

Advanced polymeric and organic-inorganic membranes for pressure driven processes

Ngoc Lieu Le, Phuoc H. H. Duong and Suzana P. Nunes

King Abdullah University of Science and Technology (KAUST)

23955-6900 Thuwal, Saudi Arabia

Abstract

The state of the art of membranes for reverse-osmosis, nanofiltration and gas separation is shortly reviewed, taking in account the most representative examples currently in application. Emphasis is done also on recent developments of advanced polymeric and organic-inorganic materials for pressure driven processes. Many of the more recent membranes are not only polymeric but contain also an inorganic phase. Tailoring innovative materials with organic and inorganic phases coexisting in a nanoscale with multi-functionalization is an appealing approach to control at the same time diffusivity and gas solubility. Other advanced materials, which are now being considered for membrane development are organic or organic-inorganic self-assemblies, metal-organic frameworks and different forms of carbon fillers.

Keywords:

block copolymers, CO₂ separation, carbon molecular sieve, carbon nanotubes, gas separation, membrane materials, nanocomposites, nanofiltration, mixed-matrix membranes, organic-inorganic, responsive membranes, reverse osmosis, self-assembly

1. Membranes for pressure driven processes

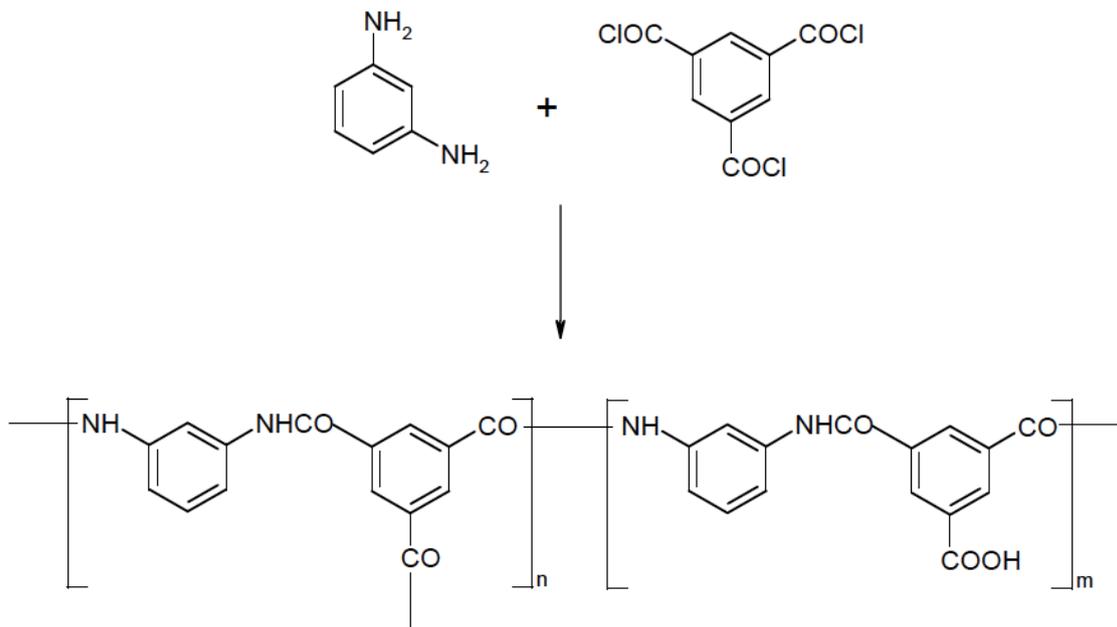
A more detailed review of membranes and membrane materials has been published before¹. In this chapter first the state-of-the-art of conventional membranes for pressure driven processes (reverse-osmosis, nanofiltration, ultrafiltration and gas separation) will be summarized, taking in account the most representative examples currently in application. After that the emphasis will be on recent developments of advanced polymeric and organic-inorganic materials for membranes.

Certainly the most used method for polymer porous membrane preparation is the so called “phase inversion”, which consists of the induction of phase separation in a previously homogeneous polymer solution either by temperature change, immersing the casting solution in a non-solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process). The wet process is the most common and is at least part of the industrial production of ultrafiltration, reverse osmosis (RO), and gas separation (GS), giving a high permeable and selective asymmetric structure. Additional thin coating steps can be further performed to give the needed selectivity for RO or GS. The preparation of asymmetric membranes by phase inversion and the influence of parameters such as casting solution composition and temperature have been topic of many reviews¹⁻⁶ and will not be detailed here.

1.1 Reverse osmosis (RO) membranes

Reverse osmosis is long established as a large scale industrial membrane processes. The large desalination plants around the world are running with reverse osmosis technology. One of the early materials used for membrane production is cellulose acetate, easily prepared by phase inversion with a solution cast on a non-woven and immersed in water. The characteristic structure of an integral asymmetric membrane is formed with a selective top layer and pores of increasing size across the membrane. Cellulose acetate (CA) is still being successfully used, especially in water treatment (in spiral wound modules) with relatively high chlorine tolerance and stability in applications where the feed water has a high fouling potential, such as in municipal effluents and surface water supplies. Thin CA hollow fibers are intensively used for seawater desalination in Saudi Arabia. The handicap of CA membranes is evident for applications in chemical and pharmaceutical industries when organic solvents are part of the feed or in processes operating at temperatures higher than 50°C or pH lower than 3 or higher than 7. For these conditions aromatic polyamides have a much higher solvent resistance and may be used in a wider pH range (pH 4-11). The main application is the treatment of brackish water and seawater. They can be produced in very thin hollow fibres with large surface area/volume. The main disadvantages are the very low chlorine tolerance and high fouling propensity. Desalination and waste water treatment need membranes with large flows. A very successful class of membranes for this application is that of “thin film composites” (TFC), prepared by interfacial polymerization on the surface of a porous support. A very good review of composite membranes was published by Petersen⁷⁻⁸. TFC membranes usually allow quite high water flows with low salt solubility. They consist of an ultrathin layer, usually of polyamide or polyetherurea, which is polymerized *in situ* and crosslinked on an asymmetric porous support, usually polysulfone. Since the dense selective layer is very thin, the membranes can operate at higher flux and lower pressure. The chemical stability is very good, although the chlorine tolerance is low. They can operate in a pH range of between 2 and 11. The membrane preparation consists of immersing the porous support in an aqueous solution containing a water-soluble monomer. After that the support is immersed in a solution of the second monomer in a non-polar solvent. Both monomers are only allowed to react at the interface between organic and aqueous solution, forming a thin polymer layer at the surface of

the porous support. As soon as the polymer layer is formed it acts as a barrier for the monomer transport and avoids the continuity of the polycondensation. On the other hand, any defect on the polymer layer is immediately repaired with a kind of self-healing mechanism, since monomer transport and polycondensation is allowed at that point. One of the most successful TFC membranes is the FilmTec FT-30, developed by Cadotte⁷⁻⁸ and now commercialized by Dow Water Solutions. The reaction involved in the preparation of the FT-30 is as follows:



The polyamide layer is formed on an asymmetric microporous polysulfone support cast on a polyester support web. The polyester web gives the major structural support and the polysulfone support with small surface pores with diameter of ca. 15 nm is the proper substrate for the formation of a 0.2 μm polyamide top layer. The maximum operating pressure of the FT 30 is about 7 MPa with free chlorine tolerance < 0.1 ppm.

Commercial TFC membranes are well optimized and are in the market for decades, being hard to beaten in terms of performance and cost, but approaches to improve even further the membranes are constantly being proposed. A widespread example is tailoring the polyamide layer with nanoparticles to improve the permeance, chlorine resistance, and fouling resistance of TFC membranes. Nanoparticles are incorporated into the traditional polyamide layer on the TFC membrane to form thin film nanocomposite (TFN) membrane that exhibits improved membrane characteristics such as better performance, increased hydrophilicity and less fouling effect. The concept of TFN RO membrane was reported by Jeong et al⁹ by embedding NaA zeolite nanoparticles into the polyamide film. Different nanoparticles (e.g. graphene and graphene oxide, graphene oxide-titanium dioxide, silica, POSS, silver, multi-walled carbon nanotubes) have been used since then as nanofillers to prepare TFN RO membranes¹⁰⁻¹¹.

Although synthetic polymeric membranes are very successful, biological systems are able to work with much higher water permeance and selectivity. Biological membranes are therefore an inspiration for further developments in RO and other fields. The most prominent examples of membranes combining biological and synthetic materials are those based on aquaporin¹². Aquaporins¹³ are membrane proteins that serve as water channels. A single aquaporin can transport water molecules at a rate of ~10⁹ molecules per second with high selectivity to water

only. Aquaporin-based biomimetic RO membranes have been prepared with structure similar to TFC RO membranes, containing aquaporin-proteoliposomes in the polyamide layer¹². The aquaporin-incorporated polyamide layer is formed on a polysulfone support by interfacial polymerization process. With the presence of aquaporin in the polyamide layer, the water flux of the aquaporin-based biomimetic RO membrane increases to $4.13 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is higher than the flux of TFC RO membrane ($2.68 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), but is still far below the expected based on aquaporin performance in biological systems.

Although the membranes for reverse osmosis are well established in the market, new membranes are required for related emerging fields. This is the case of osmotic power or pressure retarded osmosis plants, a concept, which has been independently proposed in the 70's by Norman¹⁴, Jellinek¹⁵ and Loeb¹⁶ and is now becoming reality in Norway. An introduction on this technology is given in Ref. 17. The technology takes advantage of the high osmotic pressure which is built when salt water from the sea meets water from fjords and rivers. The pressure is about 29 bar at 20°C for 35 g salt/l (sea water). The pressure is enough to move turbines and provide 2.2 MW of energy, working with water flow rate of $1 \text{ m}^3/\text{s}$. In typically large rivers water flows at about $10,000 \text{ m}^3/\text{s}$. For each MW 200,000 m^2 of membrane would be required, meaning a huge market for membranes. The requirements for these membranes are high salt rejection like in reverse osmosis, however with much higher water fluxes, as well as much thinner and opener porous supports. Membranes performance around 5 W/m^2 is needed to make the process economically competitive. Currently the best commercial cellulose derivative membranes have around 1/10 of the needed performance. The best commercial TFC membranes for reverse osmosis would give 0.1 W/m^2 . Membranes developed at the laboratory are available for up to 60 W/m^2 with 3 M NaCl draw solution under the pressure of 48 bar using a TFC flat sheet membrane¹⁸ and up to 24 W/m^2 with 1 M NaCl draw solution under the pressure of 20 bar using a TFC hollow fiber membrane¹⁹.

