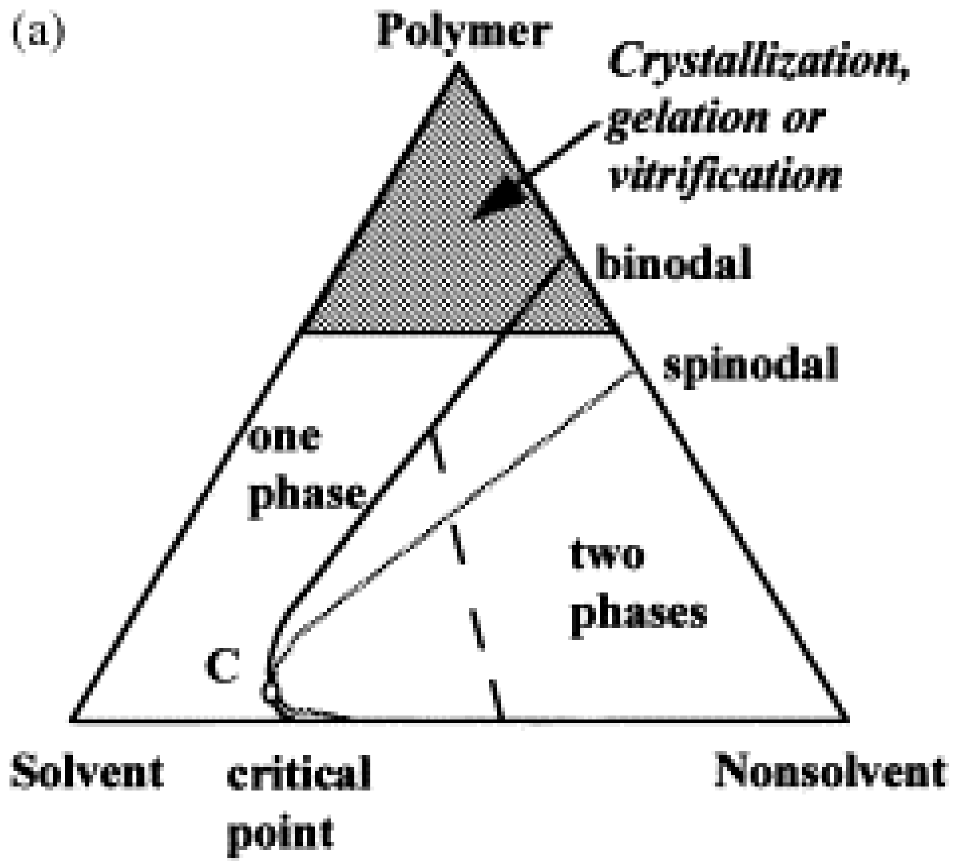
TERNARY PHASE DIAGRAM (1)

-Understanding of the phase separation-

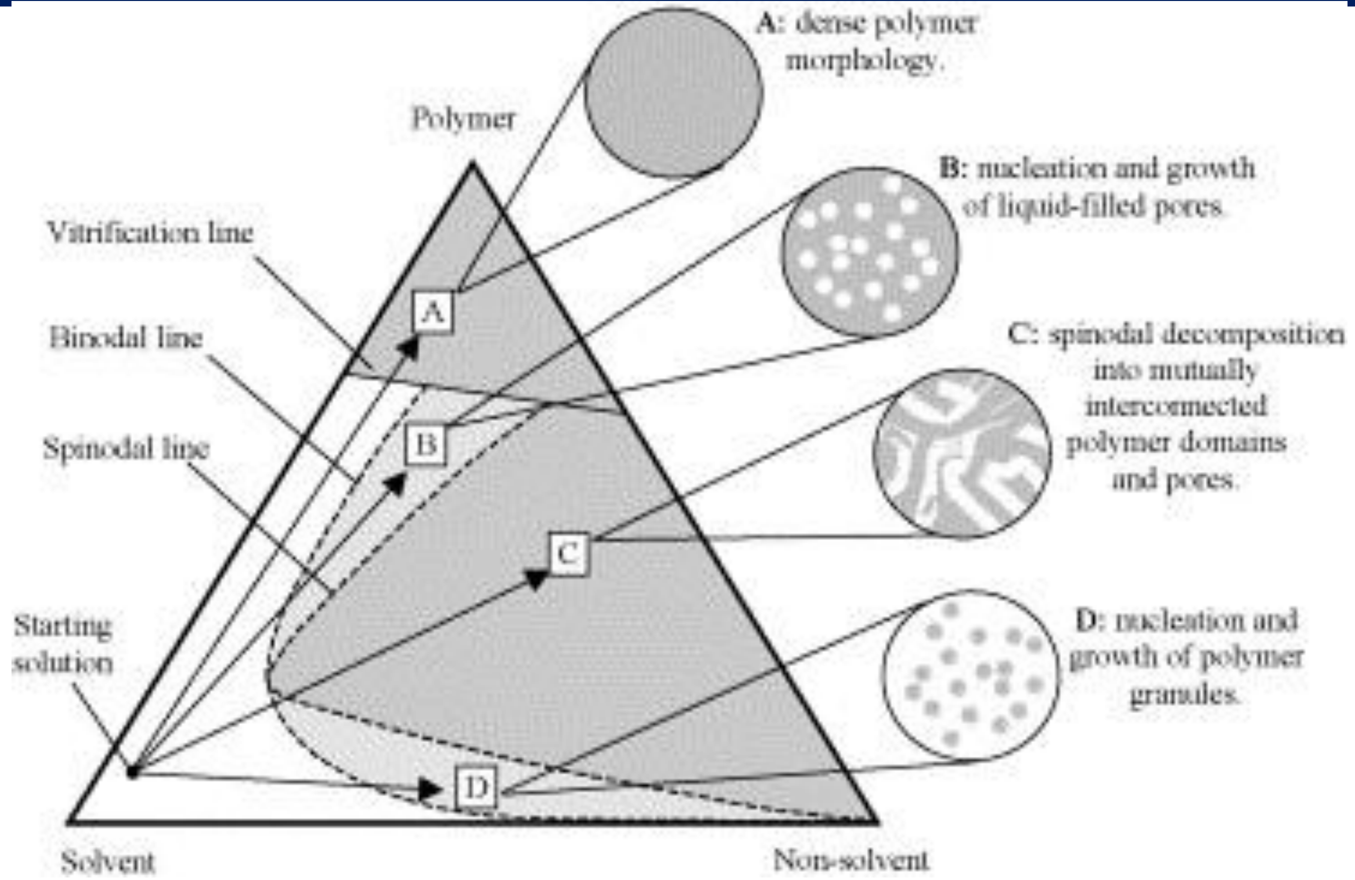


TERNARY PHASE DIAGRAM (2)

Spinodal curve: a curve that separates a metastable region from an unstable region in the coexistence region of a binary fluid. The spinodal is the limit of stability of a solution denoting the boundary of absolute instability of a solution to decomposition into multiple phases



TERNARY PHASE DIAGRAM (3)

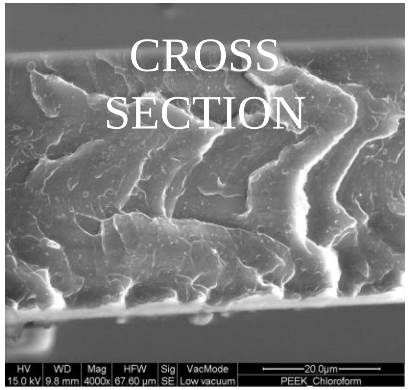


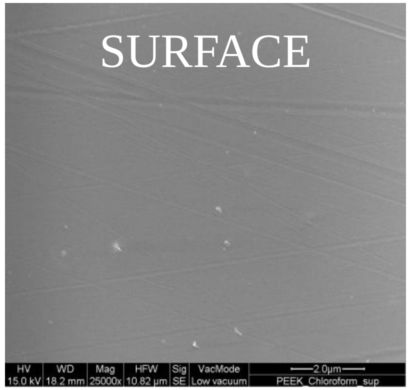
Isothermal phase diagram of a hypothetical polymer, solvent and non-solvent system showing four coagulation routes and representations of the resulting morphologies.

Polymer, Volume 43, Issue 22, 2002, p. 5827–5837

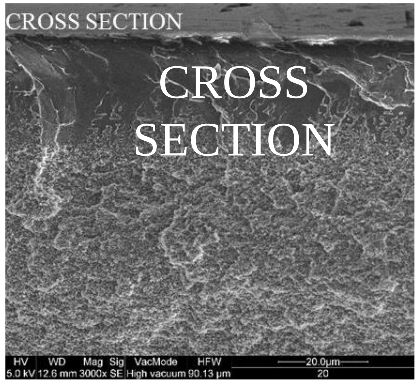
Membrane morphology - SEM

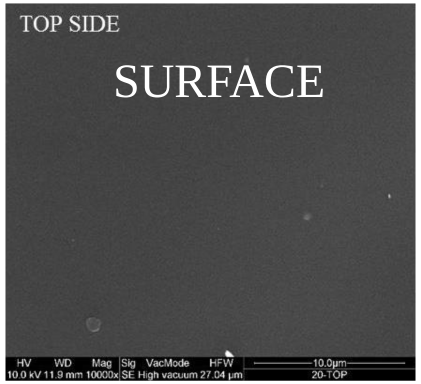
Membrane simmetriche - dense

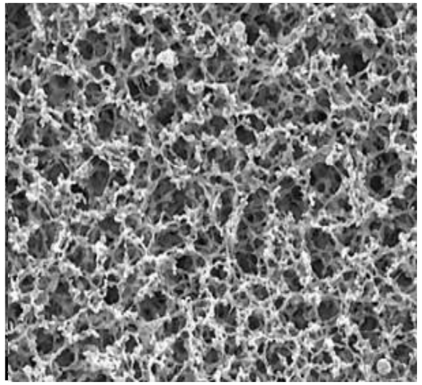




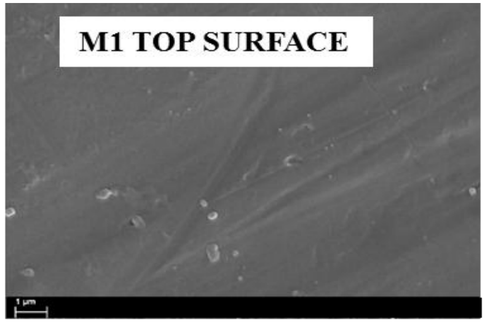
Membrane simmetriche – porose (sponge like)

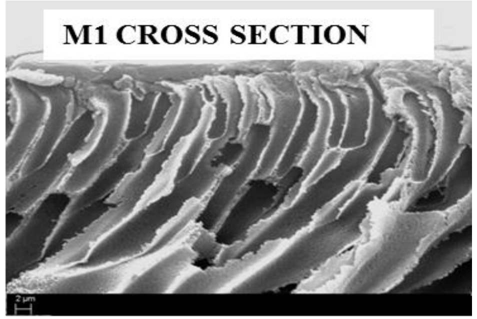


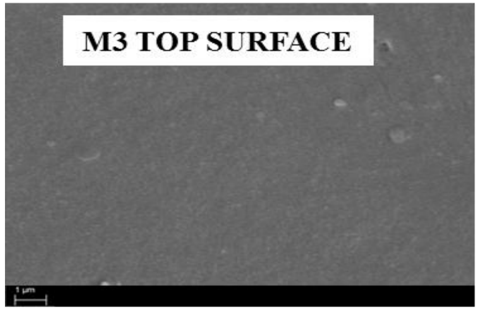


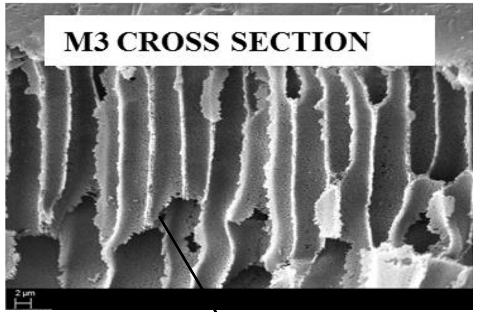


Membrane asimmetriche









finger like

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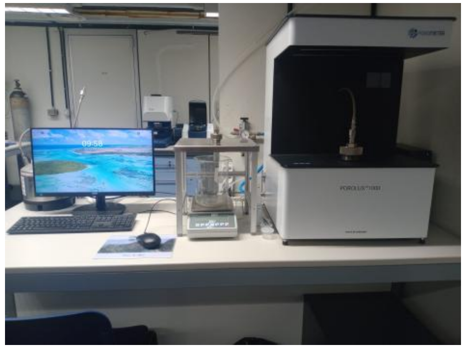
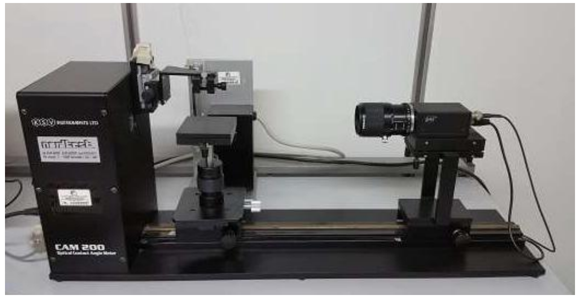
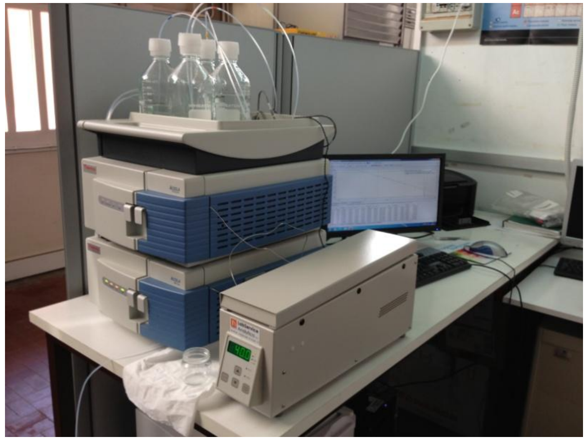
Membrane characterization (1)



Porometro gas-liquido per misura di pori passanti in membrane
Gas-liquid porometers for measuring the membrane pore size



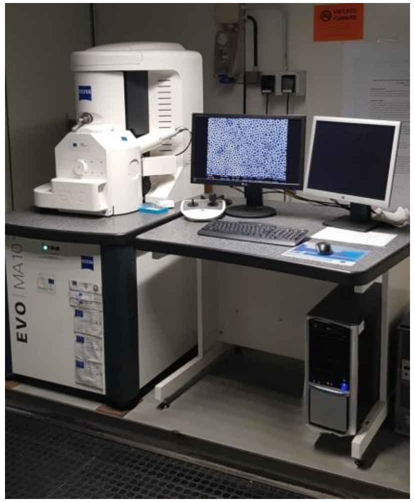
Angolo di contatto di membrane piane
Membrane static contact Angle



Molecular Weight cut-off determination (GPC – Thermoscientific)

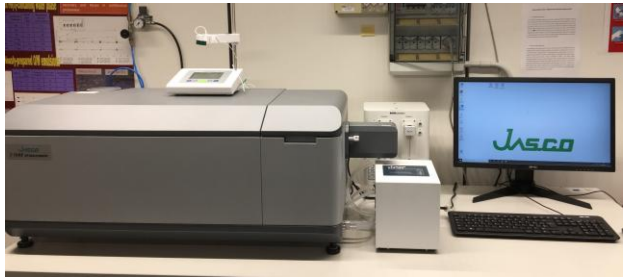
Laser Scanning Confocal Microscopy for the characterization of membranes and cells in bioartificial system.

