



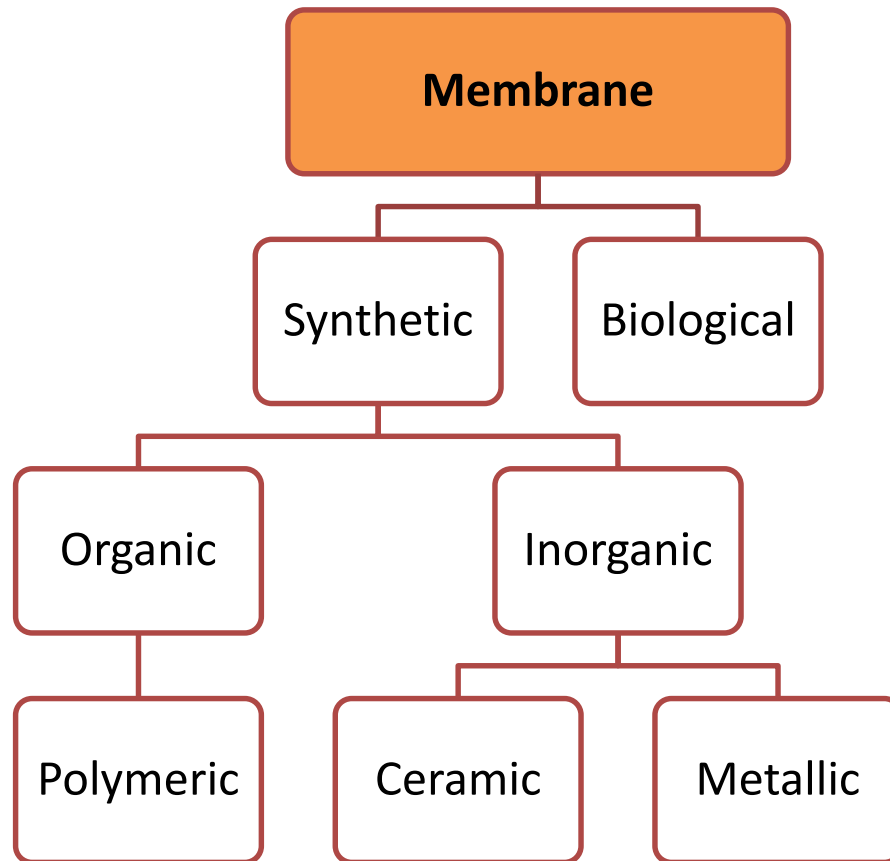
MEMBRANE TECHNOLOGY

MEMBRANE PREPARATION

ASEP MUHAMAD SAMSUDIN, S.T.,M.T.



Membrane Material



Membrane Material

Polymer (organic) >>>> Inorganic

- (i) many different types of polymeric material are commercially available,
- (ii) a large variety of different selective barriers, i.e., porous, nonporous, charged and affinity, can be prepared by versatile methods,
- (iii) production of large membrane area with consistent quality is possible in technical scale at reasonable cost based on reliable manufacturing processes, and
- (iv) various membrane shapes (flat sheet, hollow-fiber, capillary, tubular, capsule;) and formats including membrane modules with high packing density can be produced

A very well defined regular pore structure is difficult to be achieved, and the mechanical strength, the thermal stability and the chemical resistance (e.g., at extreme pH values or in organic solvents) are rather low for many organic polymers.

Polymer selection for porous barriers

1. **Film forming properties** indicate the ability of a polymer to form a cohesive film. Especially molar mass and attractive interactions between chain segments, is crucial in this regard. Poly(ether sulfones) (PES), polysulfones (PSf), polyamides (PA) or polyimides (PI) are examples for excellent film-forming materials.
2. **Mechanical properties** involve film strength, film flexibility and compaction stability. Hollow fiber membranes are self-supporting, the mechanical stability will be especially relevant. Many commercial flat-sheet membranes are prepared on a non-woven support material.
3. **Thermal stability** requirements depend very much on the application. In order to ensure the integrity of a pore structure in the nanometer dimension, the T_g of the polymer should be higher than the process temperature.

Polymer selection for porous barriers

4. ***Chemical stability*** requirements include the resistance of the polymer at extreme pH values and other chemical conditions. Cleaning agents such as strong acids or bases, or oxidation agents are usually used to clean a fouled membrane.
5. ***Hydrophilicity – hydrophobicity balance*** correlates with the wettability of the material. This can be important in order to use all pores in UF, or when a porous membrane is applied as a contactor between a liquid and a gas phase, and the phase boundary is stabilized because the liquid will not wet the dry pores of the membrane.

Polymer selection for non-porous barriers

1. **Glassy or rubbery state of the polymer.** Thermal analysis to know the T_g value is essential. The state of the non-porous polymer will determine the available free volume and the segmental mobility, and those have decisive influence on the diffusion of molecules through the polymer. Size-based diffusion selectivity will only be possible with polymers in the rigid amorphous state.
2. **Free volume** will depend on the interchain distance in the bulk of the polymer. Somewhat independent of the state (cf. above), pronounced rigidity of the main chain and very bulky side groups can lead to larger free volume and, consequently, high permeability.
3. **Hydrophilicity – hydrophobicity balance** or other more special affinities can lead to (selective) dissolution (sorption) of molecules in the membrane. When the membrane is in contact with a liquid feed, swelling can become quite large, and this effect is often dominant for selectivity
4. **Chemical stability** requirements are similar to those for porous materials. Cleaning-related instability against active chlorine is a special problem for PA-based TFC membranes for RO. Due to the increasing number of non-aqueous applications (especially in PV and NF), polymer resistance to various organic solvents is gaining particular importance.



EXAMPLES FOR MEMBRANE MATERIAL

Polysulfone (PSf) and Polyethersulfone (PES)

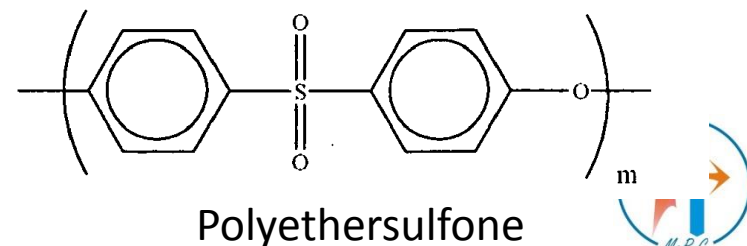
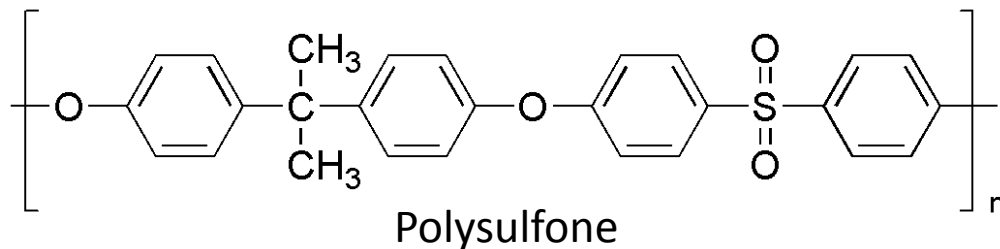
PS and PES membrane are widely used in MF and UF preparation also for support in NF and RO.

Advantages

1. High thermal stability (T_g PSf = 198 °C and T_g PES = 225 °C).
2. Wide pH tolerance (pH = 2-13).
3. Fairly good chlorine resistance.
4. Easy to fabricate membranes in a wide variety of configurations.
5. PSf and PES have a flux / high permeability

Disadvantages

1. Low pressure limit (typically 100 psig/7 atm with flat sheet membrane and 25 psig/1.7 atm with hollow fibers)
2. Hydrofobic



Cellulose acetate (CA)

CA is prepared from cellulose by acetylation, i.e., reaction with acetic anhydride, acetic acid and sulfuric acid.