1.2 Nanofiltration (NF) membranes

While reverse osmosis and ultrafiltration are long implemented in several applications, the lack of available membranes with cut offs between 400 and 4,000 g/mol has been effectively filled much later with the development of nanofiltration membranes. Nanofiltration is important for water softening, removal of organic contaminants, concentration and demineralisation of whey, concentration of sugar and juice, etc. Extensive review on principles and applications of nanofiltration have been published²⁰⁻²¹.

Analogously to the RO membranes, interfacial polymerization has been used for the development of NF membranes. Dow Water Solutions offers a series of FILMTEC membranes: NF55, NF70 and NF90 (water flow of NF55 > NF70 > NF90) with rejection of at least 95 % magnesium sulfate. The top layer is a fully aromatic crosslinked polyamide. NF270 is composed of a semi-aromatic piperazine-based polyamide layer on top of a polysulphone microporous support reinforced with a polyester non-woven²². The membrane is very hydrophilic and its surface is negatively charged leading to the repulsion of also negatively charged solutes. Hydranautics commercializes the ESNA membrane series, also a thin film composite with an aromatic polyamide layer.

GE-Osmonics (part of GE Water Technologies) commercializes the Desal™ 5 nanofiltration membranes. The membrane has 4 layers, a polyester non-woven, an asymmetric microporous polysulfone and two proprietary thin films, which might be based on sulfonated polysulfone

and polypiperazineamide⁷. Desal™ nanofiltration membranes work also at very low pH levels.

Another way to obtain nanofiltration membranes is the modification of reverse osmosis membrane²³⁻²⁵, by treatment with acid, triethanolamine or the coating of ultrafiltration membranes with different polymer solutions²⁶⁻²⁸ like hydroxyalkyl derivatives of cellulose. A new approach was proposed by Lu et al²⁹. They deposited six-arm rigid star amphiphiles on a methanol/PVA conditioned polysulfone membrane and stabilized the resulting film by stitching the building blocks. These stars are shape-persistent molecules with hydrophilic arms and a hydrophobic core, which could anchor to the support membrane through noncovalent supramolecular interactions. Rejection of organic contaminants like Rhodamine and As (III) were confirmed.

A key issue for nanofiltration today is the improvement of solvent stability of the available membranes, since it would open a wide range of potential applications in the chemical³⁰, food³¹, petrochemical³² and pharmaceutical³³ industries. The terms “organic solvent nanofiltration” (OSN) or “solvent resistant nanofiltration” (SRNF) are used for the nanofiltration processes in organic solvents. Comprehensive reviews on OSN can be found in previous publications³⁴⁻³⁶. Stable OSN membranes under harsh conditions have been investigated from both organic and inorganic materials. Major challenges of polymeric OSN membranes are swelling, solvent stability and compaction during the solvent filtration process. The first inorganic OSN membrane made from silica–zirconia is demonstrated by Tsuru et al³⁷. Compared to organic OSN membranes, inorganic OSN membranes exhibit much higher stability due to their good chemical stability and resistance to swelling and compaction. However, inorganic membranes are more brittle, less selectivity and high cost. Hence, the up-scaling of inorganic membranes for OSN is difficult.

SelRO® nanofiltration membranes, later commercialized by Koch Membrane Systems, are examples of excellent solvent resistant membranes on the market. OSN membranes are being also commercialized by Evonik and GMT. The Koch MPS-44 and 50 membranes are stable in alkanes, alcohols, acetates, ketones and aprotic solvents. The MPS 44 is a hydrophilic membrane suitable, for instance, for separation processes in solvent mixtures containing water and organics. Solutes with molecular weights around 250 g/ml can then be separated or concentrated, while the composition of the solvent mixture does not change through the membrane. The hydrophilic MPS 50 is a nanofiltration membrane for use in a pure organic medium. The membrane composition is not completely disclosed. Patents of the same company, which introduced them³⁸⁻³⁹ describes the crosslinking of porous polyacrylonitrile (PAN) membranes by immersion in metal alkoxide solutions and heating, leading to insolubility in DMF, NMP or DMSO. Crosslinked PAN membranes coated with polydimethylsiloxane have been tested for filtration of oligomers in organic solvents⁴⁰. Coating with a hydrophilic polymer (e.g. polyethylenimine), which is later crosslinked, brings the membrane cut off to the NF range. Crosslinked polyimide is among the most explored materials for OSN membranes. Recent comprehensive reviews have been recently published^{34, 41-42}. Other polymers are now being successfully explored: polyoxadiazole⁴³, polytriazole⁴⁴, polyketone⁴⁵ and polybenzimidazole⁴⁶.

1.2.1 Antifouling

One of the most common issues in pressure-driven membrane separation processes applied to liquids is fouling. Four types of fouling are observed in liquid separations including: organic fouling, scaling, colloidal fouling, and biofouling. Fouling resistant properties of membranes

are controlled by their surface characteristics including chemistry, hydrophilicity, charge, roughness, and pore size. Most of the polymers used for preparation of porous membranes have a rather hydrophobic character, which make them susceptible to adsorption of organic and biological foulants. Many strategies have been proposed in the last decades to overcome this problem, varying from chemical grafting to plasma surface modification¹. The main aims of modifications are to increase membrane surface hydrophilicity and smoothness, and to introduce anti-fouling polymers/particles onto membrane surface. Antifouling coatings using hydrophilic polymeric materials such as zwitterionic polymers⁴⁷, dendrimers⁴⁸⁻⁴⁹, and nanobrushes⁵⁰ have shown effectively reduction in the attachments of foulants. The use of plasma for surface modification of micro and ultrafiltration polymeric membranes has been reviewed by Kramer⁵¹. Surface plasma modification of TFC membranes using low pressure argon plasma activation produces smoother and more hydrophilic polyamide surfaces⁵². Grafting using plasma has been explored for instance by Belfort and Ulbricht⁵³⁻⁵⁴. Grafting promoted by UV-irradiation⁵⁵ is a common alternative to add quaternary ammonium groups to the membrane surface, increasing the positive charge and control fouling. Another strategy to increase the fouling resistance of membranes is to incorporated small amount of nanoparticles into polymer matrix of membranes or onto membrane surface. Various nanoparticles (e.g. metal based nanoparticles, carbon-based nanoparticles, and nanoparticle composites) have been investigated and are reported in recent review papers⁵⁶⁻⁵⁷. Some developments on technologies for water treatment have been summarized by Shannon et al⁵⁸, including membranes with reduced fouling susceptibility. Reducing operation prices in membrane processes can be achieved if less cleaning is necessary. Furthermore multi-step production of membranes increases price. Taking this in account an interesting approach is the use of additives like comb copolymers with hydrophobic backbones and hydrophilic side chains, which can be automatically positioned in the membrane surface and pore walls during the membrane formation⁵⁹⁻⁶².

1.3 Membranes for gas separation

Compared to other fields of membrane application like water treatment, food processing and dialysis, gas separation has still a limited market. Cellulose acetate is still widely and successfully used in the industry also for gas separation. However with the development of new membranes and with the increasing need for clean industrial processes and low emission plants the importance of gas separation is constantly increasing⁶³. A motivation is the need for modernization of the energy sector leading to clean refineries, coal power plants and cement industry⁶⁴⁻⁶⁵. Although many processes in this field require high temperature and therefore favor inorganic membranes⁶⁶, polymeric membranes can be potentially be applied for treatment of platformer off-gases (H₂/hydrocarbon separation) in refineries and for CO₂ separation from other gases in coal plants. Membranes stable till 250°C would also allow the application in water-gas shift reactors. Developments on membranes for CO₂ separation are being reported in the literature with increasing frequency.

A special class of polymers is constituted by polymers with very high free volumes, like some functionalized polyacetylenes, which are bridging the gap between microporous and “dense” polymeric materials. The best known examples for these polymers are poly (1-trimethylsilyl-1-propyne (PTMSP) and poly (4-methyl-2-pentyne (PMP). Although the PMP was already synthesized in 1982⁶⁷, its high gas permeabilities were first published in 1996 by Pinnau et al⁶⁸ at MTR, which evaluated the performance of PMP membranes for hydrocarbon separation. An attractive application of membranes in this field is natural gas hydrocarbon dew pointing, the separation of higher hydrocarbons like butane present in natural gas from methane. The performance of PTMSP and PMP for hydrocarbon separation is superior to all

other known polymers. The main reason why these membranes have not been applied in large scale is their capability to strongly absorb low vapor pressure components, leading to a drastically reduced permeability. It has been reported recently, that the flux and even the selectivity of PMP and PTMSP can be enhanced by the addition of nano-particles⁶⁹⁻⁷⁰. Merkel et al⁶⁹ added fumed silica to PMP and observed a simultaneous increase of butane flux and butane/methane selectivity. This unusual behaviour was explained by fumed-silica induced disruption of polymer chain packing and an accompanying increase in the size of free volume elements through which molecular transport occurs. Gomes et al⁷⁰ incorporated nano-sized silica particles by sol-gel technique into PTMSP and found also for this polymer a simultaneous increase in flux and selectivity. It has to be studied, if physical aging of the polyacetylenes is reduced by the addition of nano-particles.

Membrane separation is an emerging technology for CO₂ capture. With increasing energy costs methane purification from biogas becomes more and more attractive. Large international projects evaluate the possibility to capture carbon dioxide from flue gas by membrane separation. Freeman et al⁷¹ have reported an overview on material selection for membrane preparation to remove CO₂ from gas mixtures. CO₂ solubility and CO₂/gas solubility selectivity in solvents and polymers containing different polar groups have been extensively explored. Ethylene oxide (EO) units in the polymer are one of the most useful groups to achieve high CO₂ permeability and high CO₂/light gas selectivity. Homo-poly (ethylene oxide) (PEO) consists of EO monomeric units, but its disadvantage is the strong tendency to crystallize and consequently it presents low gas permeability⁷². Block copolymers containing EO units as poly (amide-*b*-ether) have been shown as alternative material for this purpose. Copolymers of this type are produced under the trade name Pebax[®] ARKEMA. The PA blocks provide the mechanical strength and gas transport occurs through the PEO phase. Block copolymers with immiscible soft and rigid blocks like Pebax[®] can form various microphase-separated structures. Varying the polyamide and polyether segment, molecular weight and the content of each block, the mechanical, chemical, and physical properties can be conventionally modeled. Pebax[®] has been demonstrated as promising membrane materials for acid gas treatment⁷³. Bondar et al⁷³ have studied CO₂/N₂ and CO₂/H₂ separation using different grade of Pebax[®] membranes. They have reported high CO₂/N₂ and CO₂/H₂ selectivity, which were attributed to high CO₂ solubility due to the strong affinity of the polar ether linkages for CO₂. Kim et al⁷⁴ have also reported high permeability and high selectivity for CO₂ over N₂ as well as SO₂ over N₂, and these properties were attributed to polarizability of gases due to PEO segments. Mesoblends of polyether block copolymers and poly (ethylene glycol) (PEG) were generated by Patel and Spontak⁷⁵ and it was found that CO₂/H₂ selectivity can be improved by incorporation of PEG. The effect of PEG in the polymer chain to CO₂ transport properties in different polymer systems was also described by other researchers⁷⁶⁻⁸⁰ and it was proven that EO units influence CO₂ transport in glassy and rubbery polymers. It was shown recently that blends of low molecular weight with Pebax exhibit exceptional properties for carbon dioxide separation⁸¹⁻⁸².