Microscopio confocale a scansione laser per la caratterizzazione di membrane e cellule in un sistema bioatificiale.



Microscopio a Scansione Elettronica
Scanning Electron Microscopy

Membrane characterization (2)



Spettropolarimetro di Dicroismo Circolare
Circular Dichroism Spectroscopy

FT-IR

Tensile strength measurements
Test di resistenza alla trazione

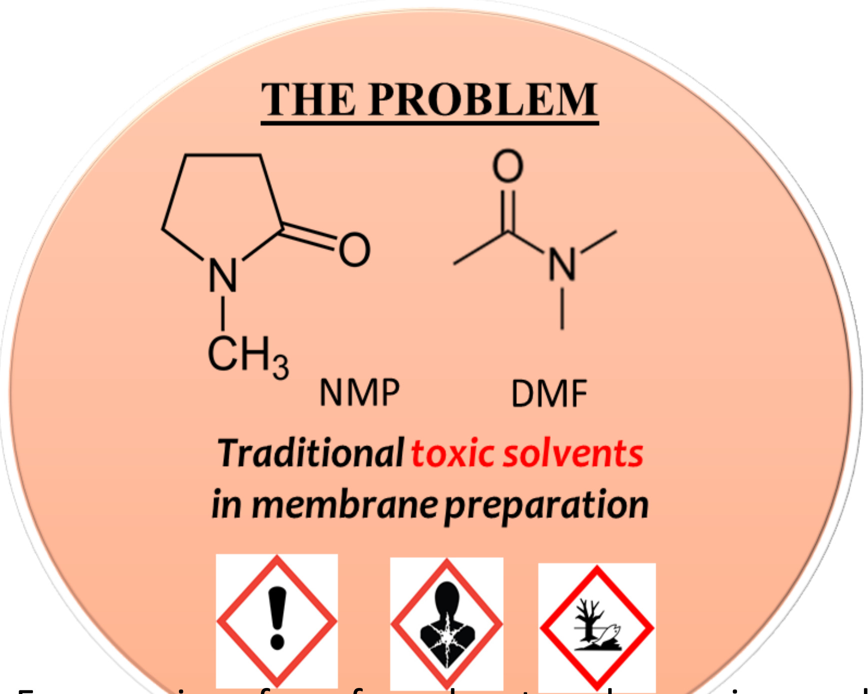
Electrokinetic analyzer for solid surface analysis
Analizzatore elettrocinetico per analisi superfici solide

RAMAN -Thermofisher

Sustainable membrane preparation

Membrane Technology can be considered a sustainable technology

however, to be really "sustainable", a membrane process should not involve the use of dangerous chemicals, in the membrane production process itself.



Frequencies of use for solvents polymers in membrane preparation

P. Yadav et al. Journal of Membrane Science 622 (2021) 1189872

Strategies of solvent replacement

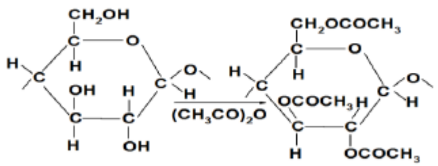
The use of renewable solvents is of great interest for producing membrane via phase separation process, in a more sustainable way, according to <u>Green Chemistry</u> design.

*D. Zou et al., Green Chemistry 23 (2021) 9815–9843

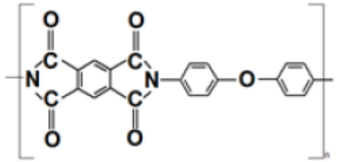
*A.Figoli, et al, Green Chemistry, 16 (2014) 4034-4059

Sustainable membrane preparation

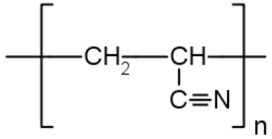
Polymers:



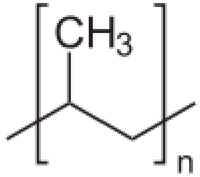
Cellulose acetate



Polyimide

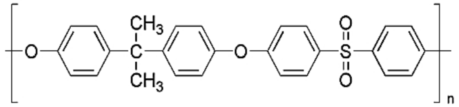


Polyacrylonitrile

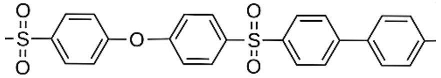


Polypropilene

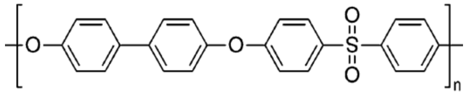
Sulfone-based polymers



Polysulfone



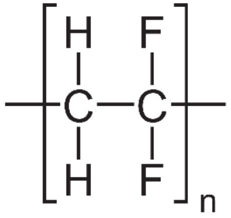
Polyether Sulfone



Polyphenyl Sulfone

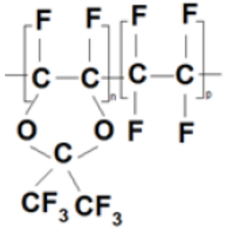
Good electrical properties
Good chemical resistance
Stable over a wide range of temperatures
High temperature resistance

Fluoropolymers



High Performance in term of chemical and mechanical stability.

Polyvinylidene difluoride (PVDF)



Teflon

Biobased polymers: New trend

- ✓ Renewable and sustainable industry
- ✓ Biodegradable
- ✓ Biocompostable
- ✓ No-Mugenic
- ✓ No-Carcinogenic
- ✓ Carbon neutral –low environmental footprint

The use of renewable biopolymers and solvents derived from biomass is of great interest for producing membrane in a more sustainable way, according to Green Chemistry design.

F. Galiano et al., Advances in biopolymer-based membrane preparation and applications, Journal of Membrane Science 564 (2018) 562–586

NEW TREND IN MEMBRANE FORMATION:

USING OF GREENER OR NON-TOXIC SOLVENT

Green Chemistry

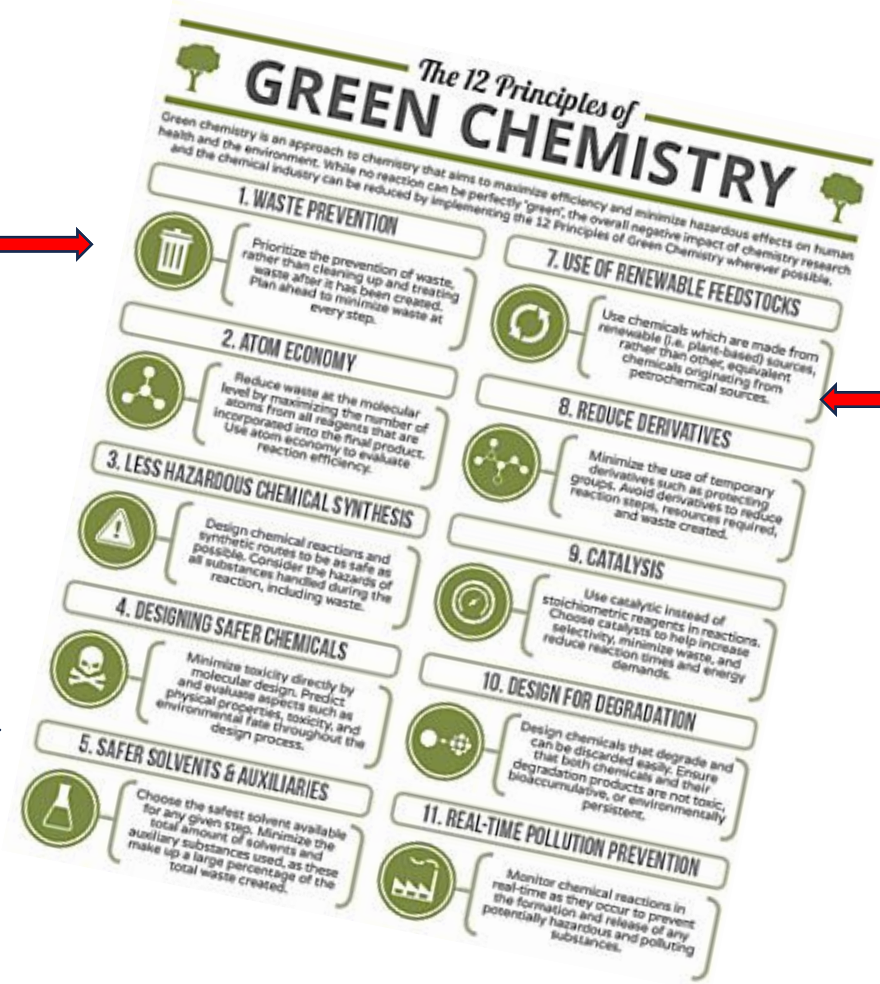
«**Green Chemistry** is on the use of a set of principles that reduces of **eliminates the use or generation of hazardous substances** in the design, manufacture and application of chemical products »

- Referes to a concept developed in the 1990_s by Paul Anastas and John Warner

- Design chemical processes in

  a less polluting,
  more efficient and
  less hazardous way

- The authors created a set of principles to guide followers of this concept



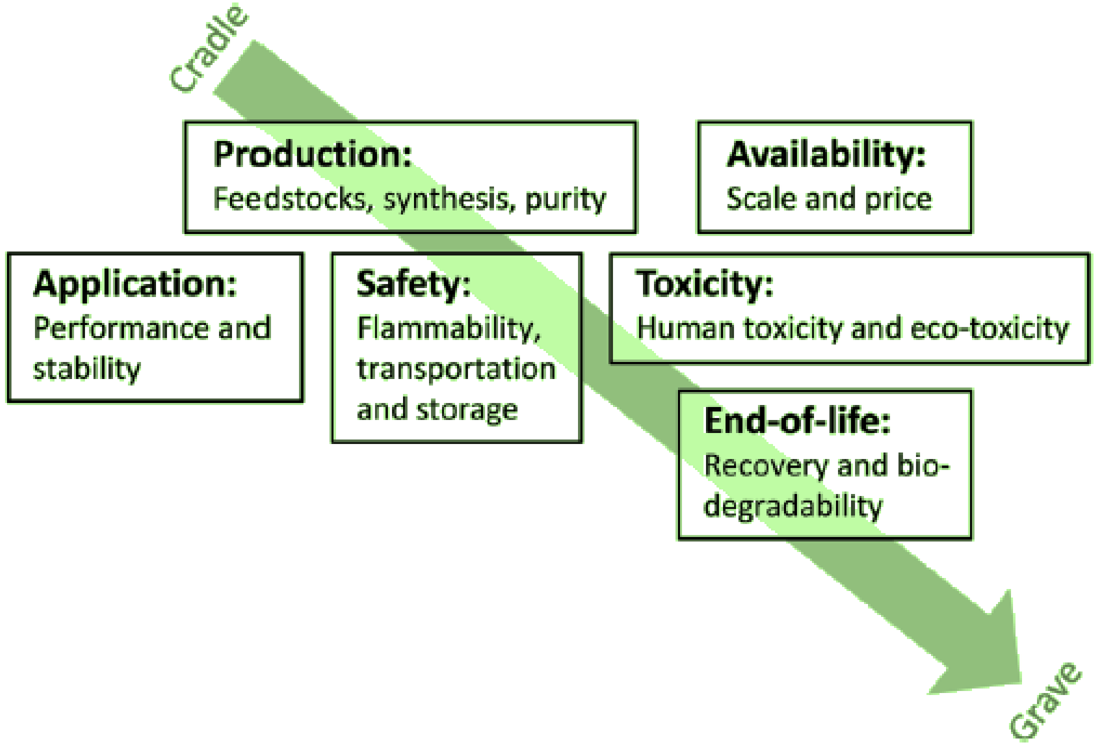
P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press New York, 1998.