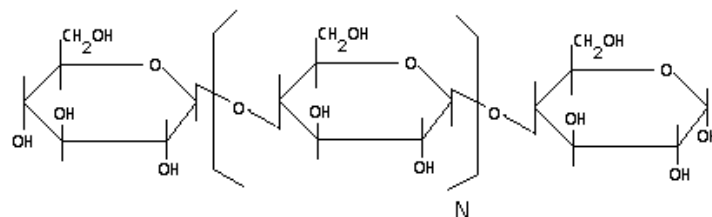
Advantages

1. Hydrophilic
2. CA membranes are relatively easy to manufacture
3. The raw material is a renewable resource
4. CA can be prepared into a membrane with a pore size range varies from MF to RO

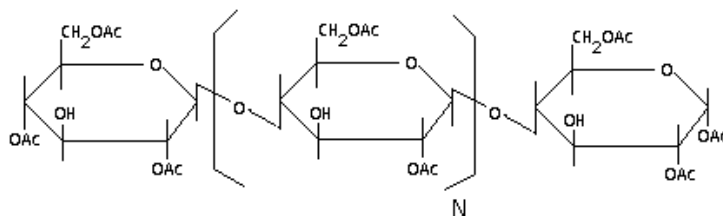
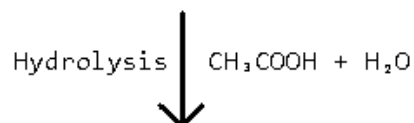
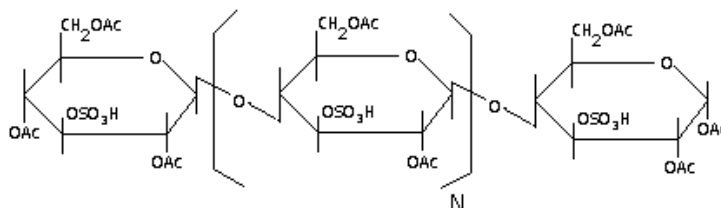
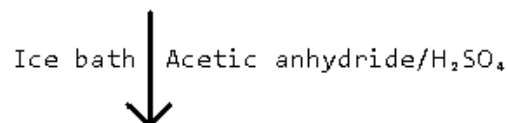
Disadvantages

1. A fairly narrow temperature range ($T_g = 198\text{ }^{\circ}\text{C}$).
2. A rather narrow pH range (3-7).
3. Poor resistance in chlorine.
4. CA is highly biodegradable.

Cellulose acetate (CA)



Cellulose



Cellulose acetate

Cellulose acetate preparation reaction from selulose

Polyamide (PA)

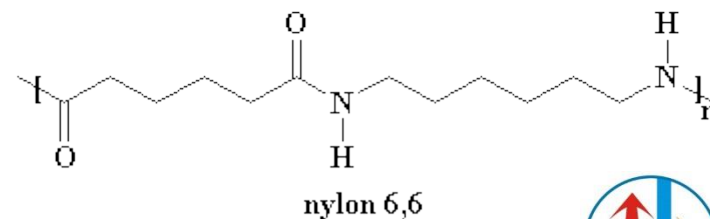
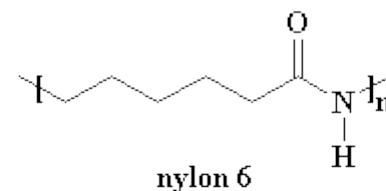
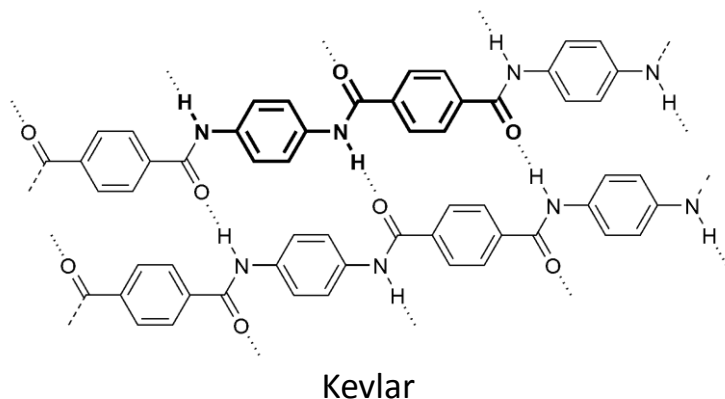
- PA is characterized by having an amide bond in structure (-CONH-).
- Polyamide can be divided into three groups, i.e. aliphatic polyamide [e.g. PA 6 (Nylon-6), PA 66 (Nylon-66)], semi-aromatic polyamides [e.g. PA 6T], aromatic polyamides [e.g. paraphenylenediamine + terephthalic acid, Kevlar]

Advantages

1. Have a wider pH and temperature range than CA.
2. Hydrophilic.

Disadvantages

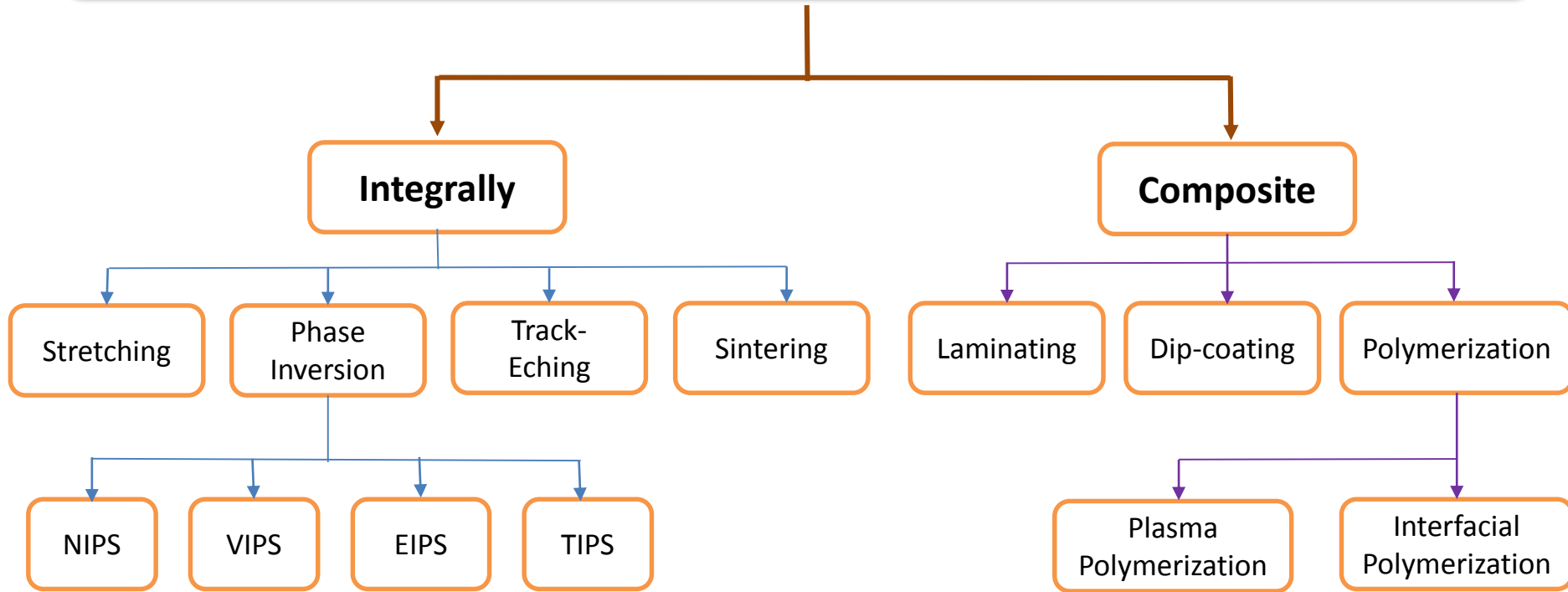
Poor resistance in chlorine.