A new class of polymers with high free volumes has been introduced recently by Budd et al⁸³. The molecular structure of these polymers contains sites of contortion (e.g. spiro-centers) within a rigid backbone (e.g. ladder polymer). The inventors call this polymer class "polymers of intrinsic microporosity (PIMs)"⁸⁴, because their porosity arises as consequence of the molecular structure and is not generated solely through processing. Recently the tertiary structure of these polymers have been confirmed by molecular modeling⁸⁵⁻⁸⁶. The gas permeation properties of membranes formed from PIM-1 were first reported in 2005⁸⁷ and since then has been explored by different groups⁸⁸⁻⁹². With an oxygen permeability of 370 Barrer and an O₂/N₂-selectivity of 4.0 PIM-1 showed an extraordinary behavior as gas

separation polymer. However, long-term measurements revealed a physical aging of PIM-1 analogous to PTMSP, which resulted in reduced permeabilities. Aging problems are still an issue⁹², but PIM-related polymers are a highly interesting polymer class for fabrication of gas separation membranes.

Another class membranes, which emerged in the last decade is that based on thermally rearranged polymers⁹³. These are membranes mainly prepared from functionalized polyimides and submitted to thermal treatment, leading to rearrangement and conversion to rigid structures with heterocyclic rings, which include polybenzoxazoles and polybenzimidazoles.

1.3.1 Mixed-matrix membranes

Many of the more recent membranes are not only polymeric but contain an inorganic phase. The advantage of organic-inorganic materials for membranes is the possibility of achieving synergetic effects on permeability and selectivity, as well as introducing new functionalizations and improving mechanical and thermal stability. Tailoring innovative materials with organic and inorganic phases coexisting in a nanoscale with multifunctionalization is an appealing approach to control at the same time free volume and gas solubility.

The most representative examples of introducing permeable inorganic fillers in a polymeric matrix for separation purposes are the so called mixed matrix membranes. Not only rather passive particles are included, but molecular sieves such as zeolites and also functionalized fillers, which might be much more active in the separation process. The term “mixed matrix membrane” has been introduced by Kulprathipanja et al⁹⁴, who performed pioneering work in the field of polymer/zeolite hybrid membranes. They showed that the CO₂/H₂ - selectivity of cellulose acetate could be reversed by addition of silicalite. The silicalite-CA membrane had a CO₂/H₂ – selectivity of 5.1, whereas the pure CA membrane exhibited a selectivity of 0.77.

Hennepe et al⁹⁵ incorporated for the first time silicalite in PDMS for pervaporation and increased the ethanol/water selectivity significantly under steady state conditions. Jia et al⁹⁶ pioneered the use of mixed matrix membranes with zeolites, using a similar approach (silicalite in PDMS). The gas selectivity could be changed due to a molecular sieving effect. However, the effects were initially too small to be of any interest for practical applications. One problem of these membranes was that the permeability ratio $P_{\text{PDMS}}/P_{\text{zeolite}}$ was too high (see equation 2).

The formation of polymer chains or networks with organic and inorganic segments has been used by different membrane groups. Molecular sieves such as zeolites have a much higher selectivity for many gas mixtures than polymeric membranes due to their well-defined pore sizes. The preparation of defect-free zeolite layers on a large scale is extremely difficult. The possibility of incorporating zeolites into a flexible organic polymer matrix enables the combination of the superior gas selectivities of these molecular sieves with the processibility of polymeric membranes⁹⁷.

The estimation of the permeability and selectivity of membranes with permeable fillers can be done using the equation derived by Maxwell⁹⁸ to calculate the electric conductivity of a metal in which small spheres of a second metal are dispersed. The permeability of the membrane to a defined gas follows equation 1:

$$P = P_c [P_d + 2 P_c - 2 \phi_d (P_c - P_d)] / [P_d + 2 P_c + \phi_d (P_c - P_d)] \quad (1)$$

The selectivity for gases 1 and 2 of a membrane prepared with a continuous phase of permeabilities P_{c1} and P_{c2} and a dispersed phase with permeabilities P_{d1} and P_{d2} can be calculated therefore by equation 2:

$$\alpha_{eff} = \alpha_c \frac{1 + 2P_{rel} - 2\phi(P_{rel} - 1)}{1 + 2P_{rel} + \phi(P_{rel} - 1)} * \frac{\frac{1}{\alpha_d} + \frac{2P_{rel}}{\alpha_c} + \phi \left(\frac{P_{rel}}{\alpha_c} - \frac{1}{\alpha_d} \right)}{\frac{1}{\alpha_d} + \frac{2P_{rel}}{\alpha_c} - 2\phi \left(\frac{P_{rel}}{\alpha_c} - \frac{1}{\alpha_d} \right)} \quad (2)$$

where α_c and α_d are the selectivity of the continuous and dispersed phases for the gas pair 1 and 2; P_{rel} is the permeability ratio between continuous and dispersed phase.

From this equation it can be seen that the selectivity is highly dependent on the permeability of the filler and of the matrix. When the polymer permeability is too high the selectivity of the mixed matrix membrane approaches the polymer selectivity. However if the permeability of the filler and the matrix are not too far apart, the properties of the membrane will have a large contribution from the highly selective filler. The compatibility between inorganic molecular sieves and polymers is very important in order to eliminate gas diffusion pathways at the interface between them, as discussed by Moore and Koros⁹⁹.

2. Next generation of organic membrane materials

The phase inversion membrane manufacture process was responsible for the breakthrough of the membrane technology and its implementation in numerous industrial applications. New advanced filtration processes are now conceivable but they require membranes with much narrower pore size distribution and better chemical resistance. A sharp pore size distribution can only be obtained with the implementation of new materials and new manufacture technologies. Approaches under investigation to tailor pore size include block and graft/comb copolymers, which self-assemble to form regular nanopores.

Furthermore new separation tasks could be fulfilled if the membrane pores would specifically respond to different stimuli and act analogously to biological gates. It is also possible to imagine membranes, which are self-cleaning with fouling-resistant surfaces, as well as self-healing membranes. The most inspiring source for new developments is nature itself, full of supramolecular chemistry, self-assemblies, controlled textures, sophisticated architectures and functional systems. The following sessions will discuss how to tailor pores using self-assembly approaches, how to produce hierarchical structures using organic-inorganic materials, how to promote a jump in the current membrane properties by using nanotubes and how to manufacture a new generation of membranes, which react to external stimuli.

2.1 Molecularly imprinted membranes

One elegant and very specific way to control pore sizes is the concept of molecularly imprinted membranes. This approach has been explored by different groups¹²⁶⁻¹²⁷. A nice review on that and other functional membranes has been published by Ulbricht¹²⁶. One

procedure to prepare imprinted membranes is the polymerization of a functional monomer in the presence of an analyte (template), which will be imprinted in the polymer and later extracted¹²⁷. The extraction gives a specific recognition site able to selectively bind analogous molecules. Other procedure is the preparation of membranes from polymer blends via phase separation. One polymer has the function of building the membrane structure and is chosen among those well investigated for phase inversion asymmetric membranes (e.g. cellulose acetate, polysulfone and polyacrylonitrile). The second polymer is added to provide strong interaction with the small molecules, which are included as templates. The small template molecules are added to the casting solution, and after a fast membrane formation by phase inversion in a coagulation bath, are extracted, leaving sites which are particularly favored for accommodating other analogous molecules in a filtration process. Since the sites are expected to have a certain chemical affinity for the original molecule, the functional mechanism is similar to antibodies or enzymes.

The challenges in molecular imprinted membranes preparation are to optimize its recognition ability and membrane transport properties simultaneously. One promising approach to overcome this problem is fabrication of composite membranes, which can be obtained by surface/pore functionalization. For instance, Son and Jegal¹²⁸ employed interfacial polymerization, a commonly used technique for the preparation of reverse osmosis membranes, to form a molecularly imprinted polymer layer on polysulfone supports for chiral separation¹²⁸. The thin layer of formed polyamide can keep high permeation rates. Similar *in situ* polymerization of molecular imprinted polymers can be performed onto the pore surface of supports to generate “smart” gates for efficient separations. Other potential strategies are development of novel materials such as functionally designed copolymers¹²⁹⁻¹³¹, novel polymer blends¹³² or incorporation of molecular imprinted polymer particles into membranes¹³³⁻¹³⁴.

2.2 Block copolymers

Block copolymers have been proposed for pore formation in membranes for a long time¹³⁵⁻¹⁴¹. Ishizu et al¹³⁷ used block copolymers to develop charge mosaic membranes, polymeric films with microphase separation containing both negatively and positively charged phases. Pebax® is an example of a commercial block copolymer of polyamide and polyethylene oxide. Lee et al¹³⁶ synthesized copolymers with one block containing isoprene and the second functional silyl groups. The immiscibility between the two different blocks led to microphase separation. The dense films were crosslinked by promoting the hydrolysis and condensation of the silyl-containing blocks. The isoprene blocks were decomposed with ozone and further leached with solvent, creating pores in a polysiloxane matrix. The pore size could be controlled, by using copolymers with blocks of different sizes. Phillip et al¹³⁸ prepared membranes based on triblock copolymer of polylactide–poly (dimethylacrylamide)–polystyrene (PLA–PDMA–PS). By controlling the relative block length, spherical domains, lamellae and cylinders of PLA coated with PDMA in a continuum of PS could be obtained. The PLA blocks were then removed by etching with aqueous base to form regular pores with a diameter of 13.7 nm. One of the main problems is however to establish a method to vertically orient microdomains and ensure pore connectivity from one side to the other. One possibility is the application of external fields¹³⁹⁻¹⁴⁰. Ikkala and ten Brinke¹⁴² summarized the potential application of self-assembly of polymeric supramolecules as basis for tunable nanoporous materials and smart membranes. Peinemann et al¹⁴¹ introduced the preparation of integral asymmetric isoporous membranes by combining self-assembly and non-solvent induced phase separation. Since then membranes from block copolymers have strongly developed¹⁴³⁻¹⁴⁴. They have been prepared as flat-sheet, hollow fibers¹⁴⁵ and porous

spheres¹⁴⁶. pH response has been demonstrated, indicating that membranes could be applied as chemical gates¹⁴⁷⁻¹⁴⁸. Photoresponse has been more recently reported¹⁴⁹. Pores can be tuned by changing the block length, by introducing additives. Pore decrease to nanofiltration range could be obtained by blending copolymers of different sizes and compositions¹⁵⁰. By incorporating metallic particles such as gold¹⁴⁵ or silver¹⁵¹, catalytic or biocide activities can be added to the membranes.