Criteria that define green solvents

The 12 criteria that define green solvents

	Criteria	Description
1	Availability	*A green solvent needs to be available on a large scale, and the production capacity should not greatly fluctuate in order to ensure a constant availability of the solvent on the market*
2	Price	*Green solvents have to be not only competitive in terms of price but also their price should not be volatile during time in order to ensure sustainability of the chemical process*
3	Recyclability	*In all chemical processes, a green solvent has to be fully recycled, of course using eco-efficient procedures*
4	Grade	*Technical grade solvents are preferred in order to avoid energy-consuming purification processes required to obtain highly pure solvents*
5	Synthesis	*Green solvents should be prepared through an energy-saving process and the synthetic reactions should have high atom-economy*
6	Toxicity	*Green solvents have to exhibit negligible toxicity in order to reduce all risks when manipulated by humans or released in nature when used for personal and home care, paints, etc.*
7	Biodegradability	*Green solvents should be biodegradable and should not produce toxic metabolites*
8	Performance	*To be eligible, a green solvent should exhibit similar and even superior performances (viscosity, polarity, density, etc.) compared to currently employed solvents*
9	Stability	*For use in a chemical process, a green solvent has to be thermally and (electro)chemically stable*
10	Flammability	*For safety reasons during manipulation, a green solvent should not be flammable*
11	Storage	*A green solvent should be easy to store and should fulfil all legislations to be safely transported either by road, train, boat or plane*
12	Renewability	*The use of renewable raw materials for the production of green solvents should be favored with respect to the carbon footprint*

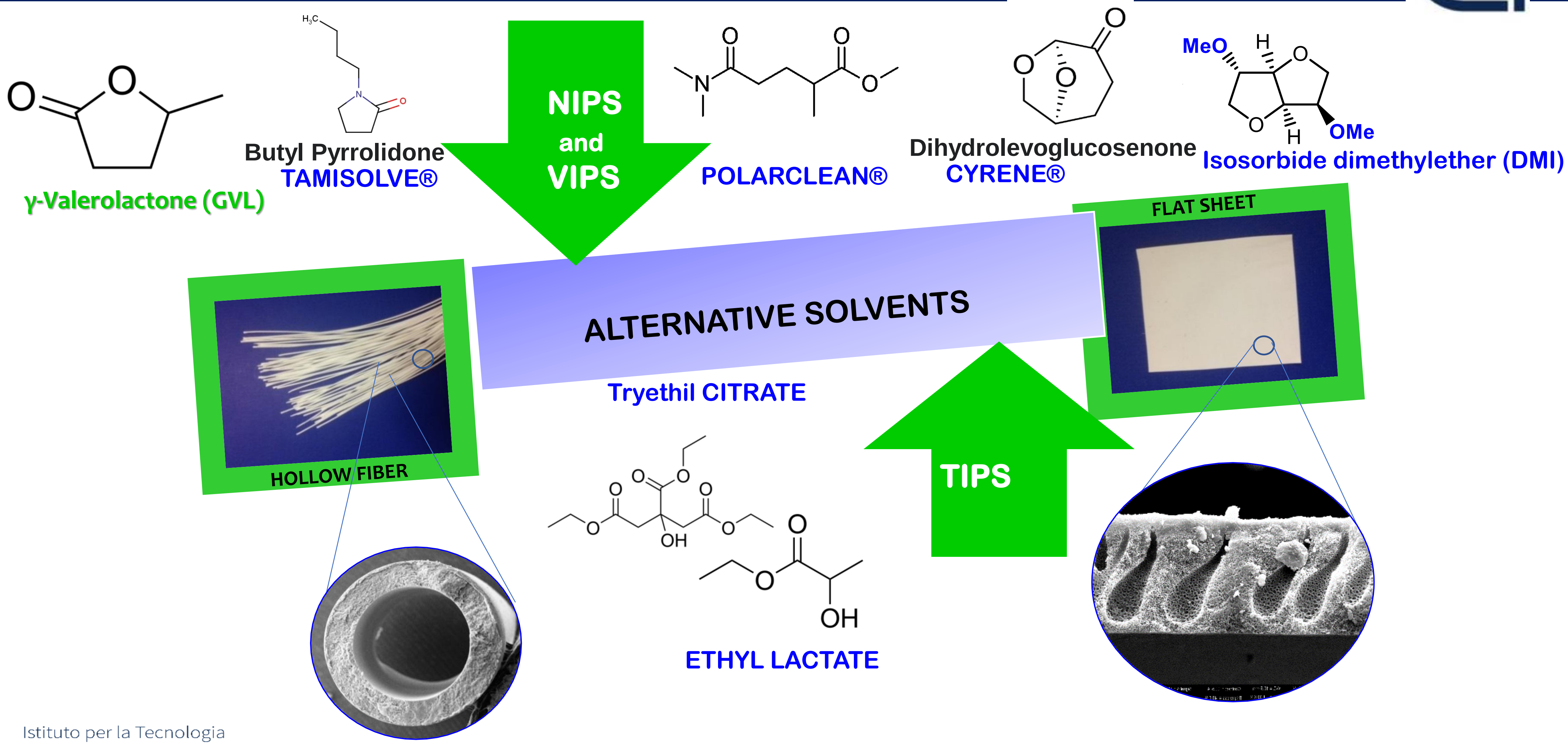
Cradle-to-grave categories of green solvents



If a solvent is renewable, it is not automatically sustainable.

J.H. Clark, T.J. Farmer, A.J. Hunt, J. Sherwood, Opportunities for Bio-Based Solvents Created as Petrochemical and Fuel Products Transition towards Renewable Resources, Int. J. Mol. Sci. 2015, Vol. 16, Pages 17101-17159.

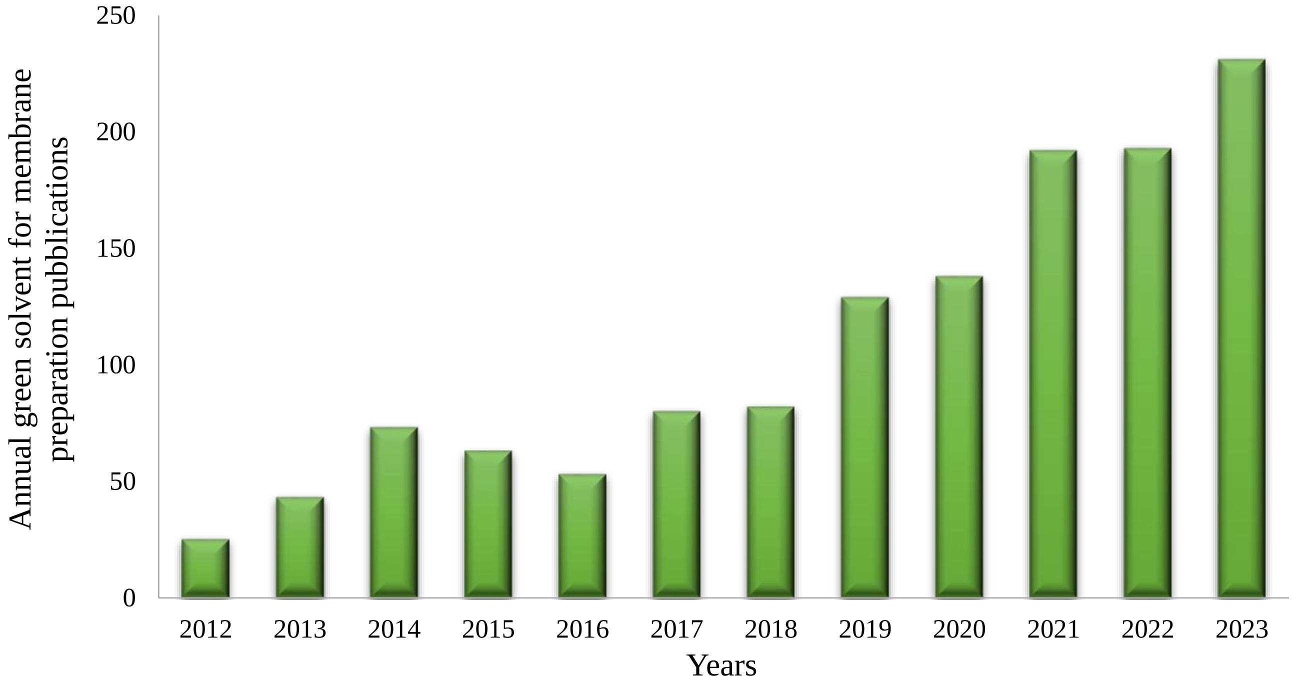
ALTERNATIVE SOLVENTS for MEMBRANE



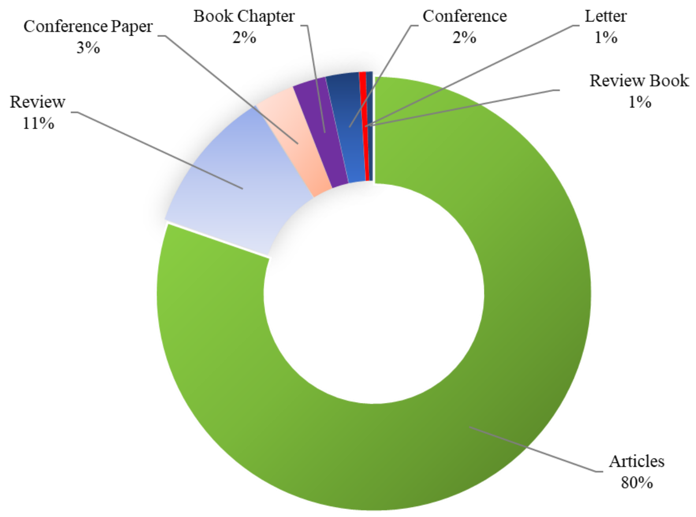
- *F. Russo, et al, ACS Sustainable Chem. Eng. (2020) 8, 1, 659–668*

Publications on Greener solvents

a)



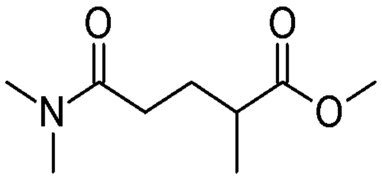
b)



a) and b) Scientific paper on green solvents for membrane preparation during the last 12 years. (updated until December 2023). Search engine: Scopus using the keywords "Green solvents for membrane preparation".

- Source: Bubalo et al., Green solvents for green technologies, J Chem Technol Biotechnol 2015; 90: 1631–1639; ** Source: A. Figoli, A. Criscuoli, Sustainable Membrane Technology for Water and Wastewater Treatment 2017, 978-9811056215; A.Figoli, T. Marino, S. Simone, E. Di Nicolò, X.-M. Li, T. He,c S. Tornaghi, E. Drioli, Green Chemistry, 2014, 16, 4034-4059; *D.. Zou , S. P. Nunes, I. F. J. Vankelecom, A. Figoli, Y. Moo Lee, Green Chem.*, 2021, **23**, 9815-9843.

POLARCLEAN®



methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate

Rhodia
Member of the Solvay group

SOLVAY

easy-to-use and to-handle.

Suitable for NIPS and TIPS procedures

high boiling point (278–282 °C)

high solvency capability

water solubility of 490 g/dm^3 at 24 °C

5° PRINCIPLE GREEN CHEMISTRY

It does not pose risks for human health and for the environment

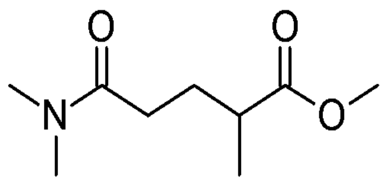
It reduces carbon foot print

TOXICOLOGICAL AND ECOTOXICOLOGICAL DATA

- **Biodegradation (dosed bottle) OECD301F/302B Inherently biodegradable**
- **Skin sensitization (local lynde node assay) OECD429 Not sensitizing**
- **Gene Mutation in bacteria (Ames test) OECD471 Not mutagenic**

"The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used."

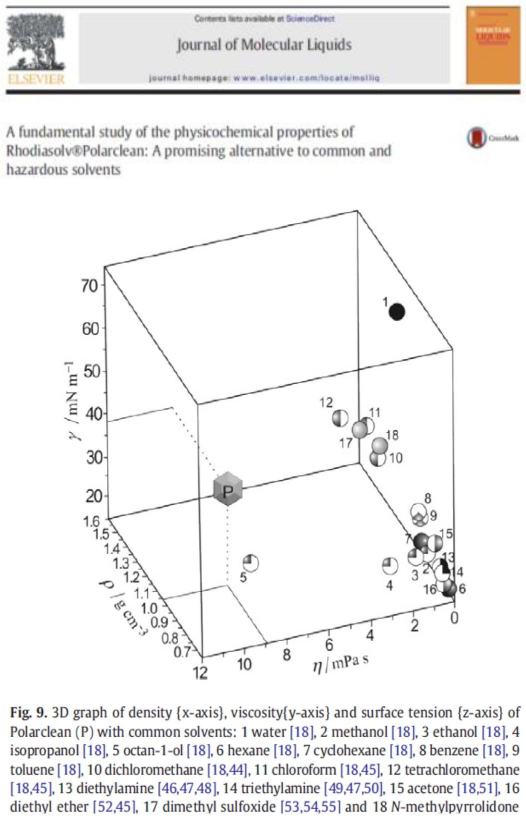
POLARCLEAN



methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate

PHYSICAL PROPERTIES	
Molar Mass	187.8
Solubility at 23°C – 50/50 v/v in water	Miscible
Refractive Index, nD at 20°C	1.4610 ± 0.0005
Density at 20°C	1.043 ± 0.001 g/cm3
Surface tension	36.3 ± 0.3 mN/m
Boiling Point (1013 hPa)	280 ± 2 °C
Vapore pressure (20°C)	<0.001 Pa
Dynamic viscosity (23 °C)	9.82 ± 0.02 Cpoises
Evaporation rate (50 °C)	0.0017 ± 0.0003 (n-butyl acetate=1)
Flash Point	145 ± 1°C (Closed cup)
Freezing Point	<-60 °C

Journal of Molecular Liquids , 234 (2016) 1163-1171


Contents lists available at ScienceDirect

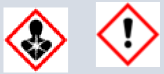
Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

A fundamental study of the physicochemical properties of Rhodiasolv®Polarclean: A promising alternative to common and hazardous solvents

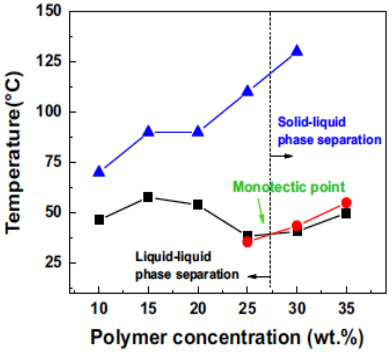
Fig. 9. 3D graph of density (x-axis), viscosity(y-axis) and surface tension (z-axis) of Polarclean (P) with common solvents: 1 water [18], 2 methanol [18], 3 ethanol [18], 4 isopropanol [18], 5 octan-1-ol [18], 6 hexane [18], 7 cyclohexane [18], 8 benzene [18], 9 toluene [18], 10 dichloromethane [18,44], 11 chloroform [18,45], 12 tetrachloromethane [18,45], 13 diethylamine [46,47,48], 14 triethylamine [49,47,50], 15 acetone [18,51], 16 diethyl ether [52,45], 17 dimethyl sulfoxide [53,54,55] and 18 *N*-methylpyrrolidone