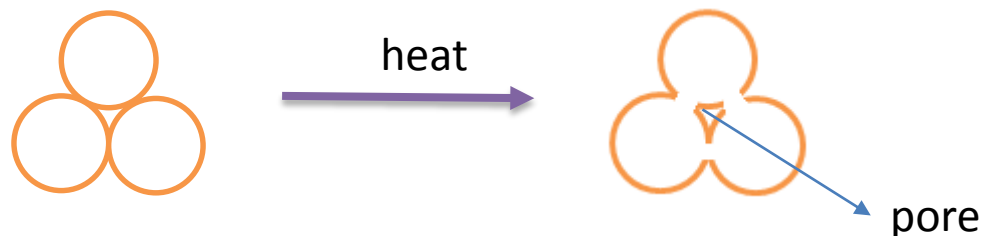
MEMBRANE PREPARATION

Membrane Preparation

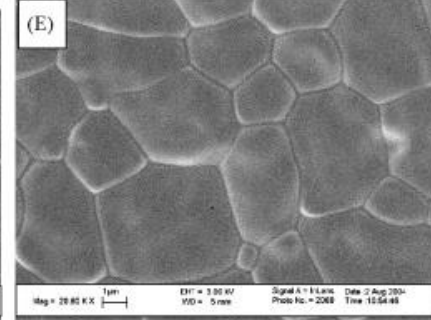
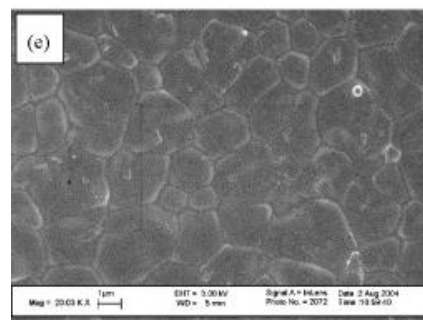
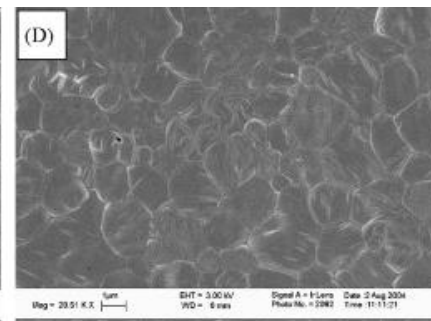
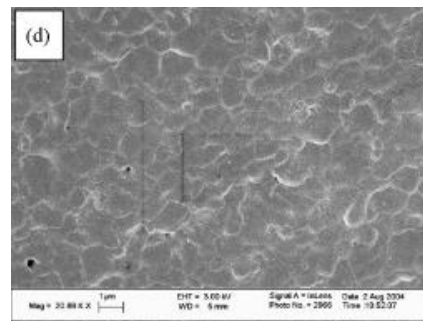
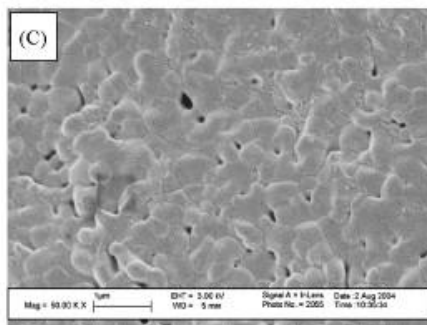
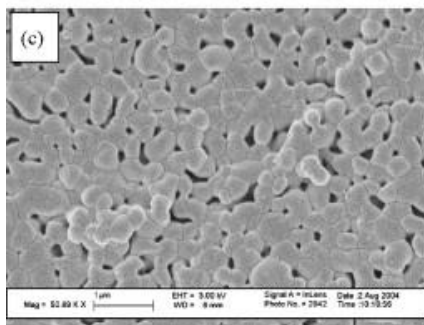
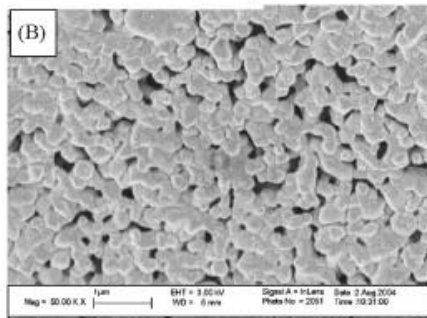
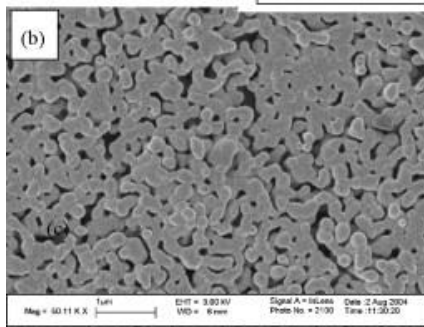
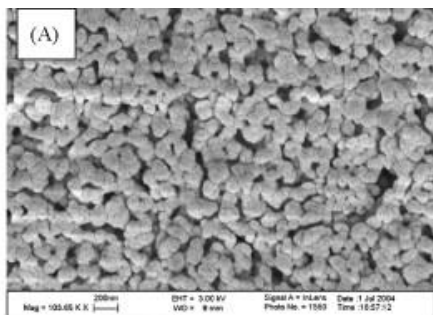


SINTERING

- Simple technique allowing porous membrane to be obtained from organic as well as from inorganic materials
- The method involves compressing a powder consisting of particles of a given size and sintering at elevated temperatures.
- The required temperature depends on the material used.
- A wide range of different materials can be used such as powders of polymers (polyethylene, polytetrafluoroethylene, polypropylene), metals (stainless steel, tungsten), ceramics (aluminium oxide, zirconium oxide), graphite (carbon) and glass (silicates).
- The pore size of resulting membrane (0.1-10 μ m) is determined by the particle size and particle distribution.
- The porosity of porous polymeric membrane is generally low (10-20 %)
- Only microfiltration membrane can be prepared by this technique.



SINTERING

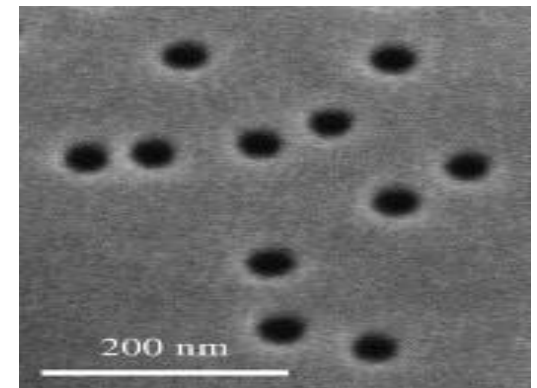
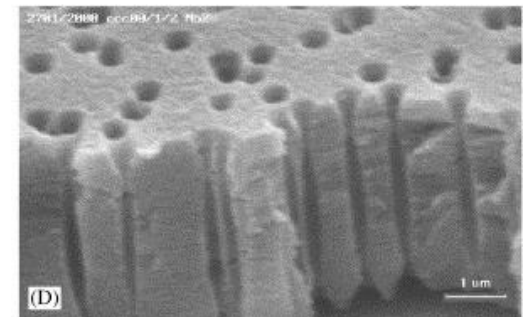
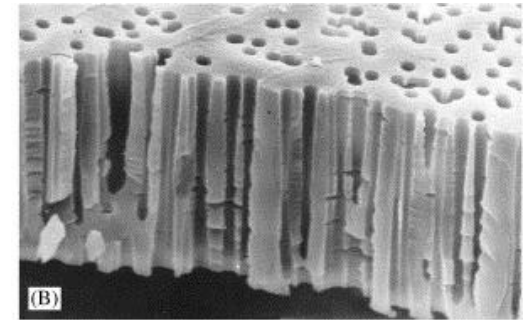
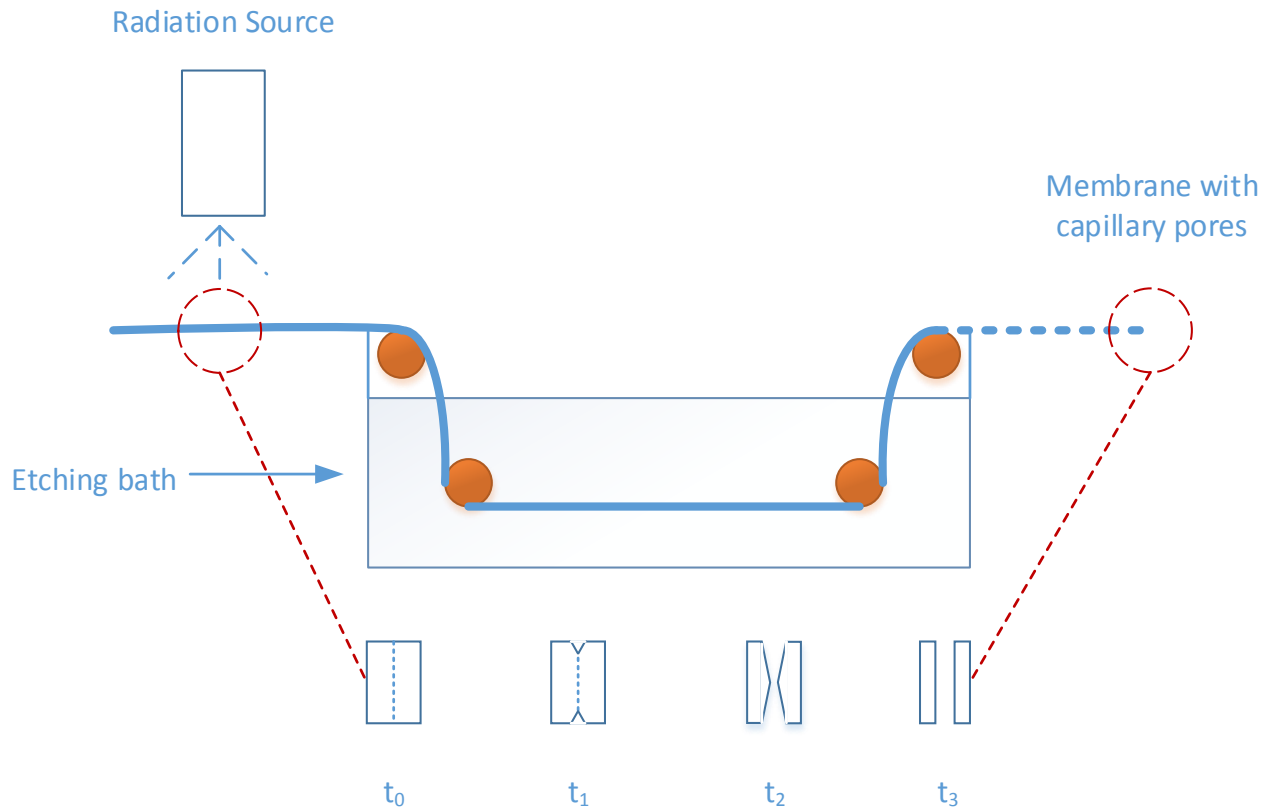