2.3 Next generation of organic-inorganic membranes

Combining organic and inorganic materials for membrane development is a versatile and successfully growing strategy. The main approaches include mixed-matrix membranes with metal oxides, zeolites, metal-organic frameworks (MOFs) and carbon fillers. The inorganic phase can be incorporated by mixing as filler or by *in-situ* generation. Briefly discussed in this section is the organic modification of previously formed inorganic membranes.

Mixed-matrix membranes (MOFs and zeolites)

There are still manufacturing problems to be solved, before mixed matrix membranes will be introduced in commercial gas separation at large scale. We see an increasing number of patents filed by big companies active in gas separation¹⁰⁰⁻¹⁰³, and it can be concluded, that mixed matrix membranes are on the brink of practical application. The development of new mixed matrix materials for gas separation will remain an attractive research field. Besides classical zeolites and carbon molecular sieves new selective adsorbants have to be considered. The research on MOFs¹⁰⁴⁻¹⁰⁵, three-dimensional nanoporous (3D)-networks of transition metal complexes, for membrane application, has substantially grown in the last decade¹⁰⁶⁻¹¹⁰. A huge number of architectures have been published in the last years. The possibility of tailoring the structures and choosing the right linkers to build networks with sieve dimensions able to discriminate gas permeants is particularly attractive for membrane development and storage¹¹¹. MOFs are analogous to zeolites, but with the chemical diversity of polymeric compounds. MOFs exhibit a very high porosity with exactly tailorable pore sizes. Preparation MOF-polymer mixed matrix membranes without cracks and defects is challenging due to compatibility. Stability is in many cases an issue. Zeolitic imidazole frameworks (ZIFs)¹¹²⁻¹¹⁴ can be seen as a sub-category with high stability, compatibility and high performance in CO₂ separation. Analogous materials, which are fully organic with strong covalent bonds, covalent organic frameworks (COFs)¹¹⁵, are more recently being considered for membrane fabrication¹¹⁶⁻¹¹⁷. COFs can be prepared as 2D or 3D structures¹¹⁷.

2D materials with layer-like structures, characterized by a high aspect ratio, are of interest in mixed matrix membranes because their nano-thin sheets can act as a barrier to restrict the diffusion of large molecules, while their nano “perforations” expanding on the layers and across their thickness will allow the transport of small molecules. As a result, the membranes can be useful in molecular sieving applications such as gas separation, water or organic purification. Graphene, which is a single-atom thick 2D carbon material, is one of the most discussed 2D materials for membranes and will be discussed later in this section.

Besides graphene, layered oxide 2D materials such as clay, AMH-3 and MFI, titanosilicates (JDF-L1) and aluminophosphates (AIPO) have been explored as molecular sieve. A single sheet of clay has a thickness of ~ 1 nm and its structure typically consists of Al-Mg octahedral sheet sandwiched between two Si-Al tetrahedral sheets. Layered clays are nonporous and their incorporation into polymer matrix have been demonstrated to improve mechanical and chemical properties or to enhance barrier properties¹¹⁸.

AMH-3, a layered silicate/zeolite with 3D 8-membered ring (MR) pores is an attractive candidate for gas separation because its 8 MR pores has small size of 0.34 nm which can be applied to separate various small-sized gases such as H₂ (0.29 nm), CO₂ (0.33 nm), O₂ (0.35 nm), N₂ (0.36 nm) and CH₄ (0.38 nm). For instance, the polybenzimidazole polymer matrix containing swollen AMH-3 displayed moderate improvement in CO₂/CH₄ selectivity¹¹⁹.

MFI, one type of zeolite, have 10 MR pores with a nominal pore size of 0.55 nm. This relatively large MR pore size can be applied to separate larger molecules such as hydrocarbon or other organics. Varoon et al demonstrated the potential of layered MFI in separating xylene mixtures with an obtained high *p*-/*o*-xylene separation factor of 65. Layered MFI can be obtained by using a new structure-directing agent (SDA) with a long-chain C₂₂ alkyl group in its synthesis process. This long-chain group restricts crystal growth in the perpendicular direction and hence a nano-thin MFI sheet of 2 nm can be generated in a one-step hydrothermal reaction.

The layered titanosilicate JDF-L1 consist of two TiO₅ square pyramids and four SO₄ tetrahedra has 6 MR pores with a small size of ~ 0.3 nm, which may be suitable for hydrogen-selective membranes. Galve et al¹²⁰ incorporated JDF-L1 into copolyimide and demonstrated a significant improvement in H₂/CH₄ separation.

Porous AIPO can be synthesized into 2D layers if using a suitable SDA. The conventional 3D AIPO has the Al/P ratio of unity. It has been demonstrated that lowering the Al/P ratio from unity decreased the dimensionality of the connectivity in the framework and hence layered AIPO is negatively charged with Al:P ratios of less than unity¹²¹. The polyimide membranes embedded with porous layered AIPO with the effective pore size of 0.44 nm × 0.33 nm × 0.32 nm showed significant improvements in O₂/N₂ and CO₂/CH₄ separations¹²². Unlike JDF-L1, however, layered AIPO has net-like morphologies with a very thin thickness of ~ 0.5 nm and hence it is more fragile leading to lower stability during swelling and exfoliation processes¹²³.

Although 2D materials have showed their great potential for future development of mixed matrix membranes, there are still challenges in their nanocomposite preparation and controlling the exfoliation of the layers in the polymer matrix is essential. Melt-bending, which is an attractive method for exfoliative dispersion, is inapplicable for perm-selective polymers such as polyimide, cellulose acetate and polyvinyl alcohol because they are not melt-processable and generally prepared by solution casting. However, attempts to exfoliate porous 2D materials in the membranes fabricated by solution casting failed because of their strong aggregation¹²⁴. To overcome this drawback, an active exfoliation process was applied by using high-shear mixing to exfoliate swollen AMH-3 in cellulose acetate solution and a high degree of exfoliation with a small number of layers (4–8) in the exfoliated flakes was obtained¹²⁵. Other techniques which may be potential for membrane fabrication with exfoliated 2D materials are *in situ* polymerization and sol-gel processing but neither of them has yet been applied¹²³.

The inorganic phase can be formed *in situ* and take advantage of self-assembly. The concept of molecular self-organization and self-assembly first from small molecules to supramolecular structures, a bottom-up strategy introduced by Lehn¹⁵². Barboiu et al¹⁵³⁻¹⁵⁴ has been using the self-organization of organic-inorganic molecules to prepare hybrid membranes by the sol-gel process. The membranes can function for instance as an ion-powered adenosine triphosphate pump. For the membrane formation molecules containing macrocyclic groups (e.g. crown

ether) are self-organized in solution forming a superstructure with strong H-bonds, which is later polymerized by sol-gel, forming a hybrid heteropolysiloxane material.

Nature can be the best inspiration for new organic-inorganic materials¹⁵⁵. Silicic skeletons of unicellular organisms Radiolaria and diatoms have a regular complex and finely porous morphology. A big challenge is to manufacture membranes with similar pores. In the last years some approaches have come, bringing some possibility in this direction. Wiesner¹⁵⁶⁻¹⁵⁸ uses block copolymers and inorganic precursors to create regular organic-inorganic structures. An example is the use of an amphiphilic poly (isoprene-*block*-ethylene oxide) block copolymer (PI-*b*-PEO) in combination with 3-(gycidyloxypropyl)trimethoxysilane, GLYMO, and aluminum *sec*-butoxide, which by sol-gel synthesis generates an organically modified aluminosilicate network. A regular porous structure results after calcination.

Another interesting organic-inorganic nanoporous materials with potential use for membranes are periodic mesoporous organosilicas with domain functionality¹⁵⁹⁻¹⁶⁰. Organic groups embedded into pore walls brought a new direction in the research of mesoporous molecular sieves. These materials are synthesized using bridged organosilica precursors ((EtO)₃Si-R-Si(OEt)₃) in conditions analogous to those for the preparation of mesoporous silicas. Compared to pure mesoporous silica the organic modification allows tuning hydrophobicity and hydrophilicity of the porous network. Compared to microporous zeolites, they feature increased pore dimensions and the ability to control the molecular recognition properties of the porous network by altering organic functionalities. Mesoporous silica with -CH₂-CH₂-/-CH=CH- bridges and with benzene rings have been reported, which can be used for further functionalization.

Membranes with Carbon Fillers

The preparation of carbon membranes has the motivation of high thermal stability (in non-oxidative environment) and the possibility of operation in the presence of organic solvents. Carbon molecular sieve (CMS) membranes are usually obtained by pyrolysis of organic polymers like cellulose¹⁶⁵ and polyimide¹⁶⁶. The porous structure can be tailored by choosing the right polymer precursor, the pyrolysis temperature and environment and the time spent at this temperature. A detailed review of carbon molecular sieve membranes is beyond the scope of this chapter. “Exotemplating” is an alternative method for preparation of hierarchically structured meso-macroporous carbon materials. In this approach a suitable template such as alumina membranes, zeolites, zirconia and mesoporous silica is impregnated with a carbon precursor such as sucrose and carbonized under non-oxidizing conditions. The template is then washed out with fluoridric acid. Carbon porous structures with aligned macrochannels were reported by Su et al¹⁶⁷.

However carbon membranes have drawbacks, which have still hindered their successful industrial application. They are brittle and the production process in large scale is much more expensive and complex than that of polymeric membranes. Promising approaches for polymeric membrane development are being reported in the last years using different geometries of carbon fillers: carbon molecular sieves, fullerenes and carbon nanotubes.