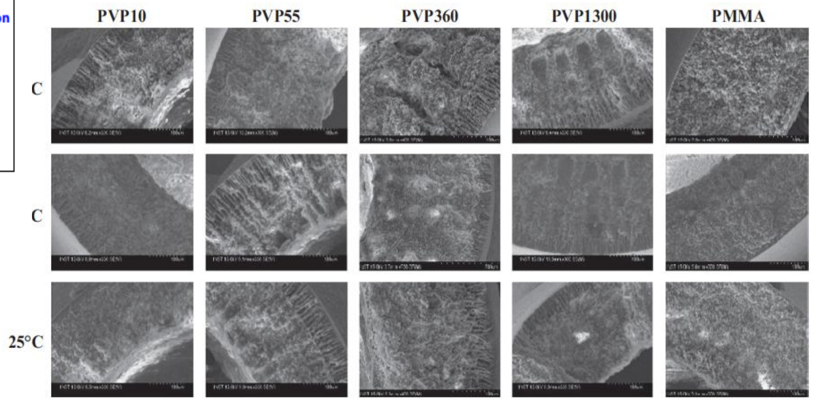
Physico-chemical comparison of standard solvents with POLARCLEAN

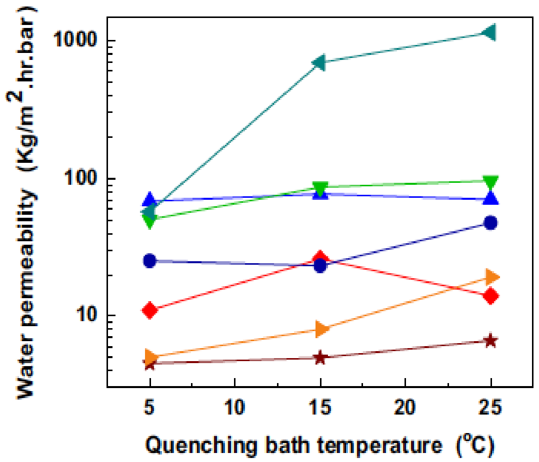
Solvent	Mp	Bp	Flash point	Vapour pressure	Viscosity	Surface tension	Evaporation rate	VOC	GHS
				@25°C	@25°C	@30°C	vs n-Butyl acetate		
	(°C)	(°C)	(°C)	mmHg	cpoises	dyne/cm			
NMP	-24	202	86	0.33	1.67	40	0,03	VOC	
DMAc	-20	166	77	1.3	0.92	32.5	0.17	VOC	
DMF	-60	153	67	3.7	0.8	36	0.2	VOC	
DMSO	18.5	189	89	0.6	2	43.5	0.026	VOC	
Polarclean	-60	280	145	0.004	9.8	36	0.001	NON VOC	

POLARCLEAN in Membranes

Prof. Drioli and Y. M. Lee group at Hanyang University (South Korea) are the pioneers for the developing and fabrication of PVDF membranes by using Polarclean membranes with TIPS and NIPS/TIPS techniques.



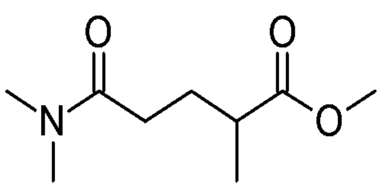




- A. Sanguineti, N. Di Nicolò, Y M Lee, E. Drioli, Z. Cui, N. T. . Hassankiadeh, S. Y. Lee, Process for manufacuring fluoropolymer membranes, WO2015051928, PCT/EP2014/060629

- N.T. Hassankiadeh, Z Cui, J.H Kim, D.W. Shin, A Sanguineti, V. Arcella, Y.M. Lee E Drioli, PVDF HF membranes prepared from green diluent via TIPS. Effect of PVDF molecolar weight, J Membrnae Science 479 (2015) 204-212

POLARCLEAN



methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate

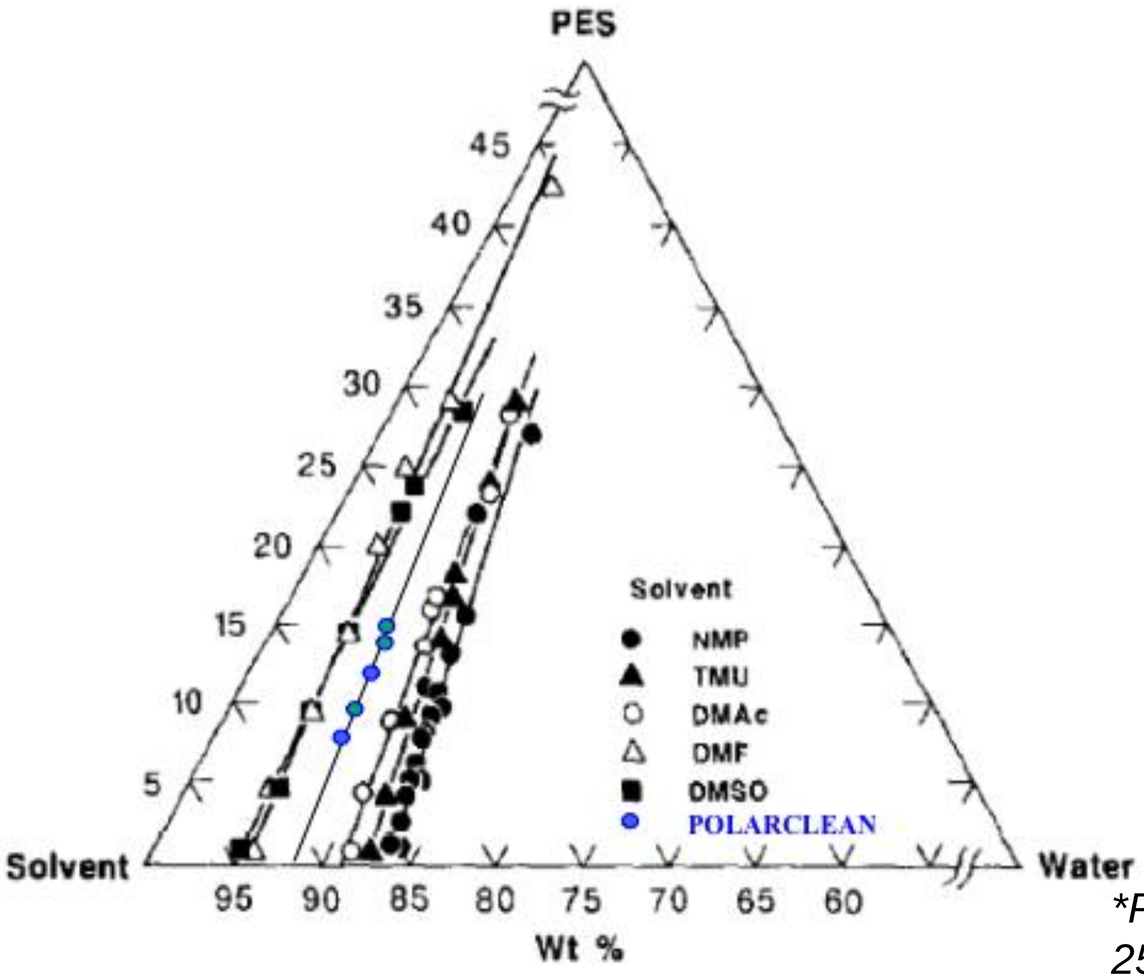
Polarclean presents **solubility parameters** similar to those of the toxic, commonly used DMF, NMP and DMA, and close to PESU, indicating that homogeneous polymeric solutions can be obtained.

Compound	δ_h $(MPa)^{1/2}$	δ_d $(MPa)^{1/2}$	δ_p $(MPa)^{1/2}$	δTotal $(MPa)^{1/2}$
Polarclean	9.2	15.8	10.7	21.2
DMSO	10.2	18.4	16.4	26.7
DMF	11.3	17.4	13.7	24.8
NMP	7.2	18.4	12.3	23
DMAc	11.8	17.8	14.1	22.8
PESU	8.4	19	11.1	23.6

Stability of the obtained clear homogeneous solutions at room temperature was proved by visual examination after 90 days storage, evidencing no phase separation nor crystallization

GOOD SOLVENT CANDIDATE FOR PESU

THERNARY PHASE DIAGRAM



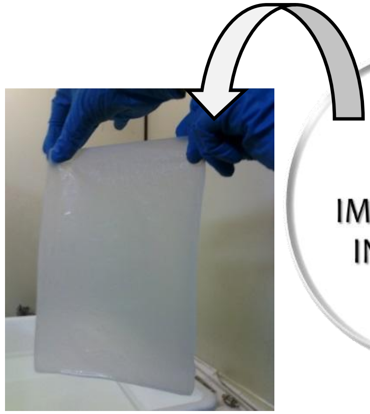
Performed with titration tests at 25°C

Adapted from Wayne W. Y. Lau, Michael D. Cuiver and T. Matsuura, Phase separation in polysulfone/solvent/water and polyethersulfone/solvent/water systems, Journal of Membrane Science, 59 (1991) 219-227.

Sulfone-based polymeric membranes prepared with Polarclean® as water soluble novel solvent

-PESU
-PEG
-2 PVP
-POLARCLEAN®

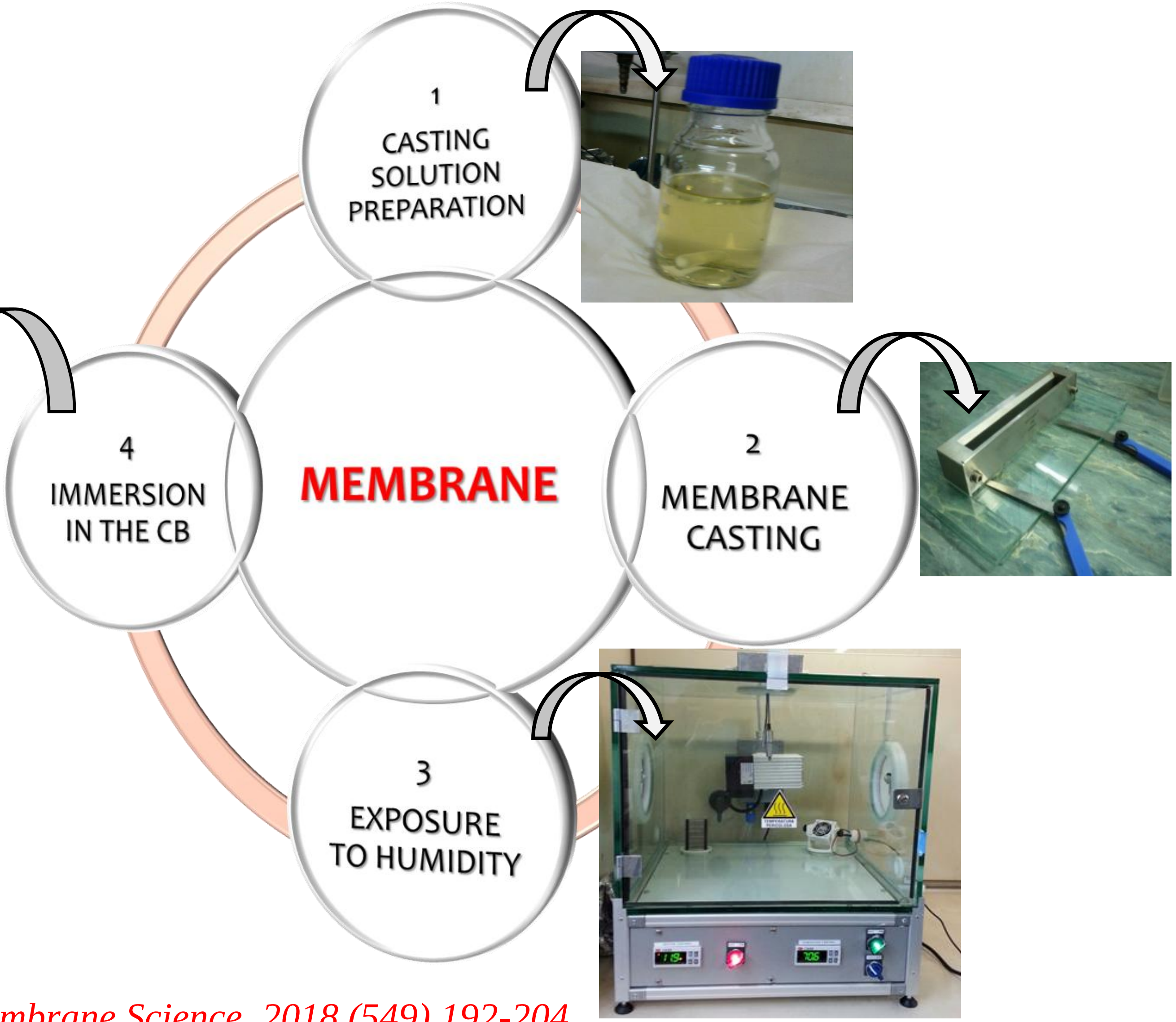
-EXPOSURE TIME TO RH AND T
0-2.5-5-7.5 MINUTES



-CB 100 wt% H_2O

-POST-TREATMENT
CONSECUTIVE WASHING WITH HOT WATER

-DRYING PROCESS



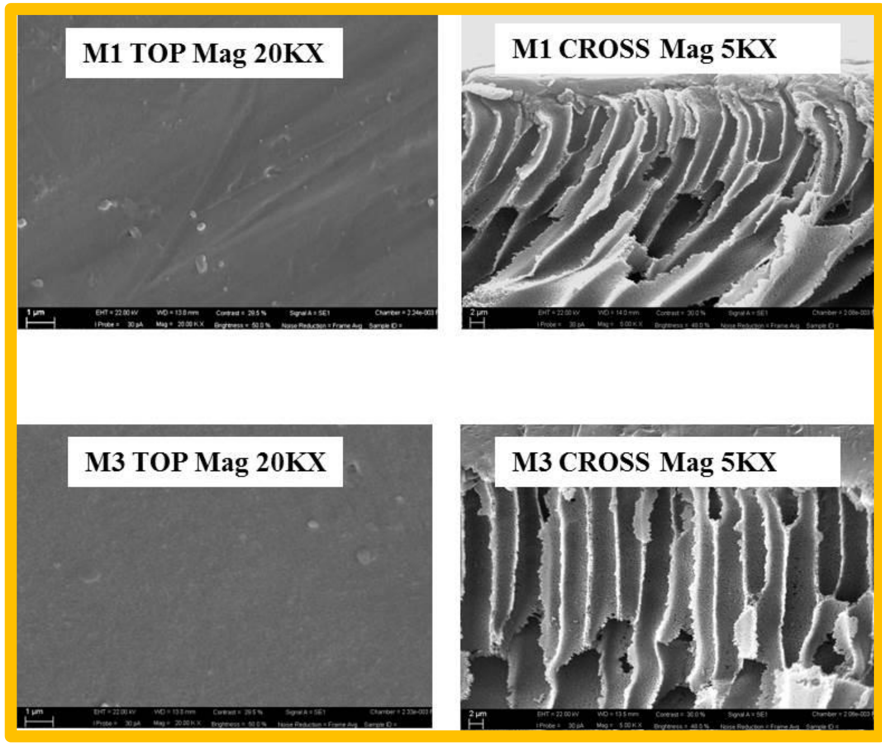
T. Marino, A. Figoli, et al. J Membrane Science, 2018 (549) 192-204