Surface morphology of the **Yttria-stabilised zirconia (YSZ)** membranes prepared using S1 and sintered at different temperatures for 4 h (b–e) and 8 h (A–E), respectively; (A): 1000 °C, (b–B): 1200 °C, (c–C): 1300 °C, (d–D): 1400 °C and (e–E) 1500 °C.

TRACK ETCHING

- Membranes with very regular pores of sizes from 0.02 to 10 μm can be prepared by track-etching.
- A relatively thin ($< 35 \mu\text{m}$) polymer film (typically from poly(ethylene terephthalate) or aromatic polycarbonate) is first bombarded with fission particles from a high energy source. These particles pass through the film, breaking polymer chains and creating damaged “tracks”.
- Thereafter, the film is immersed in an etching bath (strong acid or alkaline), so that the film is preferentially etched along the tracks, thereby forming pores.
- The porosity is determined by radiation intensity and the pore size is determined by etching time.
- The advantage of this technique is that uniform and cylindrical pores with very narrow pore size distribution can be achieved.
- In order to avoid the formation of double or multiple pores, produced when two nuclear tracks are too close together, the membrane porosity is usually kept relatively low, i.e., typically less than 10%.

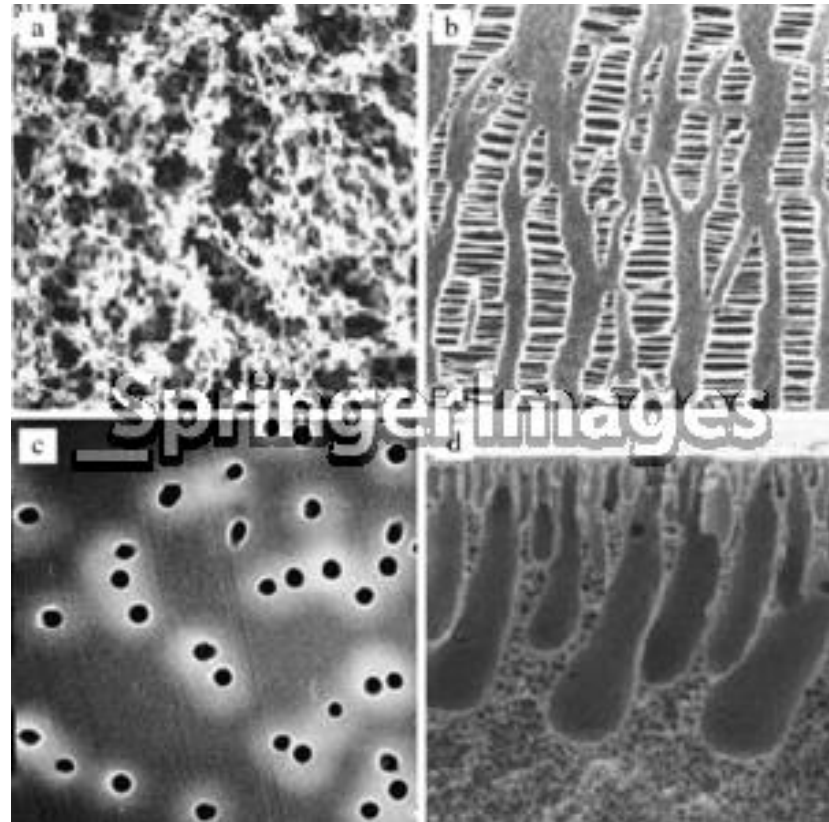
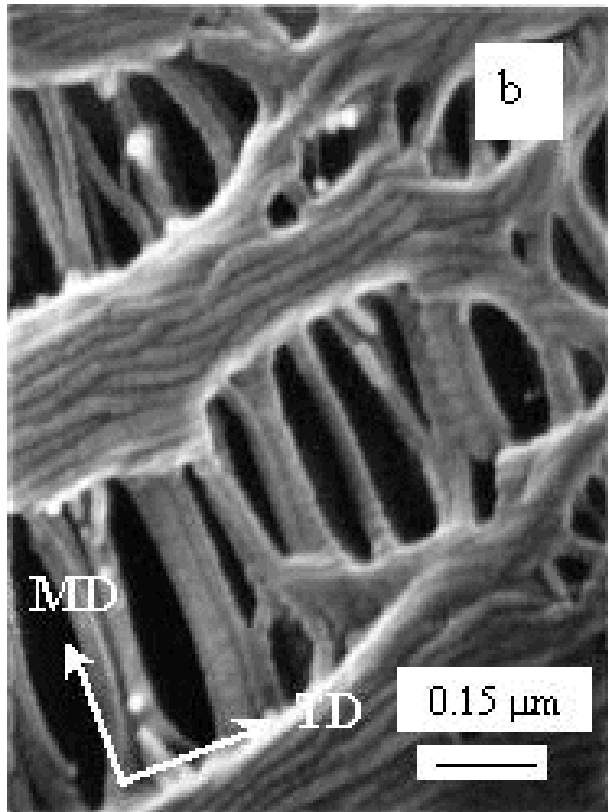
TRACK ETCHING