The dispersion of carbon molecular sieves (CMS) as filler for Matrimid[®] 5218 and Ultem[®] 1000 has been successfully explored by the group of Koros in mixed-matrix membranes¹⁶⁸. It was shown that the CMS particles produced a membrane having significantly enhanced effective permselectivities (CO₂/CH₄ and O₂/N₂) and fast-gas permeabilities (CO₂ and O₂) over the intrinsic properties of the pure polymer matrix phase alone. For the CO₂/CH₄

separation, enhancements by as much as 45% in CO₂/CH₄ permselectivity and 200% in CO₂ permeability over the corresponding intrinsic permeation properties of the pure polymer matrix phases were observed.

Homogeneously fullerene-dispersed membranes for gas separation were first prepared using a matrix of poly (1-trimethylsilyl-1-propyne) ¹⁶⁹. The fullerene in that case was just physically dispersed. Sterescu et al ¹⁷⁰ prepared poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) membranes with covalently attached fullerenes (C₆₀). The idea was that their hard-sphere properties may inhibit molecular polymer-chain packing possibly resulting in a high free volume. The PPO-bonded C₆₀ membranes exhibit significantly higher gas permeability (up to 80%) in comparison to pure PPO, without compromise in selectivity.

Carbon nanotubes (CNT) offer a unique combination of properties: high aspect ratio/high surface area, electron conductivity, superhydrophobicity and frictionless surfaces to lead to fast fluid flow, simple functionalization and dispersion in organic polymers, capability to enhance mechanical strength with small filler content as well as the potentially close control of pore dimension at the nanometer scale ¹⁷¹⁻¹⁷². Furthermore the functionalization can be directed to the entrance of the CNT, giving an excellent opportunity for developing gates for separation.

During the CNT growth process, the nanotube size is set by the diameter of the catalyst particle ¹⁷³⁻¹⁷⁴, offering a practical route for pore diameter control through well-determined catalyst synthesis. From the point of view of membranes, including nanotubes with well-defined inner core sizes into membranes shall enable a fine control of pore dimension at the nanometer scale. These characteristics started to be explored in membrane applications for gas and liquid separation ¹⁷⁵⁻¹⁷⁹. Hinds et al ¹⁷⁵ made a pioneering contribution, reporting on the preparation of an aligned CNT membrane for gas permeation and for transport of Ru(NH₃)₆³⁺ ions in aqueous solution. He followed theoretical predictions ¹⁷⁵, which suggest that the diffusivity of light gases inside CNTs with diameter around 1 nm to be orders of magnitude higher than in other porous structures like zeolites, due to the inherent molecular smoothness. After the first simulations ¹⁷⁸ of water transport in nanotubes, experimental results also demonstrated higher than expected flow rates, making CNT membranes promising candidates for water desalination with the possibility of tailoring the tube diameters to retain salt ¹⁸⁰. Salt rejection coefficients that match or exceed those of commercially available nanofiltration membranes, while exceeding their flux by up to four times ¹⁸¹.

CNTs have also been proposed for manufacturing electrodes for water desalination promoting flow through capacitor ¹⁷³. Furthermore, they are considered as mechanical support for catalysts ¹⁷⁴ and could therefore be an attractive additive in the design of a new generation of catalytic membranes. Furthermore by choosing nanotubes with suitable electron conductivity and controlling their distribution in the polymer electrolyte, an optimum catalyst-electrode-electrolyte interphase layer could be tailored ¹⁷².

However although the idea of using nanotubes for membranes is fascinating, there are many challenges involved. A first challenge is to prepare the polymer composite with aligned CNTs and free of defects. Another possible issue is the propensity for fouling given the hydrophobic nature of CNTs. CNT alignment has been claimed to be advantageous in different membrane applications. Some authors ¹⁸² predicted higher gas permeability when the CNTs are aligned. Furthermore for the aligned tubes superhydrophobicity might be much more evident. Different alignment strategies have been reported in literature ^{177, 183-185}. Nednoor et al ¹⁸³ obtained a vertically aligned array of multiwalled CNTs grown on quartz by chemical vapor

deposition (CVD). The space between the tubes was filled with polystyrene and the membrane was removed from the quartz by treatment with fluoridic acid. Prehn¹⁷² pressed a carpet of CNTs grown on silicon wafers against a thin layer of melted polystyrene, detached it from the silicon substrate and further coated the nanotubes with ionic polymer aiming the use as fuel cell membrane-electrode assemblies. The styrene was then dissolved making the CNT tips free for catalyst deposition. Mi et al¹⁸⁵ grew vertically aligned CNTs directly on a porous alumina support and filled the space between the CNTs with polystyrene as well. Kim et al¹⁷⁷ fabricated the membrane by orienting functionalized single wall CNTs with a filtration method¹⁸⁶.

A very interesting property of CNTs is the superhydrophobicity. Once water is inside the pores an exceptional flux is observed, exceeding all the initial predictions. The high flux may be due to the carbon nanotubes' atomically smooth, hydrophobic walls allowing considerable slip of water through the pores⁵⁸. However for water to wet the nanotube membranes, some work is required. Modifying the surfaces of the membrane, as discussed for nanofiltration membranes, can alter the surface properties, and thus potentially decrease the energy barrier to enter the tubes. Wang et al¹⁸⁷ studied the effect of the application of external potential on the droplet stability and wetting behavior of water on CNTs and demonstrated that water can be efficiently wet and pumped through superhydrophobic aligned multiwalled nanotube membranes by application of a small positive DC bias.

Membranes containing carbon nanotubes are therefore considered to have a great potential for water desalination¹⁷⁹. As mentioned before the water desalination with membranes is an established process and some of the currently used membranes have been developed for decades. According to recent papers, a new generation of membranes could be feasible with nanotubes, inspired by biological water pores, known as aquaporins¹⁸⁸⁻¹⁸⁹. The flow rates of water through nanotubes have been reported to be exceptionally high and independent of the tube length. The use of nanotubes in membranes might make real the dream of mimicking protein ion channels by precisely gated with selective and reversible chemical interactions. With this idea Nednoor et al¹⁸³ prepared membranes with aligned carbon nanotubes, after activating the CNT tips to have carboxylic groups, and further derivatized them with a molecule that binds to a bulky receptor. The receptor can open/close the pore entrance. Successful results were demonstrated by functionalizing nanotubes with a desthiobiotin derivative that binds reversibly to streptavidin.

Majumder et al¹⁹⁰ proposed the use of CNTs for voltage gated membranes, taking advantage of the fact that CNTs are conductors inside an insulating matrix allowing for the concentration of electric field at the tips. Modest voltages (100mV) could then be applied to control the steric environment of the channel entrance.

Besides the functionalization, technological challenges for carbon nanotube membranes will be the scaling up, increasing the pore density per area of the active layer, and decreasing the cost of membrane fabrication. However the synthesis of carbon nanotubes is becoming less expensive and at least multi-wall CNTs are already available now in large scale.

Graphene is of interest as advanced material for various membrane-based separations, because of its exceptional physical and thermal properties and atomic scale thickness. Its atomic scale pores generated by chemical or thermal treatment can play as robust channel for water transport or ion, gas and nanoparticle separations. A detailed review on graphene membranes is beyond the scope of this chapter. Pristine graphene is not promising for hybrid membranes, because it does not form homogeneous composites with polymer matrix. On the

other hand, graphene oxide (GO), the oxidation state of graphene nanosheets, could be an attractive candidate as a carbon filler because it contains epoxide, hydroxyl, and carboxylic acid groups at the edges and basal plane of the nanosheets, which can provide good compatibility with polymers. When appropriately embedded into the polymer matrix, GO can significantly improve mechanical properties of the polymer host, even at low filling amounts¹⁹¹.

When oriented horizontally in the polymer matrix, GO nanosheets may act as barrier, because they hinder diffusion pathway of permeating molecules across the membranes. A certain small amount range of GO can produce tortuous pathways which restrict the diffusion of larger molecules while still allowing smaller molecules diffuse with less resistance. This effect leads to enhancement in gas selectivity. This advantage may be lost when high fraction of GO added into the polymer matrix because the high tortuosity may not distinguish the penetrants based on their molecular size. Another application of GO in carbon-filler membranes is to prevent the aggregation of CNTs because of its strong steric effect¹⁹².

Furthermore, GO-embedded membranes are of interest in water desalination because of the hydrophilic nature of GO, which can improve water flux, salt rejection and antifouling propensity. For instance, Wang et al¹⁹³ demonstrated PVDF ultrafiltration membranes with a small GO loading amount of 0.20 wt.% achieved approximately doubled permeability and tensile strength. In addition, the increase in hydrophilicity of the membranes was validated by the decrease in contact angle, which implies a possible improvement in anti-fouling ability.

GO is preferred over CNTs because of its higher surface area, flexibility and lower cost. In comparison to isotropic CNTs, GO nanosheets with a high aspect ratio are hypothesized to provide high separation performance at a much lower loading for the polymer matrix¹²³. Regarding to membrane fabrication and scale-up, GO nanoscopically thin flakes are more favorable because of their ability of incorporation into ultra-thin active layers of membranes such as skin layers of hollow fiber membranes¹⁹⁴.

Organically modified inorganic membranes

In this chapter emphasis is given to polymeric membranes and polymeric membranes with inorganic components. On the other hand, inorganic porous sieves can be functionalized with organic segments¹⁶¹. The early efforts to graft organic groups into the micropores of zeolites generally failed, resulting in the modification of primarily the external surface of the crystals. The first microporous, crystalline silicates with organic groups covalently bound within the micropores¹⁶² were made by adding organosilanes [(CH₃O)₃SiR] to the silicate synthesis gel and incorporating into the zeolites during synthesis, yielding organic-functionalized molecular sieves with potential application for catalysis.

Ordered anodized alumina substrates are available with very regular pores, which can be functionalized by using silanes. They can work then as scaffolds with selective gates on the pores if surface bound molecules that change conformation with pH are further attached to the silanes functionalities¹⁶³⁻¹⁶⁴.

2.4 Responsive membranes

A concept which is leading to new generation of advanced membranes is that of switchable surfaces. A review on intelligent surfaces was published by Gras et al¹⁹⁵.