Sulfone-based polymeric membranes prepared with Polarclean® as water soluble novel solvent

Membrane code	PESU	PVP	PEG	Polarclean	Exposure time to RH
	wt%	wt%	wt%	wt%	minutes
M1	10	0	0	90	0.0
M2	10	0	0	90	2.5
M3	10	0	0	90	5.0
M4	10	0	0	90	7.5
M5	10	2	42	46	0.0
M6	10	2	42	46	2.5
M7	10	2	42	46	5.0
M8	10	2	42	46	7.5
M9	10	2	50	38	0.0
M10	10	2	50	38	2.5
M11	10	2	50	38	5.0
M12	10	2	50	38	7.5
M13	8	2	42	48	0.0
M14	8	2	42	48	2.5
M15	8	2	42	48	5.0
M16	8	2	42	48	7.5

Sulfone-based polymeric membranes prepared with Polarclean®
as water soluble novel solvent

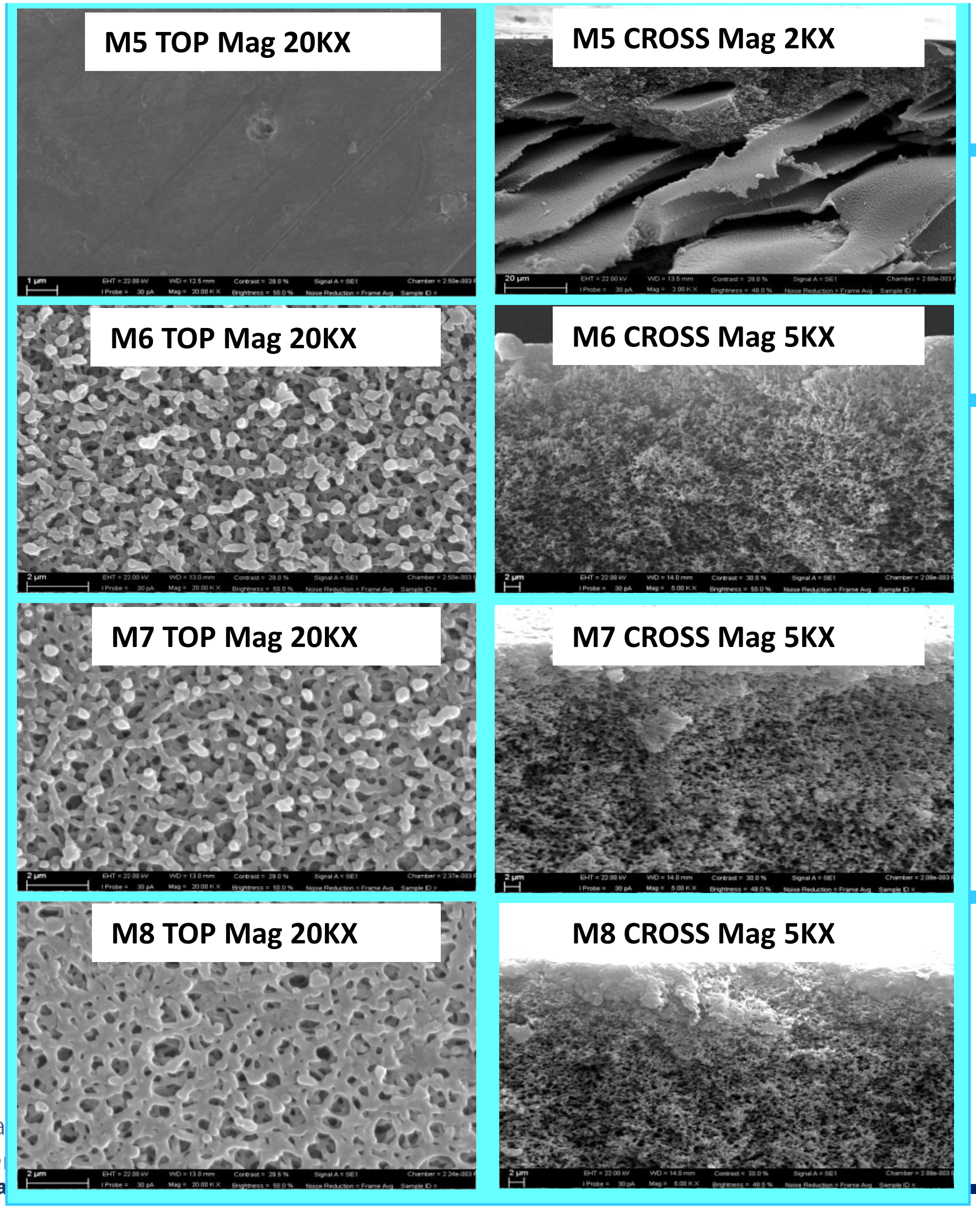
PESU	PVP	PEG	Polarclean
wt%	wt%	wt%	wt%
10	0	0	90



M1: exposure time to humidity 0 minutes
M3: exposure time to humidity 5 minutes

Typical asymmetric structure, with a dense layer on the top surface for the both the membrane types prepared via NIPS and NIPS-VIPS. A finger-like structure is characteristic of the membranes cross section.

Sulfone-based polymeric membranes prepared with Polarclean®
as water soluble novel solvent



PESU	PVP	PEG	Polarclean
wt%	wt%	wt%	wt%
10	2	42	46

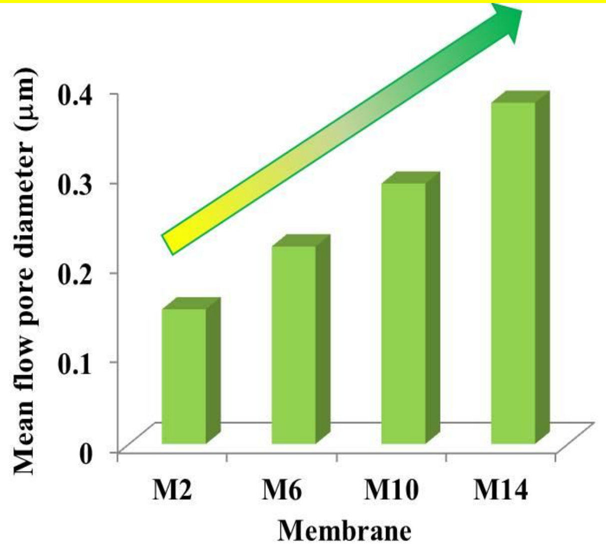
Exposure time to humidity:
M5 0 minutes
M6 2.5 minutes
M7 5 minutes
M8 7.5 minutes

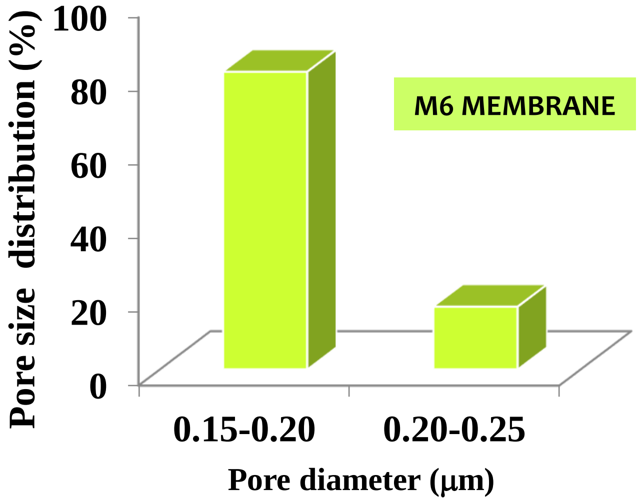
When the membranes were formed via NIPS, the dense layer still was formed on the top surface (M5) and the cross section highlighted a finger-like structure.
By combining the NIPS and the VIPS procedures, the morphology drastically changed from asymmetric finger-like to a mocrovoid-free, homogeneous sponge-like matrix.

Sulfone-based polymeric membranes prepared with Polarclean®

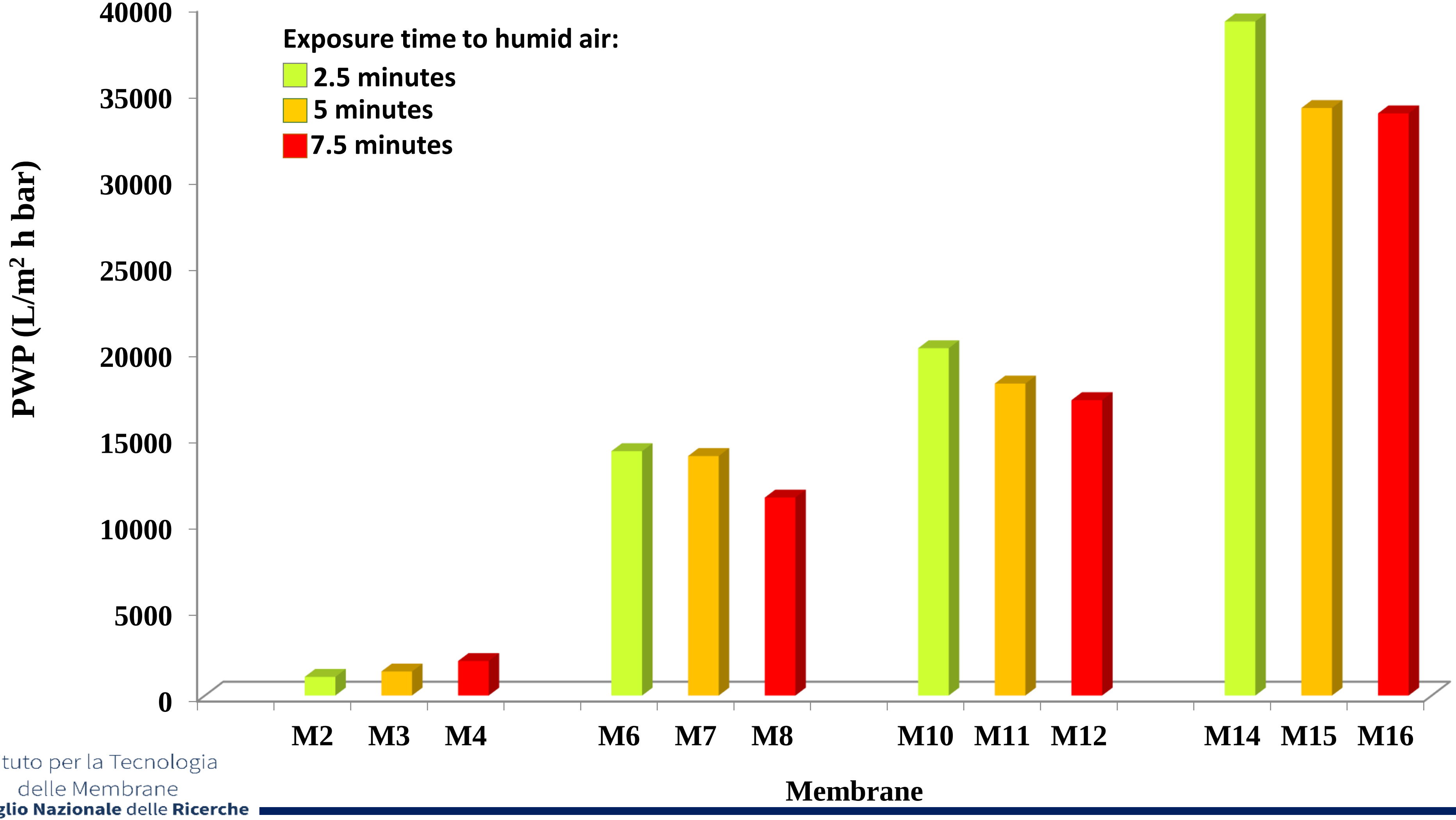
as water soluble novel solvent

Membrane code	SMALLEST PORE SIZE	MEAN FLOW PORE DIAMETER	LARGEST PORE SIZE
	μm	μm	μm
M1	-	-	-
M2	0,09±0,02	**0,15±0,00**	0,43±0,01
M3	0,10±0,00	**0,13±0,01**	0,43±0,01
M4	0,09±0,01	**0,11±0,03**	0,49±0,09
M5	0,05±0,00	**0,08±0,00**	0,29±0,01
M6	0,17±0,00	**0,22±0,05**	0,28±0,00
M7	0,14±0,01	**0,21±0,02**	0,31±0,02
M8	0,18±0,01	**0,19±0,00**	0,28±0,00
M9	0,10±0,00	**0,14±0,01**	0,31±0,01
M10	0.22±0.01	**0.29±0.00**	0.35±0.02
M11	0,14±0,07	**0,27±0,00**	0,30±0,02
M12	0,07±0,01	**0,22±0,03**	0,29±0,00
M13	0,12±0,00	**0,15±0,01**	0,38±0,03
M14	0,30±0,02	**0,38±0,02**	0,45±0,02
M15	0,31±0,04	**0,37±0,03**	0,43±0,01
M16	0,23±0,01	**0,31±0,01**	0,37±0,02

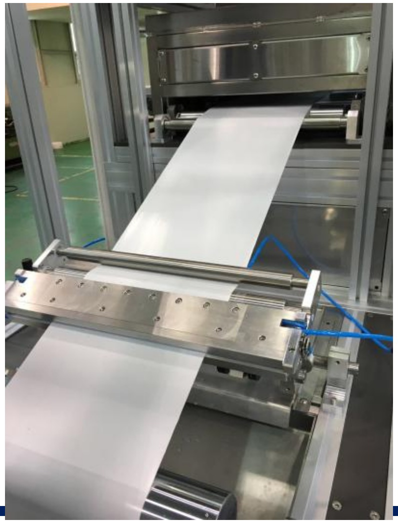




Sulfone-based polymeric membranes prepared with Polarclean® as water soluble novel solvent



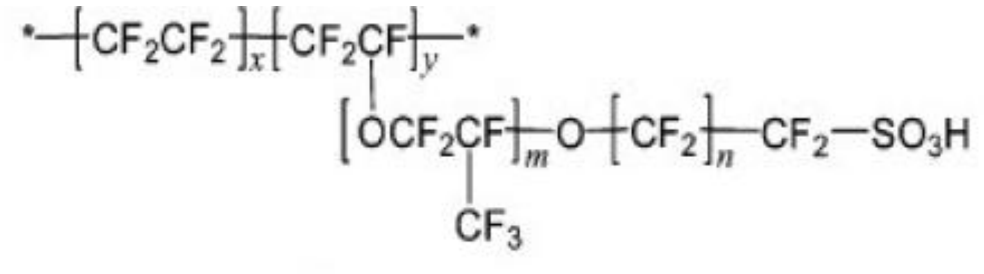
Flat sheet casting machine



✓Production of rolls of MF PES

✓A process which already utilizes non toxic solvents

Perfluorosulfonic acid (FSA) ionomers dominate the market of PEMFC



Nafion®: m=1 n=1 x=5-13.5

Flemion®: m=0,1 n=1-5 x=?