STRETCHING

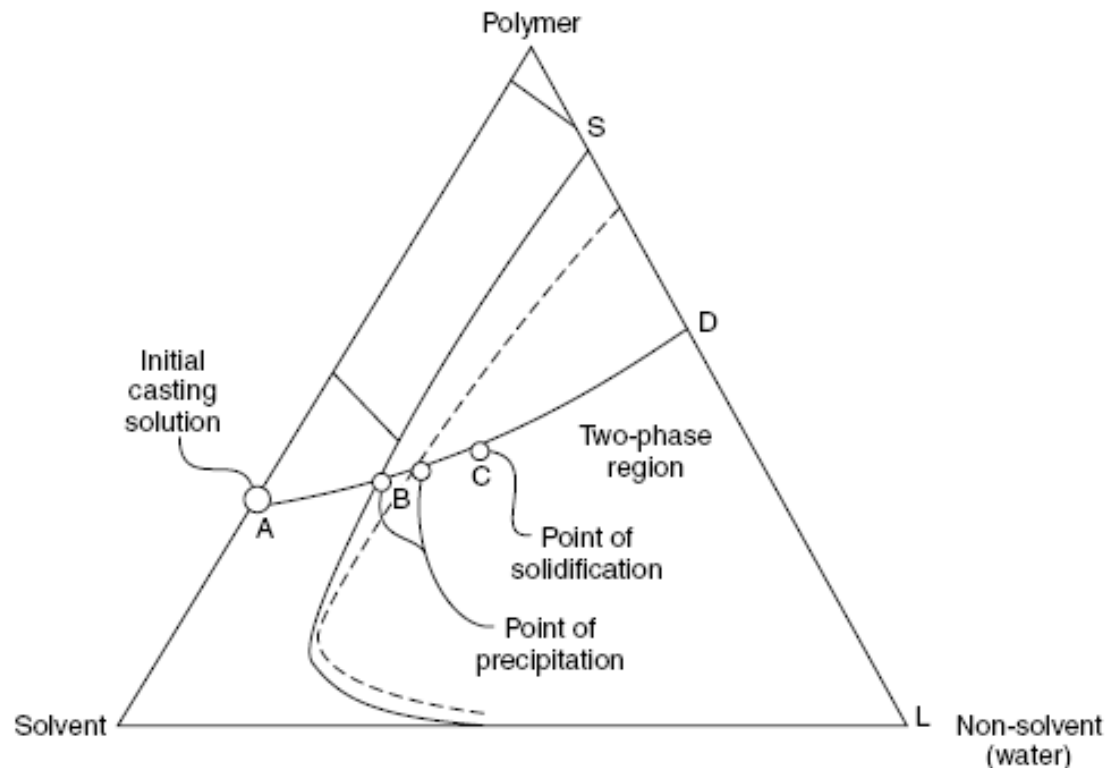
- In this method, an extruded film made from a partially crystalline polymeric material (polytetrafluoroethylene, polypropylene, polyethylene) is stretched perpendicular to the direction of the extrusion.
- When a mechanical stress is applied, small ruptures occur and a porous structure is obtained with pore size of about $0.1 - 3 \mu\text{m}$.
- Only (semi) crystalline polymeric materials can be used for this technique.
- The porosity of these membranes is much higher than that of membranes obtained by sintering, and values up to 90 % can be obtained.

STRETCHING



PHASE INVERSION

- The method is often called “**phase inversion**”, but it should be described as a **phase separation** process: a one-phase solution containing the membrane polymer is transformed by a precipitation/solidification process into two separate phases (a polymer-rich solid and a polymer-lean liquid phase).
- The “**proto-membrane**” is formed from the solution of the membrane polymer by casting a film on a suited substrate or by spinning through a spinneret together with a bore fluid.



PHASE INVERSION

- ❑ ***Nonsolvent induced phase separation (NIPS)*** – the polymer solution is immersed in a nonsolvent coagulation bath (typically water); demixing and precipitation occur due to the exchange of solvent (from polymer solution) and nonsolvent (from coagulation bath), i.e., the solvent and nonsolvent must be miscible.
- ❑ ***Vapor induced phase separation (VIPS)*** – the polymer solution is exposed to an atmosphere containing a nonsolvent (typically water); absorption of nonsolvent causes demixing /precipitation.
- ❑ ***Evaporation induced phase separation (EIPS)*** – the polymer solution is made in a solvent or in a mixture of a volatile solvent and a less volatile nonsolvent, and solvent is allowed to evaporate, leading to precipitation or demixing / precipitation.
- ❑ ***Thermally induced phase separation (TIPS)*** – a system of polymer and solvent is used which has an upper critical solution temperature; the solution is cast or spun at high temperature, and cooling leads to demixing / precipitation

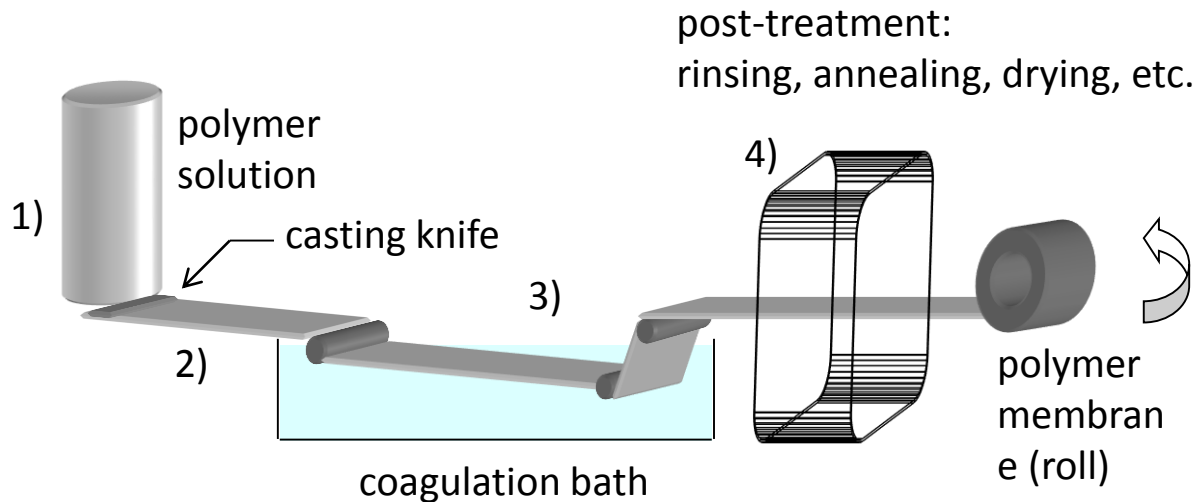
PHASE INVERSION

Nonsolvent induced phase separation (NIPS)

1. Polymer dissolution in single or mixed solvent,
2. Casting the polymer solution as film (“proto-membrane”) on suited substrate (or spinning as free liquid film, for hollow fibre),
3. Precipitation by immersion in nonsolvent coagulation bath, and
4. Post-treatments such as rinsing, annealing and drying. The membranes resulting from this process have typically a very thin ($< 1\ \mu\text{m}$, often even less than 100 nm) top skin layer (selective barrier), which is either non-porous or porous.