Response to temperature

The response of polymers to stimuli has been known for a long time. Probably the most reported and well investigated effect of this kind is the contraction and expansion of polymer chains in solution by simply changing the temperature. Heskins and Guillet¹⁹⁶ published in 1968 their investigation on poly (N-isopropylacrylamide) reporting that the system has a lower critical solution temperature (LCST) at 32°C. Polymer-solvent interactions in general can improve or deteriorate as the temperature increases. Numerous systems are known for which the thermodynamic conditions for polymer dissolution improves with the temperature. In this case the thermodynamic phase diagram is determined by upper critical solution temperatures, below which demixing occurs. This is the case for instance for water/poly (ethylene glycol) and many polymers in organic solvents. On the opposite the solubility of poly (N-isopropylacrylamide) increases when the temperature decreases. Above LCST water becomes a bad solvent for this polymer. The polymer chains react then by contracting themselves above the LCST and expanding below it. In the particular case of this polymer, the expansion is due to strong hydrogen bonds between the amide groups in the polymer chains and the surrounding water molecules. Water is in this form retained in the polymer gel. As the temperature increases above the LCST, the polymer hydrophobic groups are exposed and the hydrogen bonds with water are interrupted. The water molecules are squeezed out of the gel while the polymer chains shrink¹⁹⁷.

With an LCST near the body temperature this system was predestinated for biomedical applications, being the object of investigation for drug delivery¹⁹⁸, bioseparation¹⁹⁹, enzyme immobilization²⁰⁰ and cell culture for tissue engineering²⁰¹.

Another very interesting aspect of analogous systems is that the LCST can be shifted if additional factors like pH or ionic strength are changed. However although thermo-responsive gels have been found applications for instance in chromatography, their application in the membrane manufacture came much later, since as a film they are not self-supportable. Different approaches have been used to overcome this disadvantage, mainly the copolymerization and preparation of phase inversion porous membranes²⁰²⁻²⁰⁴ and the manufacture of composite membranes by grafting onto high-strength polymeric micro-porous membranes like track-etched polycarbonate^{197, 205}, PET²⁰⁶⁻²⁰⁷, polysulfone²⁰⁸, poly(vinylidene fluoride)²⁰⁹, polypropylene²¹⁰ or alkali-modified cellulose acetate membranes²¹¹; and nanofiber membranes like polyurethane²¹². Different *in situ* polymerization techniques are used for grafting like plasma-induced²¹³, photo-initiated²⁰⁶, surface-initiated atom transfer radical²¹⁴ and reversible addition fragmentation chain transfer polymerization²¹⁵.

Besides temperature there is a large variety of external stimuli, which can trigger changes in surface hydrophobicity, including electrical, electrochemical and photonic effects.

Electrochemical response

By applying voltage to a surface, electric charge is generated and wettability and even chemical properties can change²¹⁶⁻²²⁵. This effect is achieved for instance by changing the redox state. A conceivable membrane could have redox-active groups attached to its pore walls. The groups could be oxidized by the electric charge, forming cations and making the membrane hydrophilic, analogously to what is observed for surfactants. After withdrawing the voltage, the membranes would become hydrophobic again. Bulky molecules like rotaxanes can respond to electrochemical impulses or to changes in proton concentration

nearby by changing their conformation. They are being considered for potential application as artificial molecular muscles, but could be also useful if attached to membrane surfaces ²²⁶.

In addition to wettability, the pore size of certain electric-responsive gels (e.g. polyelectrolyte) can be changed by applying voltage and the membrane can act as an electrically activated “permeation valve” regulating the transport of specific solutes through the membrane ²²⁷. The changes in pore size is attributed to the gel deformation under an electric field which causes anisotropic swelling or deswelling when its charged ions are directed toward the anode or cathode side of the gel. The deformation and hence the pore size is influenced by several factors such as pH or salt concentration, position of the gel relative to the electrodes, thickness, shape and chemical properties of the gel, and the applied voltage. The advanced techniques of grafting gels onto membranes were aforementioned.

Another method to tailor a membrane with electro-responsive properties is to integrate the β -cyclodextrin (β -CD)/ferrocene (Fc) complexes into the membrane ²²⁸. Applying an electric field would charge the Fc and induce the complex to dissociate and turn the membrane into electro-responsive. In the study, poly(tetrafluoroethylene) was used as the base membrane, which was initially grafted with Fc and subsequently crosslinked with β -CD. Under an electric field, the membrane expressed self-cleaning capability by efficiently removing foulants and restoring their original filtration performance.

Electrochemically responsive surfaces, which could be useful for membranes could be prepared by attaching hydrophobic chains with negatively charged tips. This was demonstrated by Lahann et al ²²⁹ for mercaptohexadecanoic acid molecules on gold surface. If electrical potential is applied, the negatively charged tips (carboxylic groups) are bended to the surface exposing the hydrophobic part of the chain.

Photo-response

It is has been reported that molecules like azobenzene suffer reversible isomeric changes of conformation by illumination with UV light ²³⁰. The *cis* form is more hydrophobic and less expanded than the *trans*. The introduction of similar segments into membranes would also selectively change their flow rates through changes in wettability or formation of photo-adaptative membrane gates for ion or molecule permeation. Isomerization under UV light is also observed for other photo-chromic molecules like pyrimidine ²³¹, diarylethene ²³², viologen ²³³ and spiropyran ²³⁴. Photo-responsive membranes can be obtained by preparing from monomers or polymers containing photo-chromic groups ²³⁵, functionalizing membrane pores/surfaces with photo-responsive polymers ²³⁶ or embedding photo-switchable carriers into membranes ²³⁷. A comprehensive review on photo-responsive polymeric membranes was recently done by Nicoletta et al ²³⁸.

pH- and ionic strength-response

pH and ionic strength are other stimuli to lead to changes in membrane properties. Response to pH changes is generally due to protonation/deprotonation of ionizable side groups of polyelectrolytes such as carboxyl, pyridine, imidazole, and dibutylamine groups ²³⁹⁻²⁴⁰. For non-porous membranes embedded with pH-sensitive carriers, swelling/deswelling of the carriers caused by pH changes can control membrane permeability and selectivity. For porous membranes, layers of pH-sensitive polymers grafted on pore walls can reversibly change their pore size which eventually affects permeability and/or selectivity. For instance, an high pH environment causes deprotonation of poly(acrylic acid) gels which leads to its swelling to

enhance solute permeation²⁴¹. Opposite phenomenon occurs under low pH conditions. These responses make pH-responsive membranes potential in applications such as solute permeation control, self-cleaning or size and charge selective filtration and fractionation. The response of these membranes to various pH values also depends on solution ionic strength and hence ionic strength is also considered as a stimulus.

3. Final remarks

The research on nanotechnology is dramatically growing in the last years. Many of the innovative approaches reported for other applications can be adapted to tailor membrane surface and pore size. Micro-patterning of membranes has been successfully used to increase their surface and flow²⁴². Taking in account the different approaches mentioned in this paper and combining other nanofabrication methods like photolithography, layer-by-layer assembling²⁴³ and conventional methods of membrane preparation it will be possible to tune pores and surface functionalities. Some years ago, the membrane field seemed to be stagnated, after testing a large range of available homopolymers for manufacture, which in many cases was up-scaled and brought to successful implementation in industrial separation processes. With the application of recent achievements of nanoscience, new challenges for membrane development are now becoming reality and it is clear that innumerable possibilities are still open for exploration.

4. Acknowledgement

The authors thank Klaus-Viktor Peinemann, King Abdullah University of Science and Technology (KAUST) for his contribution to the previous version of this chapter.

5. References

1. Nunes, S. P.; Peinemann, K. V., Presently available membranes for liquid separation. *Membrane Technology: in the Chemical Industry, Second, Revised and Extended Edition* **2006**, 15-38.
2. Kesting, R. E., Synthetic polymeric membranes: a structural perspectives. **1985**.
3. Strathmann, H., Membrane separation processes. *Journal of membrane science* **1981**, 9 (1), 121-189.
4. Baker, R.; Cussler, E.; Eykamp, W.; Koros, W.; Riley, R., Membrane separation system: Recent developments and future directions. *Noyes Data Corporation, Park Ridge, NJ. 1991. 451* **1991**.
5. Mulder, J., Basic principles of membrane technology. *Springer Science & Business Media* **2012**.
6. Nunes, S. P., Recent advances in the controlled formation of pores in membranes. *Trends in polymer science* **1997**, 5 (6), 187-192.
7. Petersen, R. J., Composite reverse osmosis and nanofiltration membranes. *Journal of membrane science* **1993**, 83 (1), 81-150.
8. Cadotte, J.; Petersen, R.; Larson, R.; Erickson, E., A new thin-film composite seawater reverse osmosis membrane. *Desalination* **1980**, 32, 25-31.
9. Jeong, B. H.; Hoek, E. M. V.; Yan, Y.; Subramani, A.; Huang, X.; Hurwitz, G.; Ghosh, A. K.; Jawor, A., Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes. *Journal of Membrane Science* **2007**, 294 (1-2), 1-7.
10. Giwa, A.; Akther, N.; Dufour, V.; Hasan, S. W., A critical review on recent polymeric and nano-enhanced membranes for reverse osmosis. *RSC Advances* **2016**, 6 (10), 8134-8163.