Aciplex®: m=0,3 n=2-5, x=1,5-14

Aquivion®: m=0 n=1 x=3-7

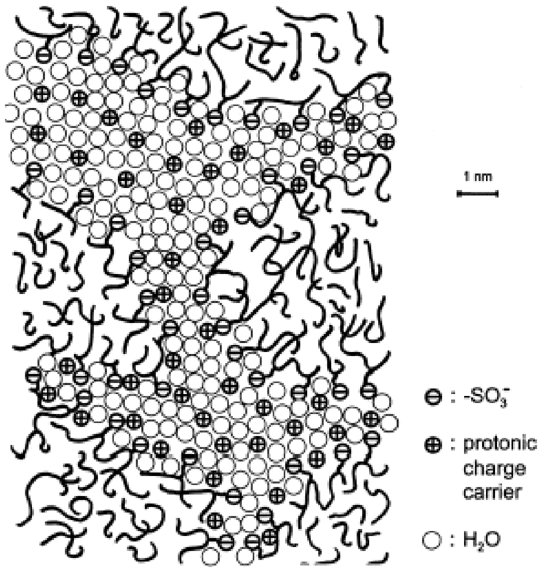
NODES
Nord Ovest Digitale E Sostenibile

Advantages:

- High proton conductivity
- Excellent chemical, mechanical and thermal stability

Disadvantages:

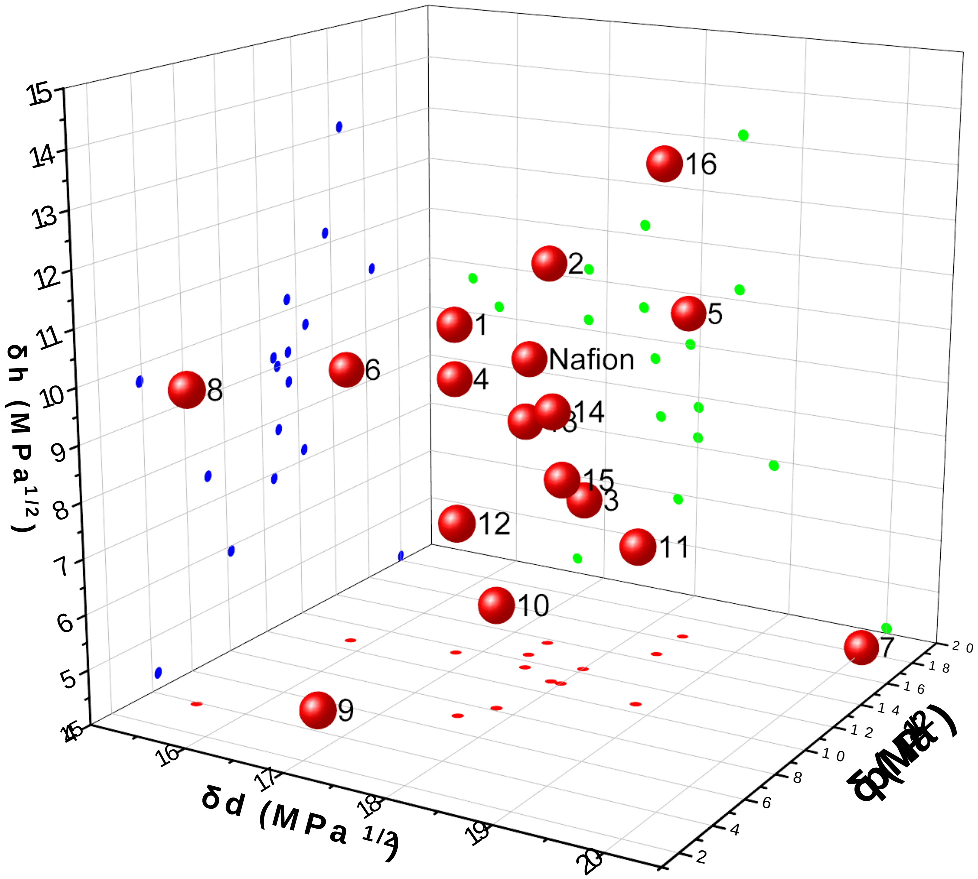
- High cost ; Loss of proton conductivity above 80-90°C because of dehumidification problems
- High hydrogen, water and methanol crossover



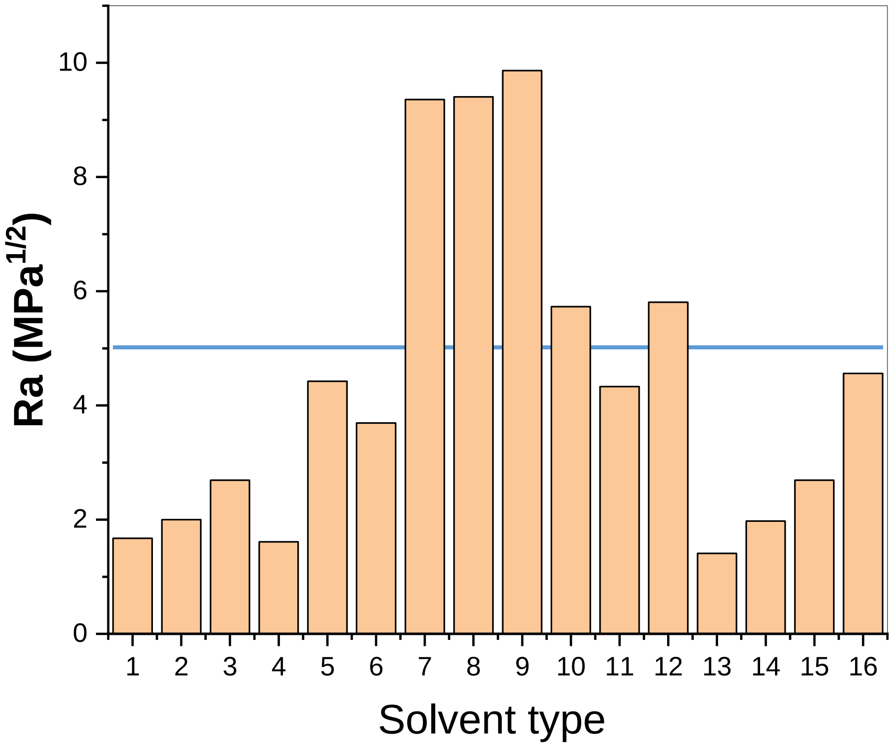
K.D. Kreuer, Journal of Membrane Science 185 (2001) 29–39

Hansen solubility parameters Nafion and solvents

(a)



(b)



(a) Distribution and (b) calculated distance polymer/solvent (R_a) in HSPs space

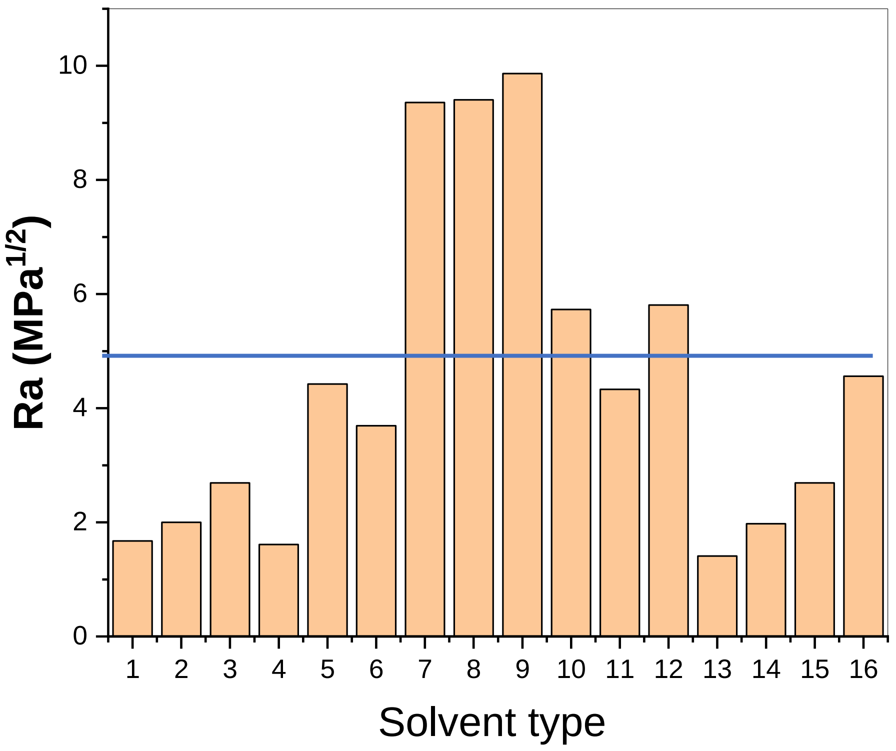
Solvents 1-3: SVHC

Solvents 4-16: solvents with acceptable toxicological and ecological profile, REACH and EPA compliant

NODES
Nord Ovest Digitale E Sostenibile

Hansen solubility parameters
Nafion and solvents

		Calc.	Exp.
1	DMA	Yes	Yes
2	DMF	Yes	Yes
3	NMP	Yes	Yes
4	Synthesized solvents (fossil-based)	Yes	**Yes**
5		Yes	**Yes**
6		Yes	**Yes**
7		No	No
8		No	No
9		No	No
10		No	**Yes**
11	Biosolvents	Yes	No
12		No	No
13	Blend of biosolvents	Yes	**Yes**
14		Yes	**Yes**
15		Yes	**Yes**
16		Yes	**Yes**



Solvents 1-3: SVHC

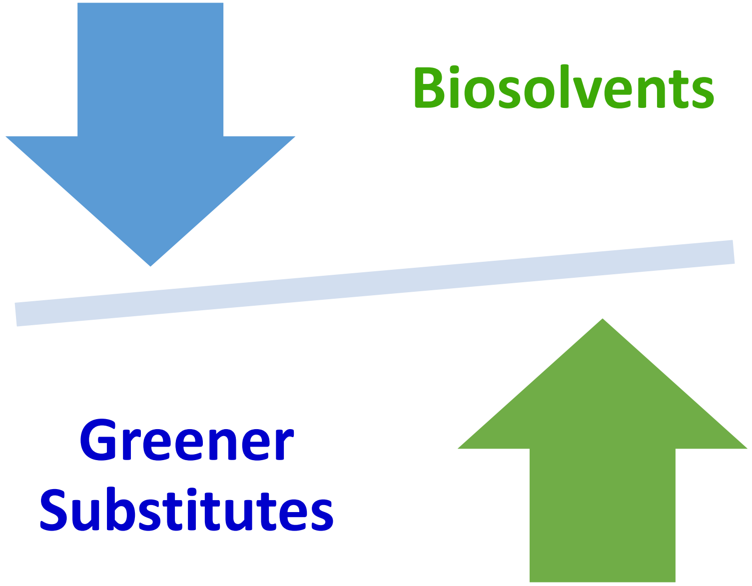
Solvents 4-16: solvents with acceptable toxicological and ecological profile, REACH and EPA compliant

Patent Pending

Hansen solubility parameters Nafion and solvents

#	Type of solvent	Sol. Calc.	Sol. Exp.
1	DMA	Yes	Yes
2	DMF	Yes	Yes
3	NMP	Yes	Yes
4	Synthesized solvents (fossil-based)	Yes	**Yes**
5		Yes	**Yes**
6		Yes	**Yes**
7		No	No
8		No	No
9		No	No
10		No	**Yes**
11	Biosolvents	Yes	No
12		No	No
13	Blend of biosolvents	Yes	**Yes**
14		Yes	**Yes**
15		Yes	**Yes**
16		Yes	**Yes**

NODES
Nord Ovest Digitale E Sostenibile



***Biosolvents** are sourced from renewable, sustainable biobased materials, significantly lowering their environmental impact.*