PHASE INVERSION

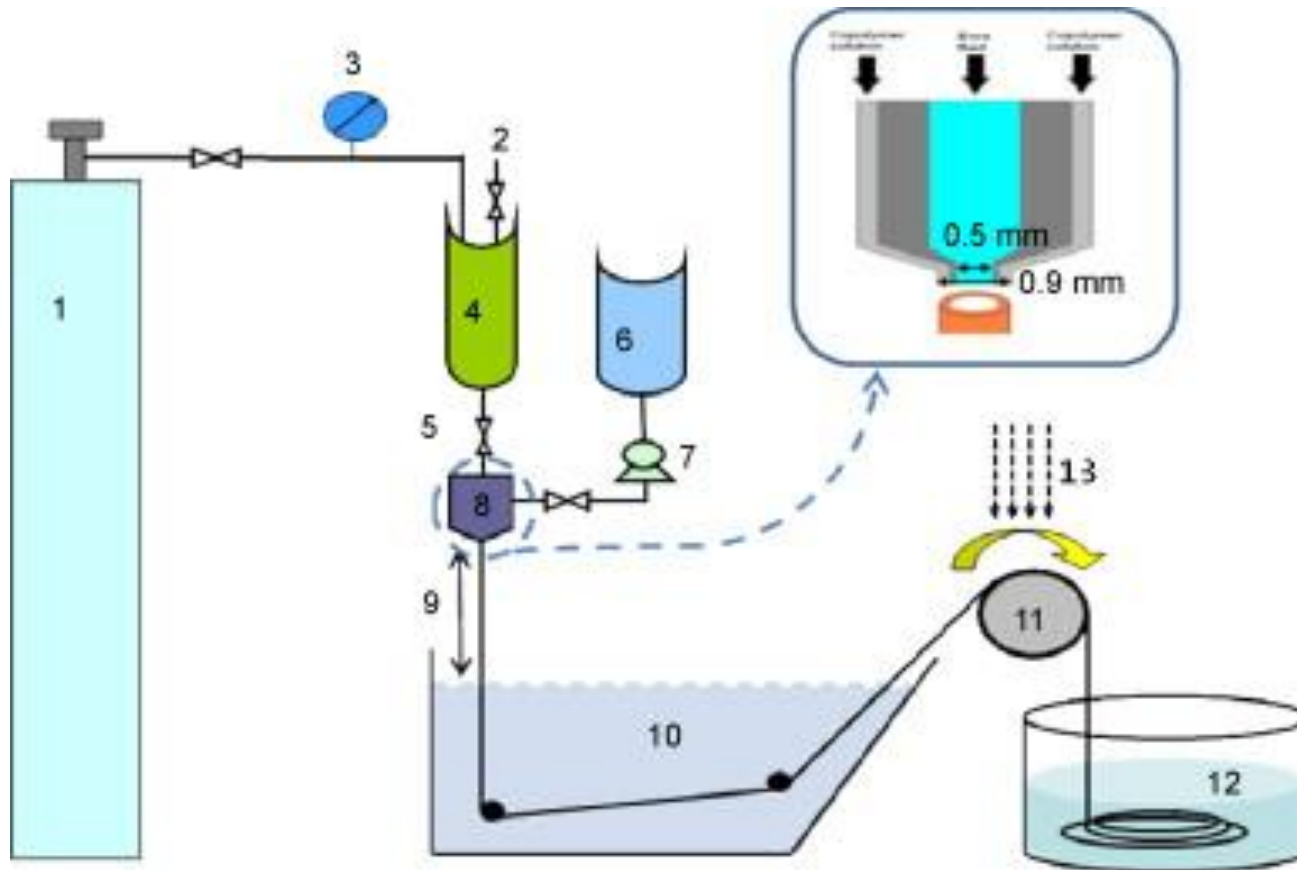
Schematic depiction of the continuous manufacturing process of polymeric membranes by the NIPS process



Factors:

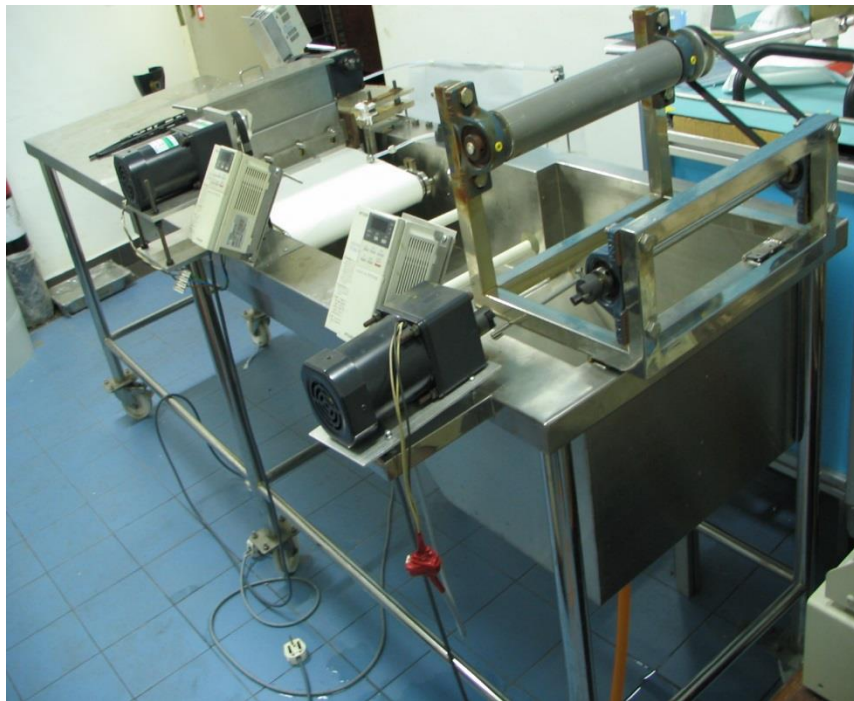
- Thermodynamic aspect
- The rate of precipitation in the liquid film; the mass-transfer (non-solvent in-flow, and solvent out-flow) can have tremendous influence:
 - i. Instantaneous liquid-liquid demixing, which will result in a porous membrane,
 - ii. Delayed onset of liquid-liquid demixing, which can result in a membrane with nonporous barrier skin layer

PHASE INVERSION



(1) nitrogen cylinder; (2) regulating pressure valve; (3) pressure gauge; (4) spinning dope tank; (5) dope solution valve; (6) bore liquid vessel; (7) bore fluid pump; (8) spinneret; (9) air gap length; (10) external coagulation bath; (11) wind-up drum; (12) fiber collecting reservoir and (13) distilled water wash.

CASTING MACHINE



CASTING MACHINE



PHASE INVERSION PARAMETERS

- ❑ **Characteristics of the casting solution.** Most important is the selection of a suitable solvent for the polymer. Polymer concentration also plays a vital role to determine the membrane porosity. Increasing polymer concentration in the casting solution leads to higher fraction of polymer and consequently decreases average membrane porosity and pore size. In addition, increasing of polymer concentration could also suppress macrovoid formation and enhance the tendency to form sponge-like structure. However, this can also increase the thickness of the skin layer.
- ❑ **Solvent / nonsolvent system.** The solvent must be miscible with the nonsolvent (here aqueous system). An aprotic polar solvent like N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl acetamide (DMAc) or dimethylsulfoxide (DMSO) is preferable for rapid precipitation (instantaneous demixing) upon immersion in the nonsolvent water. As consequence, a high porosity anisotropic membrane can be achieved. For slow precipitation, yielding low porosity or nonporous membrane, solvents having a relatively low Hildebrand solubility parameter, like tetrahydrofuran (THF) or acetone should be preferable.

PHASE INVERSION PARAMETERS

- ❑ **Additives.** For certain purposes, additive or modifier is added in the casting solution. Indeed, this additive can determine performance of the ultimate membrane and is often not disclosed for commercial membranes. Usually, additives include
 - ❑ **(i) co-solvent with relatively high solubility parameter**
 - ❑ **(ii) pore forming agents** such as poly(vinyl pyrrolidone) (PVP) or poly(ethylene glycol) (PEG) (these hydrophilic additives can enhance not only membrane pore size but also membrane hydrophilicity; at least partially, these polymers form stable blends with membrane polymers such as PSf or PES),
 - ❑ **(iii) non-solvent** (should be added only in such amounts that demixing of the casting solution does not occur; promotes formation of more porous structure and could also reduce macrovoid formation),
 - ❑ **(iv) addition of cross-linking agent** into casting solution (is less frequently used, but could also reduce macrovoid formation).

PHASE INVERSION PARAMETERS

- ❑ ***Characteristics of coagulation bath.*** The presence of a fraction of solvent in the coagulation bath can slow down liquid-liquid demixing rate. Consequently, a less porous barrier structure should be obtained. However, the opposite effect can also occur, i.e., addition of solvent can decrease polymer concentration (in the proto-membrane) leading to a more open porous structure. The amount of the solvent to be added strongly depends on the solvent – non-solvent interactions. As mutual affinity of solvent and nonsolvent increases, more solvent is required to achieve an effect onto membrane structure.
- ❑ ***Exposure time of proto-membrane before precipitation.*** The effect of exposing to atmosphere before immersion is dependent on the solvent property (e.g., volatility, water absorption) and atmosphere property (e.g., temperature, humidity). This step (i.e., combination of EIPS or VIPs with NIPS; cf. above) has significant effects on the characteristics of the skin layer and the degree of anisotropy of the resulting membrane