11. Lau, W. J.; Gray, S.; Matsuura, T.; Emadzadeh, D.; Paul Chen, J.; Ismail, A. F., A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches. *Water Research* **2015**, *80*, 306-324.
12. Qi, S.; Wang, R.; Chaitra, G. K. M.; Torres, J.; Hu, X.; Fane, A. G., Aquaporin-based biomimetic reverse osmosis membranes: Stability and long term performance. *Journal of Membrane Science* **2016**, *508*, 94-103.
13. Agre, P.; Brown, D.; Nielsen, S., Aquaporin water channels: unanswered questions and unresolved controversies. *Current opinion in cell biology* **1995**, *7* (4), 472-483.
14. Norman, R. S., Water salination: a source of energy. *Science* **1974**, *186* (4161), 350-352.
15. Jellinek, H. H., Osmosis process for producing energy. Google Patents: **1976**.
16. Loeb, S.; Norman, R. S., Osmotic Power Plants. *Science* **1975**, *189* (4203), 654-655.
17. Peinemann, K. V.; Nunes, S. P., Membrane Technology, Volume 2: Membranes for Energy Conversion. *John Wiley & Sons* **2008**.
18. Straub, A. P.; Yip, N. Y.; Elimelech, M., Raising the bar: Increased hydraulic pressure allows unprecedented high power densities in pressure-retarded osmosis. *Environmental Science & Technology Letters* **2014**, *1* (1), 55-59.
19. Chou, S.; Wang, R.; Fane, A. G., Robust and high performance hollow fiber membranes for energy harvesting from salinity gradients by pressure retarded osmosis. *Journal of Membrane Science* **2013**, *448*, 44-54.
20. Schäfer, A. I.; Fane, A.; Waite, T. D., Nanofiltration: principles and applications. *Elsevier* **2005**.
21. Mohammad, A. W.; Teow, Y. H.; Ang, W. L.; Chung, Y. T.; Oatley-Radcliffe, D. L.; Hilal, N., Nanofiltration membranes review: Recent advances and future prospects. *Desalination* **2015**, *356*, 226-254.
22. Mänttari, M.; Pekuri, T.; Nyström, M., NF270, a new membrane having promising characteristics and being suitable for treatment of dilute effluents from the paper industry. *Journal of Membrane Science* **2004**, *242* (1), 107-116.
23. Cadotte, J. E.; Walker, D. R., Novel water softening membranes. Google Patents: **1989**.
24. Wheeler, J. W., Process for opening reverse osmosis membranes. Google Patents: **1993**.
25. Mickols, W. E., Method of treating polyamide membranes to increase flux. Google Patents: **1998**.
26. Nunes, S. P.; Sforça, M. L.; Peinemann, K. V., Dense hydrophilic composite membranes for ultrafiltration. *Journal of Membrane Science* **1995**, *106* (1), 49-56.
27. Schmidt, M.; Peinemann, K. V.; Paul, D.; Röddicker, H., Celluloseether als trennschichten hydrophiler polymermembranen. *Die Angewandte Makromolekulare Chemie* **1997**, *249* (1), 11-32.
28. Livazovic, S.; Li, Z.; Behzad, A. R.; Peinemann, K. V.; Nunes, S. P., Cellulose multilayer membranes manufacture with ionic liquid. *Journal of Membrane Science* **2015**, *490*, 282-293.
29. Lu, Y.; Suzuki, T.; Zhang, W.; Moore, J. S.; Mariñas, B. J., Nanofiltration membranes based on rigid star amphiphiles. *Chemistry of materials* **2007**, *19* (13), 3194-3204.
30. Valadez-Blanco, R.; Ferreira, F. C.; Jorge, R. F.; Livingston, A. G., A membrane bioreactor for biotransformations of hydrophobic molecules using organic solvent nanofiltration (OSN) membranes. *Journal of Membrane Science* **2008**, *317* (1-2), 50-64.
31. Peshev, D.; Peeva, L. G.; Peev, G.; Baptista, I. I. R.; Boam, A. T., Application of organic solvent nanofiltration for concentration of antioxidant extracts of rosemary (*Rosmarinus officinalis* L.). *Chemical Engineering Research and Design* **2011**, *89* (3), 318-327.

32. White, L. S., Development of large-scale applications in organic solvent nanofiltration and pervaporation for chemical and refining processes. *Journal of Membrane Science* **2006**, *286* (1-2), 26-35.
33. Székely, G.; Bandarra, J.; Heggie, W.; Sellergren, B.; Ferreira, F. C., Organic solvent nanofiltration: A platform for removal of genotoxins from active pharmaceutical ingredients. *Journal of Membrane Science* **2011**, *381* (1-2), 21-33.
34. Marchetti, P.; Jimenez Solomon, M. F.; Szekely, G.; Livingston, A. G., Molecular separation with organic solvent nanofiltration: A critical review. *Chemical Reviews* **2014**, *114* (21), 10735-10806.
35. Amirilargani, M.; Sadrzadeh, M.; Sudhölter, E. J. R.; de Smet, L. C. P. M., Surface modification methods of organic solvent nanofiltration membranes. *Chemical Engineering Journal* **2016**, *289*, 562-582.
36. Vandezande, P.; Gevers, L. E. M.; Vankelecom, I. F. J., Solvent resistant nanofiltration: Separating on a molecular level. *Chemical Society Reviews* **2008**, *37* (2), 365-405.
37. Tsuru, T.; Sudou, T.; Kawahara, S. I.; Yoshioka, T.; Asaeda, M., Permeation of liquids through inorganic nanofiltration membranes. *Journal of Colloid and Interface Science* **2000**, *228* (2), 292-296.
38. Linder, C.; Perry, M.; Nemas, M.; Katraró, R., Solvent stable membranes. Google Patents: **1991**.
39. Perry, M.; Yacubowicz, H.; Linder, C.; Nemas, M.; Katraró, R., Polyphenylene oxide-derived membranes for separation in organic solvents. Google Patents: **1992**.
40. Ebert, K.; Koll, J.; Dijkstra, M.; Eggers, M., Fundamental studies on the performance of a hydrophobic solvent stable membrane in non-aqueous solutions. *Journal of membrane science* **2006**, *285* (1), 75-80.
41. Szekely, G.; Jimenez-Solomon, M. F.; Marchetti, P.; Kim, J. F.; Livingston, A. G., Sustainability assessment of organic solvent nanofiltration: from fabrication to application. *Green Chemistry* **2014**, *16* (10), 4440-4473.
42. Hołda, A. K.; Vankelecom, I. F., Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes. *Journal of Applied Polymer Science* **2015**, *132* (27).
43. Maab, H.; Nunes, S. P., Porous polyoxadiazole membranes for harsh environment. *Journal of membrane science* **2013**, *445*, 127-134.
44. Chisca, S.; Duong, P. H.; Emwas, A. H.; Sougrat, R.; Nunes, S. P., Crosslinked copolyazoles with a zwitterionic structure for organic solvent resistant membranes. *Polymer Chemistry* **2015**, *6* (4), 543-554.
45. da Silva Burgal, J.; Peeva, L. G.; Kumbharkar, S.; Livingston, A., Organic solvent resistant poly (ether-ether-ketone) nanofiltration membranes. *Journal of membrane science* **2015**, *479*, 105-116.
46. Valtcheva, I. B.; Kumbharkar, S. C.; Kim, J. F.; Bhole, Y.; Livingston, A. G., Beyond polyimide: crosslinked polybenzimidazole membranes for organic solvent nanofiltration (OSN) in harsh environments. *Journal of Membrane Science* **2014**, *457*, 62-72.
47. Marré Tirado, M. L.; Bass, M.; Piatkovsky, M.; Ulbricht, M.; Herzberg, M.; Freger, V., Assessing biofouling resistance of a polyamide reverse osmosis membrane surface-modified with a zwitterionic polymer. *Journal of Membrane Science* **2016**, *520*, 490-498.
48. Sarkar, A.; Carver, P. I.; Zhang, T.; Merrington, A.; Bruza, K. J.; Rousseau, J. L.; Keinath, S. E.; Dvornic, P. R., Dendrimer-based coatings for surface modification of polyamide reverse osmosis membranes. *Journal of Membrane Science* **2010**, *349* (1-2), 421-428.

49. Zhu, W. P.; Gao, J.; Sun, S. P.; Zhang, S.; Chung, T. S., Poly(amidoamine) dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber membranes for heavy metal removal. *Journal of Membrane Science* **2015**, *487*, 117-126.
50. Rahaman, M. S.; Therien-Aubin, H.; Ben-Sasson, M.; Ober, C. K.; Nielsen, M.; Elimelech, M., Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes. *Journal of Materials Chemistry B* **2014**, *2* (12), 1724-1732.
51. Kramer, P.; Yeh, Y.; Yasuda, H., Low temperature plasma for the preparation of separation membranes. *Journal of Membrane Science* **1989**, *46* (1), 1-28.
52. Reis, R.; Dumée, L. F.; Tardy, B. L.; Dagastine, R.; Orbell, J. D.; Schutz, J. A.; Duke, M. C., Towards enhanced performance thin-film composite membranes via surface plasma modification. *Scientific Reports* **2016**, *6*.
53. Ulbricht, M.; Belfort, G., Surface modification of ultrafiltration membranes by low temperature plasma. I. Treatment of polyacrylonitrile. *Journal of applied polymer science* **1995**, *56* (3), 325-343.
54. Ulbricht, M.; Belfort, G., Surface modification of ultrafiltration membranes by low temperature plasma II. Graft polymerization onto polyacrylonitrile and polysulfone. *Journal of Membrane Science* **1996**, *111* (2), 193-215.
55. Wang, D., Hydrophobic membrane having hydrophilic and charged surface and process. Google Patents: **1992**.
56. Jhaveri, J. H.; Murthy, Z. V. P., A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. *Desalination* **2016**, *379*, 137-154.
57. Yang, Q.; Mi, B., Nanomaterials for membrane fouling control: Accomplishments and challenges. *Advances in Chronic Kidney Disease* **2013**, *20* (6), 536-555.
58. Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M., Science and technology for water purification in the coming decades. *Nature* **2008**, *452* (7185), 301-310.
59. Deratani, A.; Li, C. L.; Wang, D. M.; Lai, J. Y. In New trends in the preparation of polymeric membranes for liquid filtration, *Annales de chimie, Lavoisier* **2007**; pp 107-118.
60. Hester, J.; Banerjee, P.; Mayes, A., Preparation of protein-resistant surfaces on poly (vinylidene fluoride) membranes via surface segregation. *Macromolecules* **1999**, *32* (5), 1643-1650.
61. Hester, J.; Mayes, A., Design and performance of foul-resistant poly (vinylidene fluoride) membranes prepared in a single-step by surface segregation. *Journal of Membrane Science* **2002**, *202* (1), 119-135.
62. Wang, Y. Q.; Wang, T.; Su, Y. L.; Peng, F. B.; Wu, H.; Jiang, Z. Y., Remarkable reduction of irreversible fouling and improvement of the permeation properties of poly (ether sulfone) ultrafiltration membranes by blending with pluronic F127. *Langmuir* **2005**, *21* (25), 11856-11862.
63. Baker, R. W.; Low, B. T., Gas separation membrane materials: a perspective. *Macromolecules* **2014**, *47* (20), 6999-7013.
64. Merkel, T. C.; Lin, H.; Wei, X.; Baker, R., Power plant post-combustion carbon dioxide capture: an opportunity for membranes. *Journal of membrane science* **2010**, *359* (1), 126-139.
65. Merkel, T. C.; Zhou, M.; Baker, R. W., Carbon dioxide capture with membranes at an IGCC power plant. *Journal of membrane science* **2012**, *389*, 441-450.
66. Pera-Titus, M., Porous inorganic membranes for CO₂ capture: present and prospects. *Chemical reviews* **2013**, *114* (2), 1413-1492.