Patent Pending

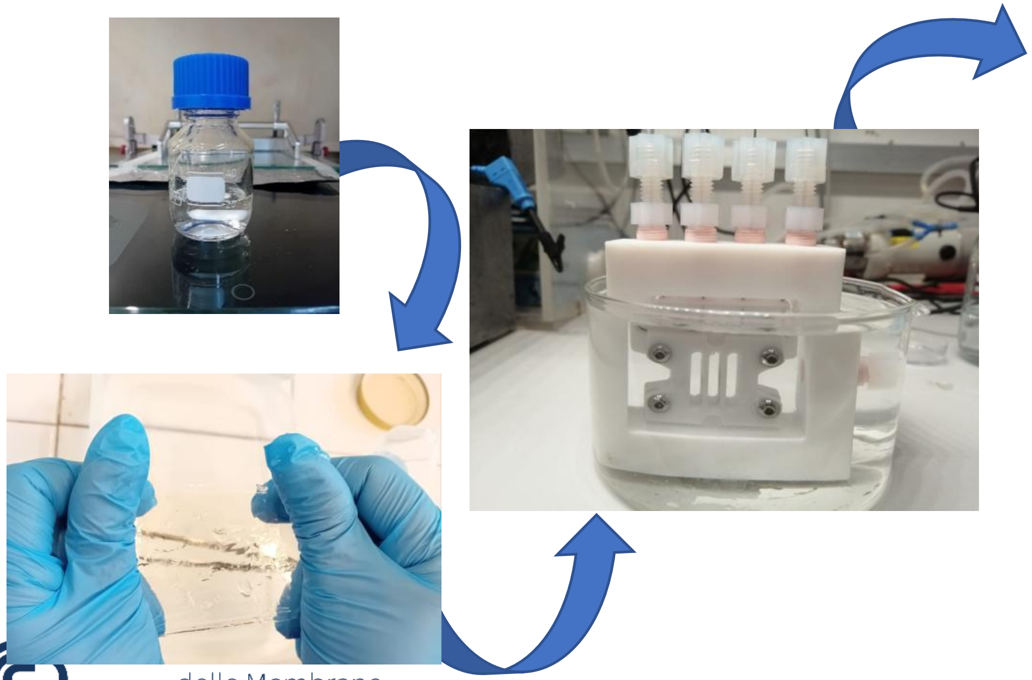
Membrane Preparation

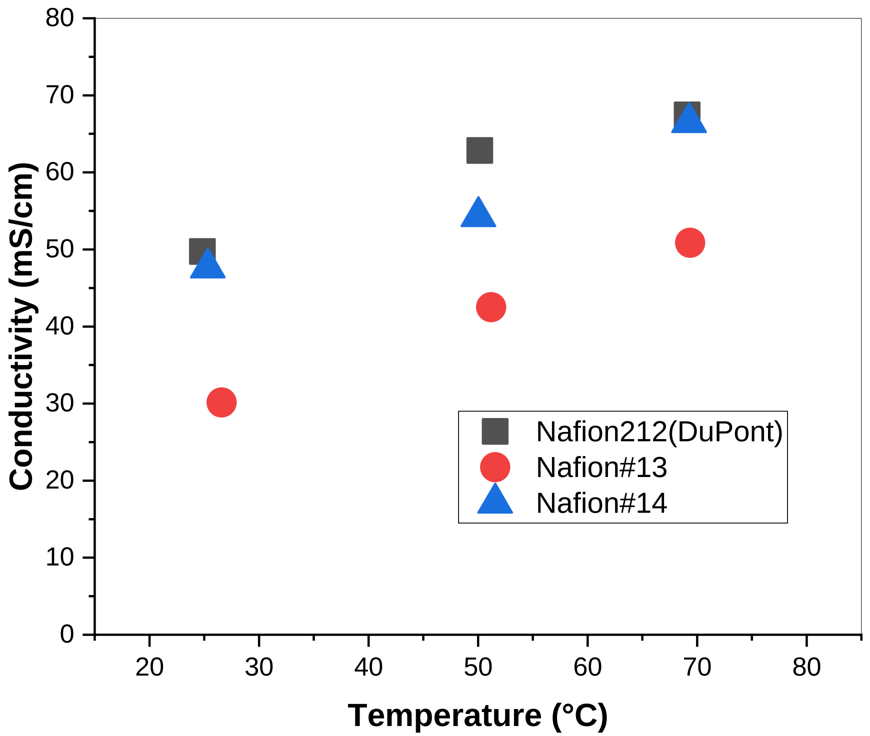
- Polymer solubilization
- Solution casting
- Solvent evaporation
- Thermal treatment
- Membrane activation

Nafion membrane preparation with selected solvents

#	Type of solvent	R_a ($MPa^{1/2}$)	Nafion wt%
13	Blend of biosolvents	1.44	20
14		1.98	15
15		2.69	15
16		4.56	10

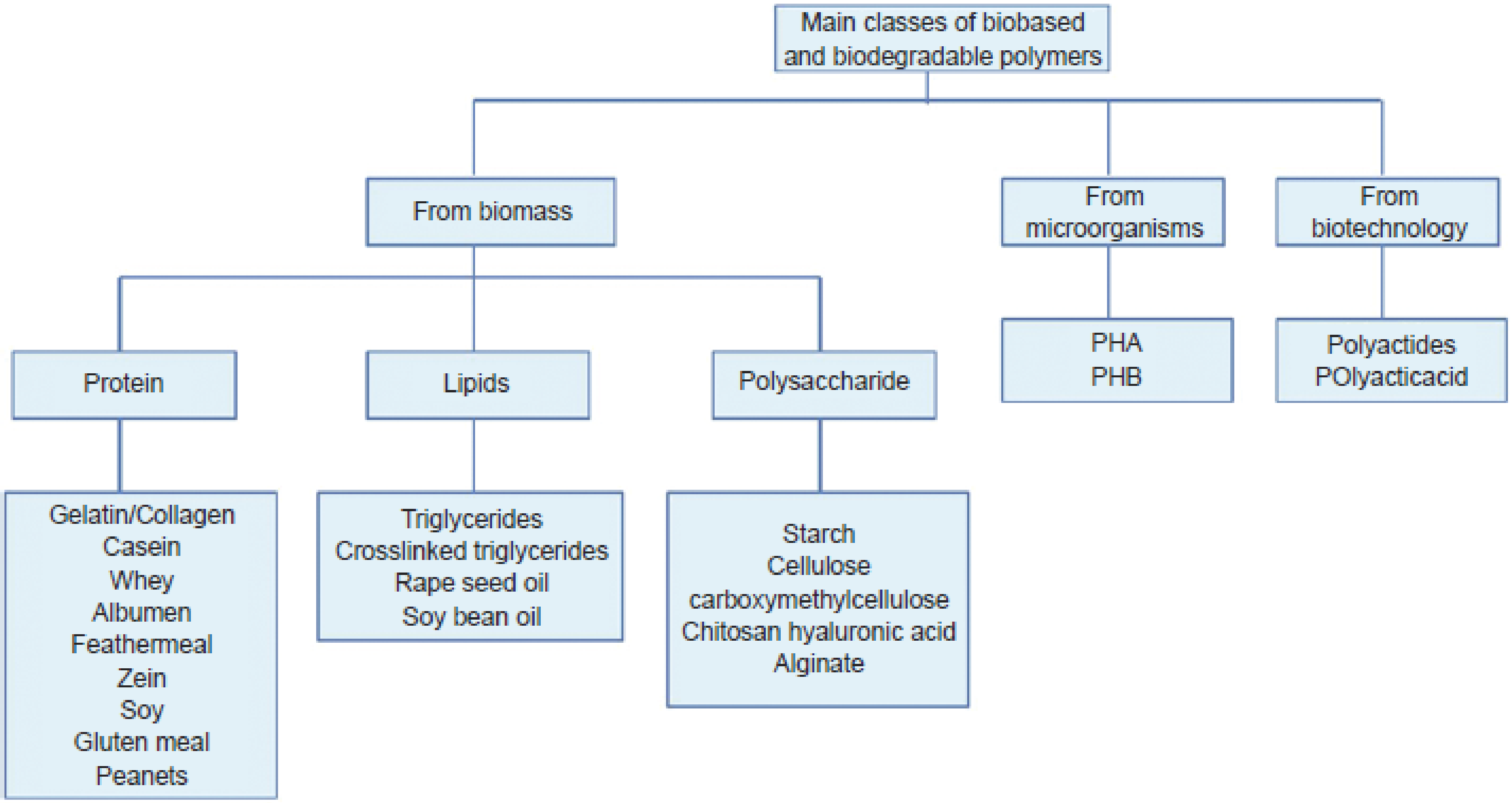
Nafion#14





✓ **Nafion membrane prepared with the green solvents #14 has similar conductivity to Nafion 212 (DuPont) and excellent stability (Elongation at break 62%; E_{breack} 7 Mpa)**

CLASSES OF BIOPOLYMERS



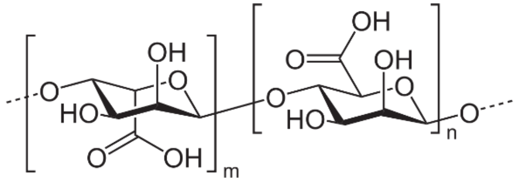
eXPRESS Polymer Letters Vol.8, No.11 (2014) 791–808

CLASSES OF BIOPOLYMERS

Bio-polymers: New trend

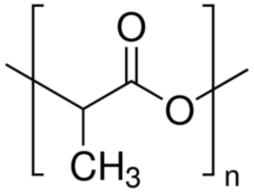
- ✓ Renewable and sustainable industry
- ✓ Biodegradable
- ✓ Biocompostable
- ✓ No-Mugenic
- ✓ No-Carcinogenic
- ✓ Carbon neutral –low environmental footprint

The use of renewable biopolymers and solvents derived from biomass is of great interest for producing membrane in a more sustainable way, according to Green Chemistry design.



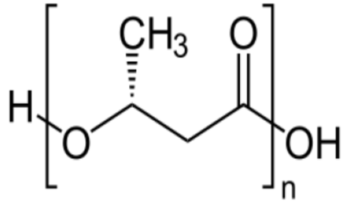
Alginate (Alginate acid)

Polysaccharide derived from brown seaweed



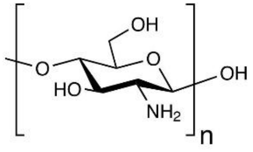
Poly-lactic acid (PLA)

Poly(lactic acid) PLA is a rigid thermoplastic polymer that can be semicrystalline or totally amorphous.



Poly-3-hydroxybutyrate (PHB)

Pruduced by microbial aerobic fermentation

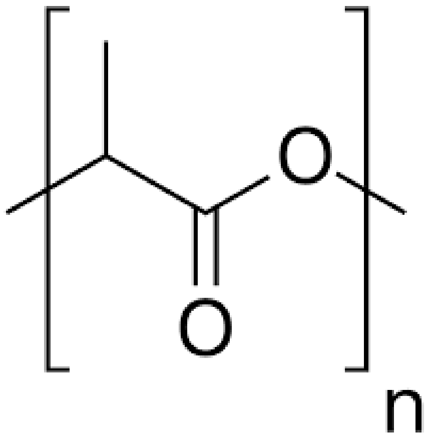


Chitosan

Poly lactic acid (PLA) as a biopolymer

PLA can be obtained from lactic acid in two different ways: by direct **polycondensation of hydroxyl acid** or by **ring opening polymerization of lactide**.

Lactic acid is a chiral molecule existing in L and D form. Depending on the percentage of D-lactide acid, PLA can be highly crystalline (< 2%), semi-crystalline (2-20%) or amorphous (>20%).



renewable source

reduce carbon foot print

high thermodinamic performance

The physical and mechanical properties of PLA

Properties	
Polymer density (g/cm3)	1.21–1.30
Tensile strength (MPa)	15.5–150
Tensile modulus (GPa)	2.7–16
Ultimate strain (%)	2–10
Specific tensile strength (Nm/g)	16.8–66.8
Specific tensile strength (Nm/g)	16.8–66.8
Specific tensile modulus (kNm/g)	0.28–3.85
Melting temperature (◦C)	130–180
Glass transition temperature (◦C)	**50–65**

*Russo et al., Fuel Processing Technology 213 (2021) 106643.

Case Study: Poly lactic acid (PLA) membrane for gas separation

Poly lactic acid (PLA) as a biopolymer

PLA is a biodegradable polyester that can be chemical synthesized from renewable resources such as corn or sugarcane increasing its strength and reducing the dependence on fossil fuels.

It can be used in many end-user industries due to its versatile characteristics such as:

PROCESSABILITY
RENEWABILITY
ENERGY SAVING
BIOCOMPATIBILITY.

The polymer possesses thermal properties that are greater than other bio-based materials; therefore,

PLA can be processed by injection molding, fiber spinning, extrusion, film casting, and blow molding.

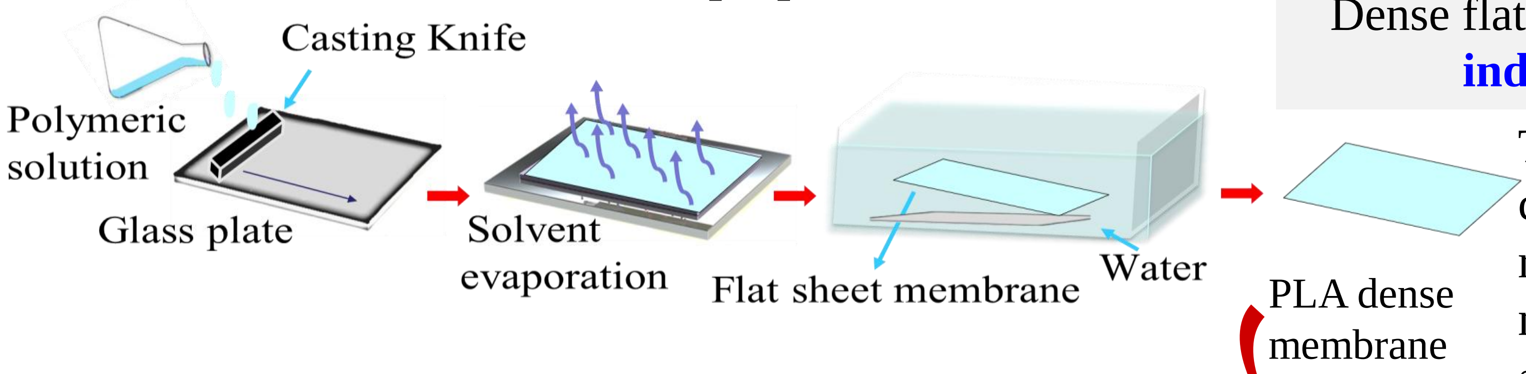
The leading vendors in the market are:

- BASF
- Corbion
- NatureWorks
- Synbra Technology

*Russo et al., Fuel Processing Technology 213 (2021) 106643.