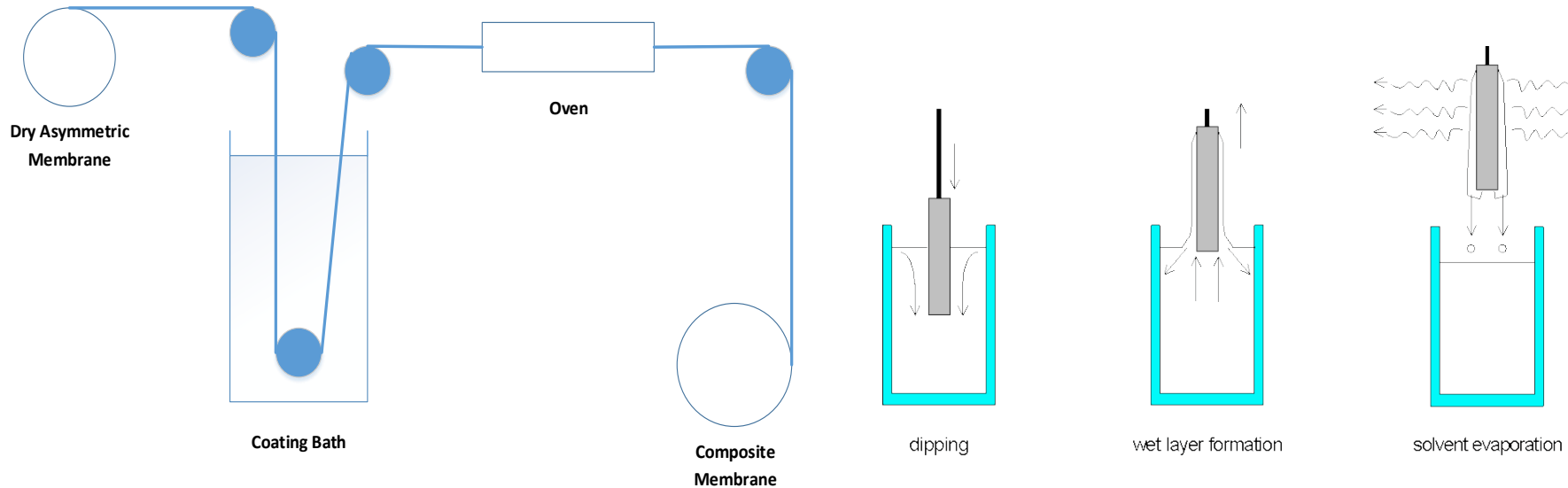
COMPOSITE MEMBRANE PREPARATION

- (i) preparation of porous support which is usually made by phase separation
- (ii) deposition of a selective barrier layer on this porous support.

LAMINATING

An ultrathin film is cast and then laminated to a (micro)porous support. This method has been used for preparing early RO membranes for water desalination .

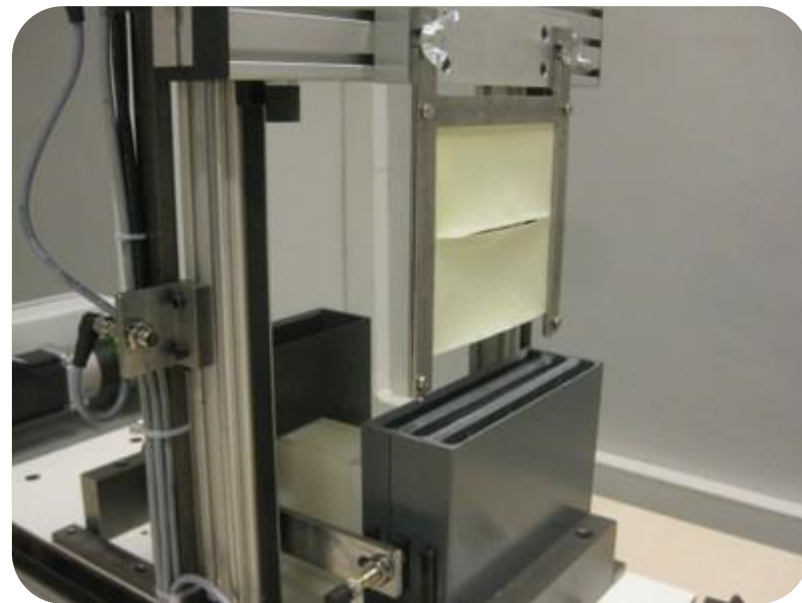
DIP-COATING



- Asymmetric membrane (often UF or MF) is immersed in the coating solution (polymer, pre-polymer or monomer). Concentration of polymer often less than 1 %.
- A thin layer than adheres on asymmetric membrane is then put in oven where the solvent evaporates and where crosslinking also occurs.
- Membranes obtained by this method are used in reverse osmosis, gas separation and pervaporation.
- The final thickness can be calculated with the Navier-Stokes equation.

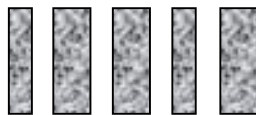
$$h_{\infty} = \frac{2}{3} \sqrt{\frac{\eta v}{\rho g}}$$

DIP-COATING

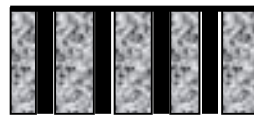


INTERFACIAL POLYMERIZATION

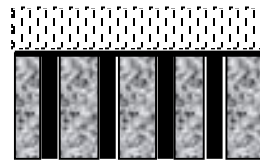
- A polymerization reaction occurs between two very reactive monomers (or one pre-polymer) at the interface of two immiscible solvents.
- The resulting film thickness extremely thin about the 50 nm range.
- The support layer is generally an UF or MF membrane.



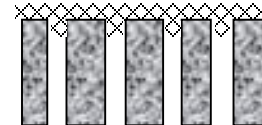
porous support
membrane



... after immersed
in aqueous
solution of first
monomer

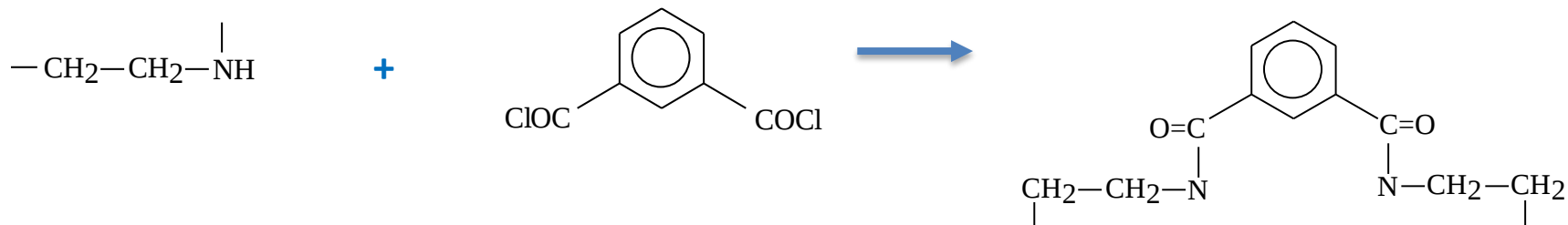
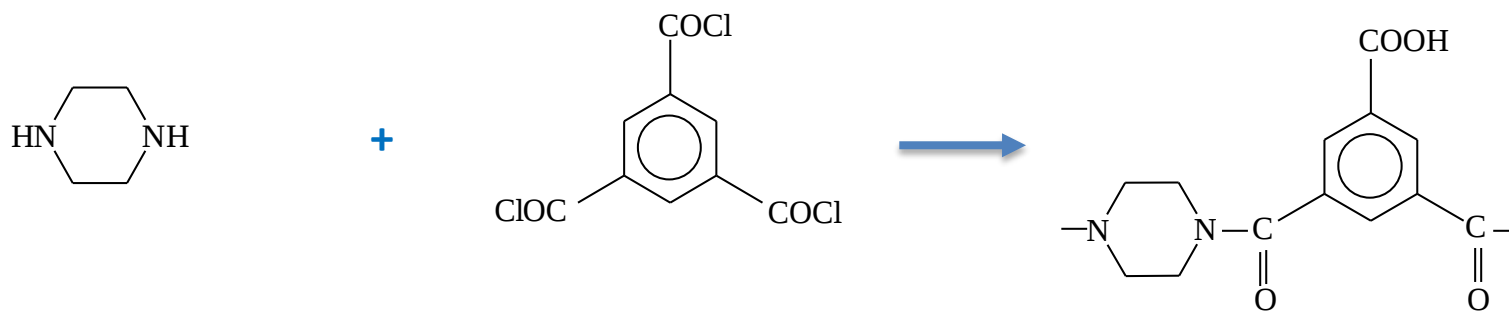
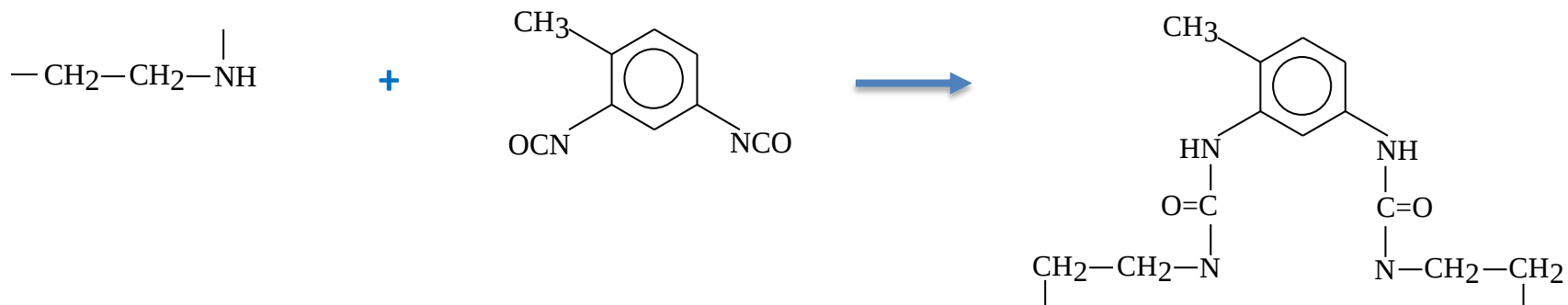