Case Study: Poly lactic acid (PLA) membrane for gas separation

PLA dense membrane preparation

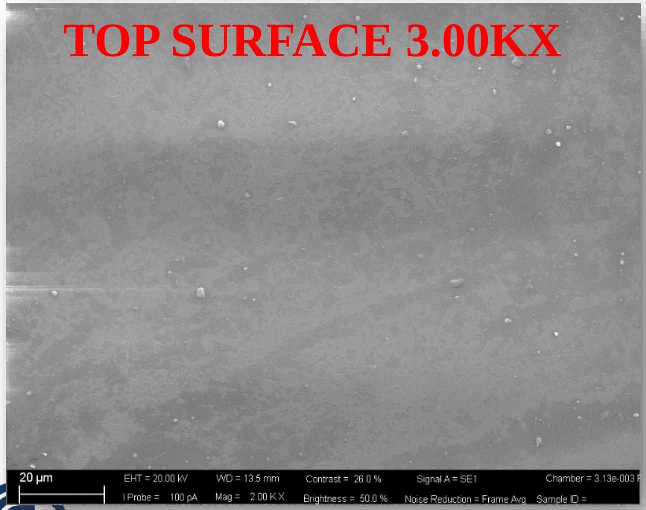


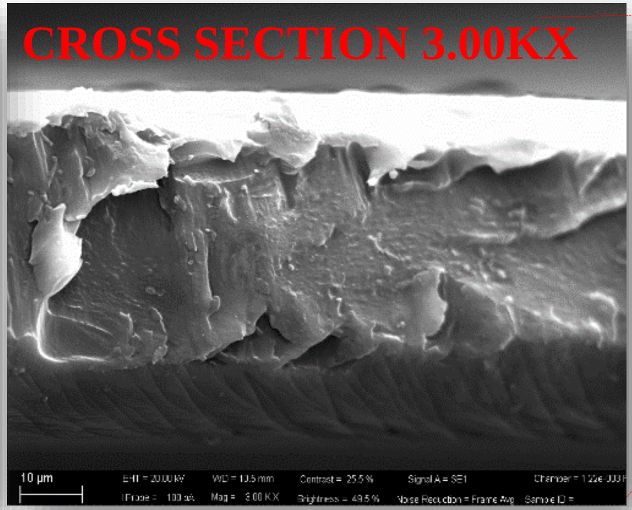
Dense flat-sheet membranes were prepared by **evaporation induced phase separation (EIPS)** technique.

The dope solution was cast on a glass plate using a casting knife set with a thickness of ~ 250 µm and relative humidity around 40%. Successively, all the membrane samples were firstly air exposed at 25 ◦C for 4 h to induce the evaporation of the **DMI.**

PLA dense membrane characterization

SEM analysis illustrates the cross section and top surface of the membrane, confirming its symmetrical structure.





PLA membrane

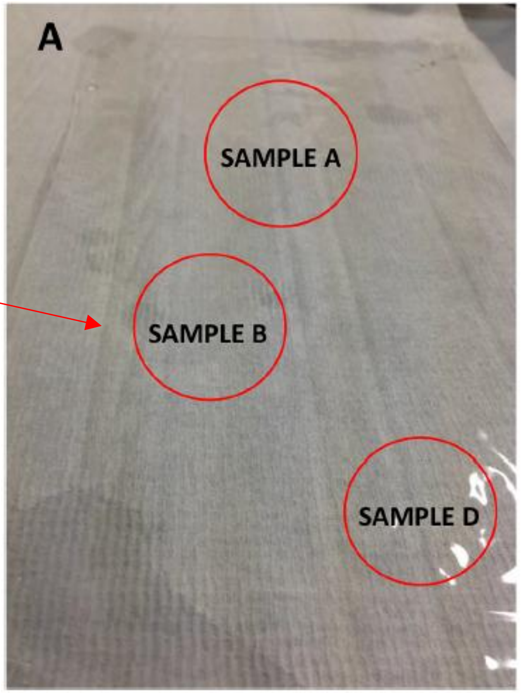
*Iulianelli et al., International Journal of Greenhouse Gas Control 117 (2022) 103657; Iulianelli et al., Greenhouse Gas Sci Technol. 9: (2019) 360–369.

Case Study: Poly lactic acid (PLA) membrane for gas separation

PLA dense membrane preparation

The PLA polymer (Nature Green 2100D - D% co-monomer of up to 1.47 _ 0.2%; highly crystalline) used in this work was was provided by NatureWorks by Cargill Dow (Minnetonka, MN, US).

NatureWorks



List of membranes

Membrane	Sample	Thickness [μm]	Permeation tests
PLA-17331	A	26	+++
	B	26	+
	C	24	*
PLA-17427	A	26	+++
	B	24	*
PLA-17613	A	28	+++
	B	28	+++
	C	23	*
	D	28	+++
PLA-17720	A	23	*
	B	23	*
PLA-17730	A	23	*
	B	26	+
	C	23	*
PLA-17807	A	23	*
	B	23	*
	C	23	*
PLA-17929	A	26	+++

+++ = experimental tests valid and reproduced
\+ = experimental data non-valid due to the membrane failure under testing
* = membrane broken

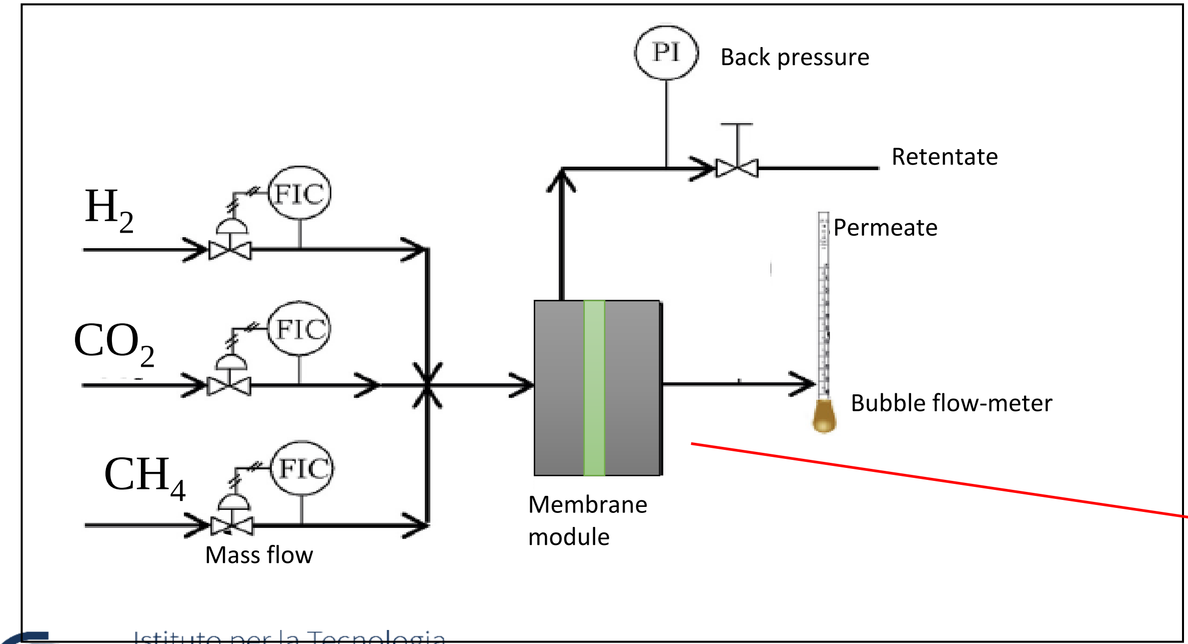
Case Study: Poly lactic acid (PLA) membrane for gas separation

Gas permeation tests

For each PLA membrane sheet, various membrane samples were selected in order to be tested under single gas permeation tests with the scope of ensuring the reproducibility of the experimental results in terms of **gas permeating flux**, **permeability** and **ideal gas selectivity.**

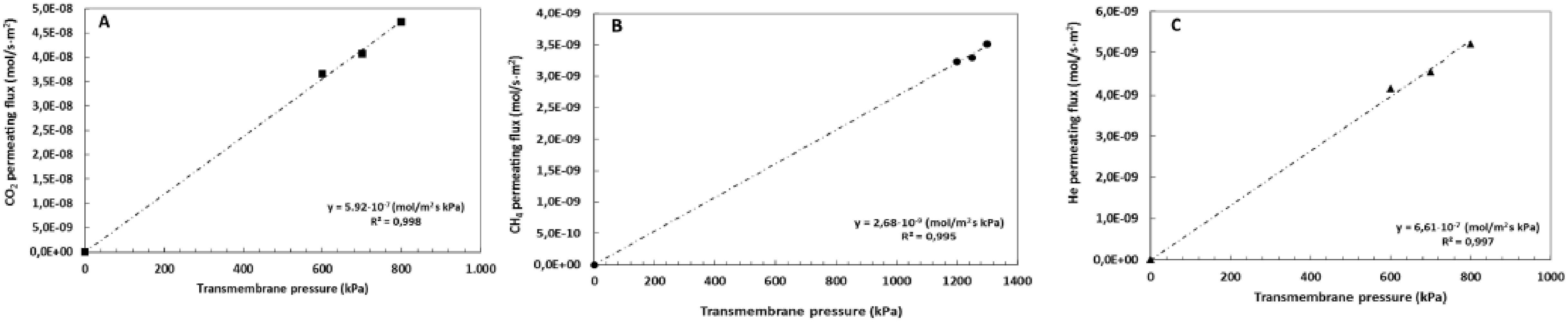
Single-gas (**H_2, He, CO_2 and CH_4**) permeation tests were performed on various membrane samples using a cell (inner diameter 4.0 cm).

Each single gas was supplied by means of mass flow controllers controlled by software. The **transmembrane pressure** between feed and permeate sides was varied in the range **100–1200 kPa** by means of a back pressure controller, placed on the retentate side.



*Iulianelli et al., International Journal of Greenhouse Gas Control 117 (2022) 103657; Iulianelli et al., Greenhouse Gas Sci Technol. 9: (2019) 360–369.

Gas permeation properties in terms of single gas permeating flux

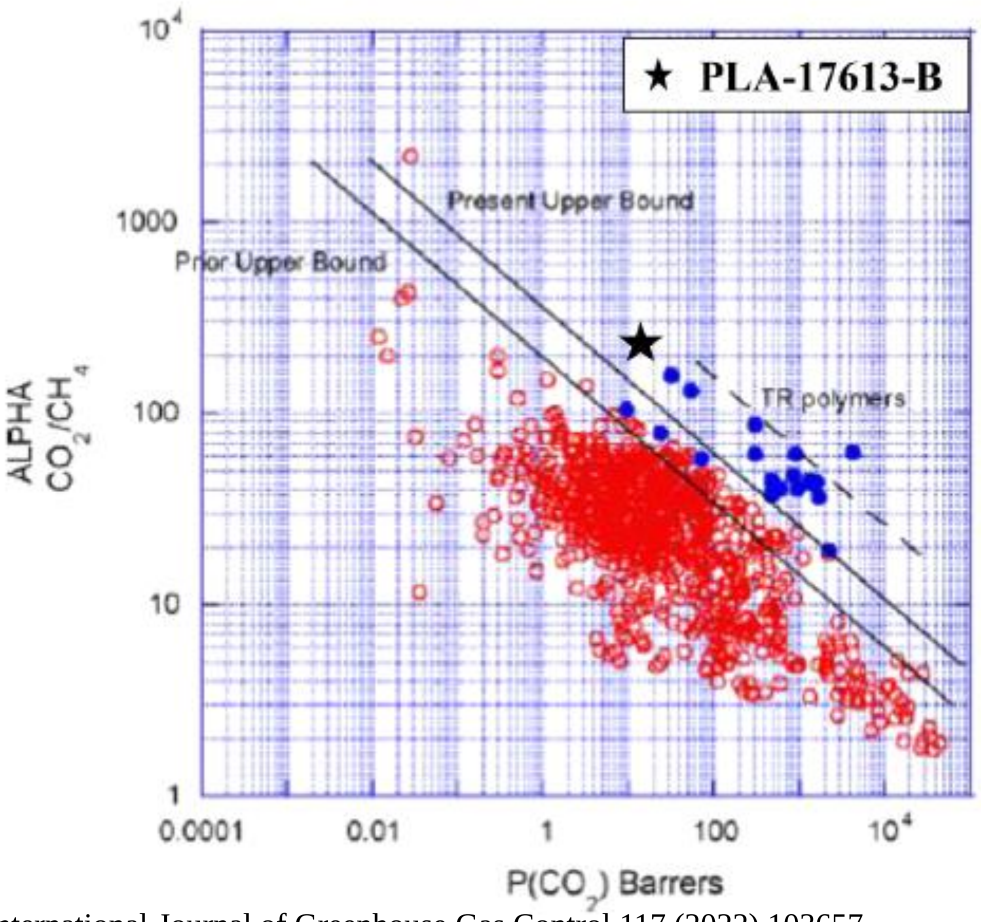


Membrane	T of the residual solvent evaporation [°C]	δ(μm)	$P(CO_2)$ [Barrer]	$P(CH_4)$ [Barrer]	P(He) [Barrer]	Ideal selectivity (-)		
						$\alpha_{(CO2/CH4)}$	$\alpha_{(He/CH4)}$	$\alpha_{(He/CO2)}$
PLA-17331	40	26	11.58	0.05	14.83	231	296	1.28
PLA-17427	40	26	13.38	0.06	12.32	223	205	0.85
PLA-17613-A	30	28	11.46	0.05	15.84	229	316	1.40
PLA-17929	30	26	11.30	0.05	14.95	226	299	1.32

*Iulianelli et al., International Journal of Greenhouse Gas Control 117 (2022) 103657

Gas permeation properties

Ideal CO2/CH4 selectivity vs CO2 permeability Robeson's upper-bound and PLA membrane result (PLA-17613-B)



*Iulianelli et al., International Journal of Greenhouse Gas Control 117 (2022) 103657

Conclusions

- Many efforts have been carried out in order to make the membrane fabrication process **greener** by **replacing the traditional toxic solvents with greener alternative**

- In the selection of the fabrication method, an important aspect is the **interaction between the polymers and greener solvents**. **Hansen solubility parameters** make it possible to understand the dissolution mechanism and the affinity between the polymer and the solvents

- A series of green solvents (e.g. Cyrene, DMI) have been already identified and **successfully applied for the preparation of membranes** employing the most common polymers (PES and PVDF)

- The replacement of toxic diluents with safer alternatives, together with the use of **biodegradable polymers** (e.g. PLA, PHA) that are not oil-derived, will strongly contribute to the development of green membrane production. A case study showing the potentiality of PLA in gas separation is an example

MEASURED

MEMBRANE SCALE-UP FOR CHEMICAL INDUSTRIES

WP3: Membranes development and Scale-up

Task 3.1: Development of polymeric membranes for MD

Funded by the European Union

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4th International Workshop on Membrane Distillation and Innovating Membrane Operations in Desalination and Water Reuse

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THANK YOU!