... after contacting
with nonaqueous
solution
of second monomer



composite membrane
with ultrathin polymer
film as top layer

INTERFACIAL POLYMERIZATION



Aqueous phase

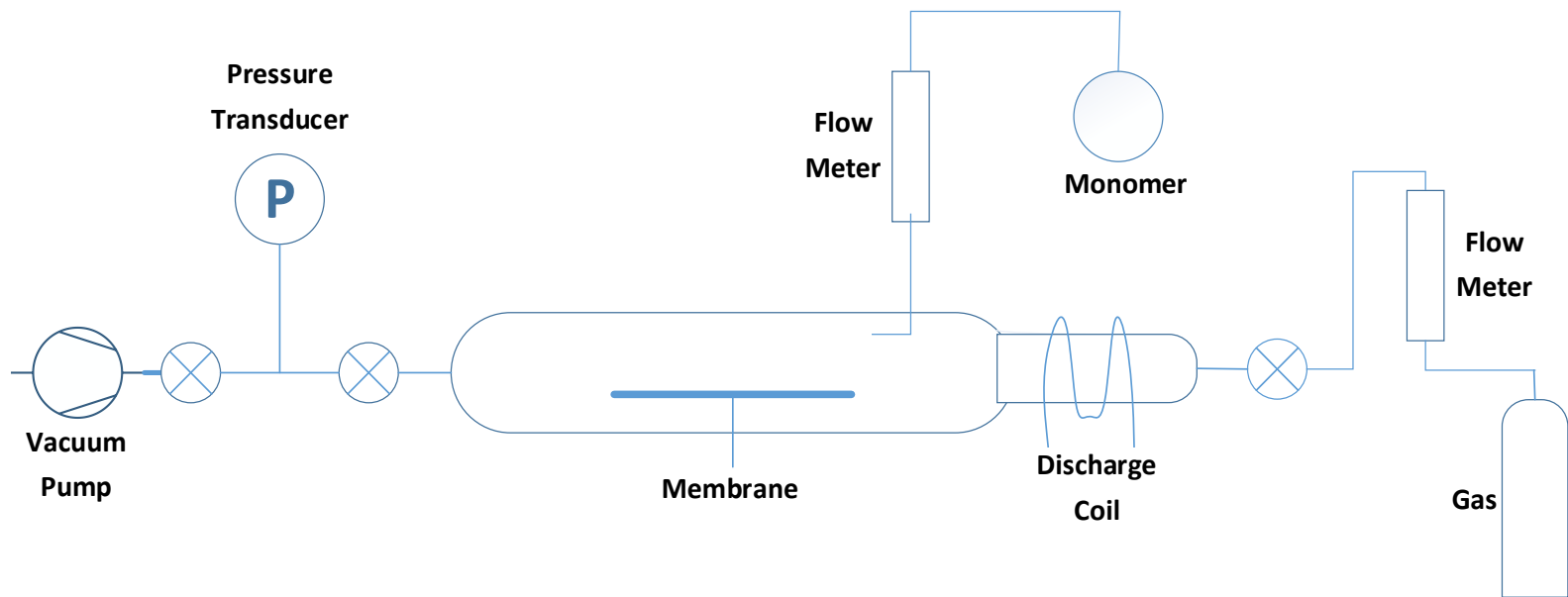
Organic phase

Product

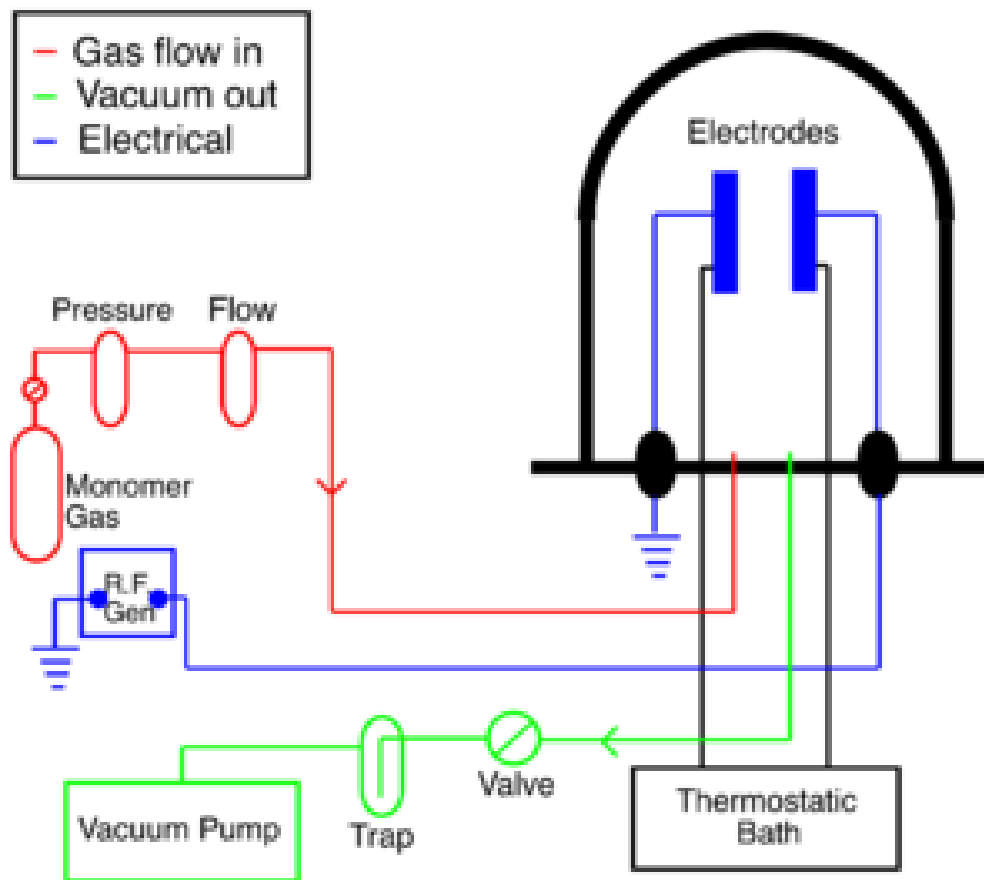


PLASMA POLIMERIZATION

- Gas phase deposition of the barrier layer on a porous support is conducted from glow discharge plasma via plasma polymerization.
- The plasma being obtained by the ionization of a gas by means of the electrical discharge at high frequencies up to 10 MHz.
- To type of plasma reactors are used :
 - Type 1 : The electrodes are located inside the reactor
 - Type 2 : The coil is located outside the reactor
- The structure of the resulting polymer is generally difficult to control and is often highly cross-linked.



PLASMA POLIMERIZATION



Type 2 : The coil is located outside the reactor