67. Masuda, T.; Kawasaki, M.; Okano, Y.; Higashimura, T., Polymerization of methylpentynes by transition metal catalysts: monomer structure, reactivity, and polymer properties. *Polymer Journal* **1982**, *14* (5), 371-377.
68. Morisato, A.; Pinnau, I., Synthesis and gas permeation properties of poly (4-methyl-2-pentyne). *Journal of membrane science* **1996**, *121* (2), 243-250.
69. Merkel, T.; Freeman, B.; Spontak, R.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A., Ultrapermeable, reverse-selective nanocomposite membranes. *Science* **2002**, *296* (5567), 519-522.
70. Gomes, D.; Nunes, S. P.; Peinemann, K. V., Membranes for gas separation based on poly (1-trimethylsilyl-1-propyne)-silica nanocomposites. *Journal of Membrane Science* **2005**, *246* (1), 13-25.
71. Lin, H.; Freeman, B. D., Materials selection guidelines for membranes that remove CO₂ from gas mixtures. *Journal of Molecular Structure* **2005**, *739* (1), 57-74.
72. Lin, H.; Freeman, B. D., Gas solubility, diffusivity and permeability in poly (ethylene oxide). *Journal of Membrane Science* **2004**, *239* (1), 105-117.
73. Bondar, V.; Freeman, B.; Pinnau, I., Gas sorption and characterization of poly (ether-b- amide) segmented block copolymers. *Journal of Polymer Science Part B: Polymer Physics* **1999**, *37* (17), 2463-2475.
74. Kim, J. H.; Ha, S. Y.; Lee, Y. M., Gas permeation of poly (amide-6-b-ethylene oxide) copolymer. *Journal of Membrane Science* **2001**, *190* (2), 179-193.
75. Patel, N. P.; Spontak, R. J., Mesoblends of polyether block copolymers with poly (ethylene glycol). *Macromolecules* **2004**, *37* (4), 1394-1402.
76. Okamoto, K. I.; Fuji, M.; Okamoto, S.; Suzuki, H.; Tanaka, K.; Kita, H., Gas permeation properties of poly (ether imide) segmented copolymers. *Macromolecules* **1995**, *28* (20), 6950-6956.
77. Patel, N. P.; Hunt, M. A.; Lin-Gibson, S.; Bencherif, S.; Spontak, R. J., Tunable CO₂ transport through mixed polyether membranes. *Journal of Membrane Science* **2005**, *251* (1), 51-57.
78. Kawakami, M.; Iwanaga, H.; Hara, Y.; Iwamoto, M.; Kagawa, S., Gas permeabilities of cellulose nitrate/poly (ethylene glycol) blend membranes. *Journal of Applied Polymer Science* **1982**, *27* (7), 2387-2393.
79. Li, J.; Wang, S.; Nagai, K.; Nakagawa, T.; Mau, A. W., Effect of polyethyleneglycol (PEG) on gas permeabilities and permselectivities in its cellulose acetate (CA) blend membranes. *Journal of membrane science* **1998**, *138* (2), 143-152.
80. Kim, J. H.; Ha, S. Y.; Nam, S. Y.; Rhim, J. W.; Baek, K. H.; Lee, Y. M., Selective permeation of CO₂ through pore-filled polyacrylonitrile membrane with poly (ethylene glycol). *Journal of Membrane Science* **2001**, *186* (1), 97-107.
81. Car, A.; Stropnik, C.; Yave, W.; Peinemann, K. V., PEG modified poly (amide-b-ethylene oxide) membranes for CO₂ separation. *Journal of Membrane Science* **2008**, *307* (1), 88-95.
82. Car, A.; Stropnik, C.; Yave, W.; Peinemann, K. V., Pebax®/polyethylene glycol blend thin film composite membranes for CO₂ separation: performance with mixed gases. *Separation and Purification Technology* **2008**, *62* (1), 110-117.
83. Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E., Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. *Chemical Communications* **2004**, (2), 230-231.
84. McKeown, N. B., Polymers of intrinsic microporosity. *ISRN Materials Science* **2012**, *2012*.
85. Heuchel, M.; Fritsch, D.; Budd, P. M.; McKeown, N. B.; Hofmann, D., Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1). *Journal of Membrane Science* **2008**, *318* (1), 84-99.

86. Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Fritsch, D., Polymers of intrinsic microporosity derived from bis (phenazyl) monomers. *Macromolecules* **2008**, *41* (5), 1640-1646.
87. Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanem, B. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D., Gas separation membranes from polymers of intrinsic microporosity. *Journal of Membrane Science* **2005**, *251* (1), 263-269.
88. Song, Q.; Cao, S.; Pritchard, R. H.; Ghalei, B.; Al-Muhtaseb, S. A.; Terentjev, E. M.; Cheetham, A. K.; Sivaniah, E., Controlled thermal oxidative crosslinking of polymers of intrinsic microporosity towards tunable molecular sieve membranes. *Nature communications* **2014**, *5*.
89. Du, N.; Dal-Cin, M. M.; Robertson, G. P.; Guiver, M. D., Decarboxylation-induced cross-linking of polymers of intrinsic microporosity (PIMs) for membrane gas separation. *Macromolecules* **2012**, *45* (12), 5134-5139.
90. Carta, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B., Gas permeability of hexaphenylbenzene based polymers of intrinsic microporosity. *Macromolecules* **2014**, *47* (23), 8320-8327.
91. Mitra, T.; Bhavsar, R. S.; Adams, D. J.; Budd, P. M.; Cooper, A. I., PIM-1 mixed matrix membranes for gas separations using cost-effective hypercrosslinked nanoparticle fillers. *Chemical Communications* **2016**, *52* (32), 5581-5584.
92. Swaidan, R.; Ghanem, B.; Litwiller, E.; Pinnau, I., Physical aging, plasticization and their effects on gas permeation in “rigid” polymers of intrinsic microporosity. *Macromolecules* **2015**, *48* (18), 6553-6561.
93. Kim, S.; Lee, Y. M., Rigid and microporous polymers for gas separation membranes. *Progress in Polymer Science* **2015**, *43*, 1-32.
94. Kulprathipanja, S.; Neuzil, R. W.; Li, N. N., Separation of fluids by means of mixed matrix membranes. Google Patents: **1988**.
95. Te Hennepe, H.; Bargeman, D.; Mulder, M.; Smolders, C., Zeolite-filled silicone rubber membranes: Part 1. Membrane preparation and pervaporation results. *Journal of Membrane Science* **1987**, *35* (1), 39-55.
96. Jia, M.; Peinemann, K.-V.; Behling, R.-D., Molecular sieving effect of the zeolite-filled silicone rubber membranes in gas permeation. *Journal of Membrane Science* **1991**, *57* (2-3), 289-292.
97. Nunes, S. P.; In: Mallada, R.; Menéndez, M., Inorganic membranes: synthesis, characterization and applications. *Elsevier* **2008** Vol. 13.
98. Maxwell, J. C., A Treatise on Electricity and Magnetism. *Dover Publication* **1873** Vol. 1.
99. Moore, T. T.; Koros, W. J., Non-ideal effects in organic–inorganic materials for gas separation membranes. *Journal of Molecular Structure* **2005**, *739* (1), 87-98.
100. Miller, S. J.; Kuperman, A.; Vu, D. Q., Mixed matrix membranes with small pore molecular sieves and methods for making and using the membranes. Google Patents: **2007**.
101. Koros, W. J.; Wallace, D.; Wind, J. D.; Miller, S. J.; Staudt-Bickel, C.; Vu, D. Q., Crosslinked and crosslinkable hollow fiber mixed matrix membrane and method of making same. Google Patents: **2004**.
102. Kulprathipanja, S.; Charoenphol, J., Mixed matrix membrane for separation of gases. Google Patents: **2004**.
103. Ekiner, O. M.; Kulkarni, S. S., Process for making hollow fiber mixed matrix membranes. Google Patents: **2003**.
104. Kitagawa, S.; Kitaura, R.; Noro, S. i., Functional porous coordination polymers. *Angewandte Chemie International Edition* **2004**, *43* (18), 2334-2375.
105. Rowsell, J. L.; Yaghi, O. M., Metal–organic frameworks: a new class of porous materials. *Microporous and Mesoporous Materials* **2004**, *73* (1), 3-14.

106. Rodenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; i Xamena, F. X. L.; Gascon, J., Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nature materials* **2015**, *14* (1), 48-55.
107. Lin, J. Y., Molecular sieves for gas separation. *Science* **2016**, *353* (6295), 121-122.
108. Nenoff, T. M., Hydrogen purification: MOF membranes put to the test. *Nature Chemistry* **2015**, *7* (5), 377-378.
109. Sabetghadam, A.; Seoane, B.; Keskin, D.; Duim, N.; Rodenas, T.; Shahid, S.; Sorribas, S.; Guillouzer, C. L.; Clet, G.; Tellez, C., Metal organic framework crystals in mixed matrix membranes: Impact of the filler morphology on the gas separation performance. *Advanced Functional Materials* **2016**.
110. Brown, A. J.; Brunelli, N. A.; Eum, K.; Rashidi, F.; Johnson, J.; Koros, W. J.; Jones, C. W.; Nair, S., Interfacial microfluidic processing of metal-organic framework hollow fiber membranes. *Science* **2014**, *345* (6192), 72-75.
111. Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T., Prospects for nanoporous metal-organic materials in advanced separations processes. *AIChE journal* **2004**, *50* (6), 1090-1095.
112. Lai, L. S.; Yeong, Y. F.; Lau, K. K.; Azmi, M. S., Zeolite imidazole frameworks membranes for CO₂/CH₄ separation from natural gas: A review. *Journal of Applied Sciences* **2014**, *14* (11), 1161.
113. Yang, T.; Shi, G. M.; Chung, T. S., Symmetric and asymmetric zeolitic imidazolate frameworks (ZIFs)/polybenzimidazole (PBI) nanocomposite membranes for hydrogen purification at high temperatures. *Advanced Energy Materials* **2012**, *2* (11), 1358-1367.
114. Yao, J.; Wang, H., Zeolitic imidazolate framework composite membranes and thin films: synthesis and applications. *Chemical Society Reviews* **2014**, *43* (13), 4470-4493.
115. Ding, S. Y.; Wang, W., Covalent organic frameworks (COFs): from design to applications. *Chemical Society Reviews* **2013**, *42* (2), 548-568.
116. Kharul, U. K.; Banerjee, R.; Biswal, B.; Chaudhari, H. D., Chemically stable covalent organic framework (COF)-polybenzimidazole hybrid membranes: Enhanced gas separation through pore modulation. *Chemistry—A European Journal* **2016**.
117. Kang, Z.; Peng, Y.; Qian, Y.; Yuan, D.; Addicoat, M. A.; Heine, T.; Hu, Z.; Tee, L.; Guo, Z.; Zhao, D., Mixed matrix membranes (MMMs) comprising exfoliated 2D covalent organic frameworks (COFs) for efficient CO₂ separation. *Chemistry of Materials* **2016**, *28* (5), 1277-1285.
118. Choudalakis, G.; Gotsis, A., Permeability of polymer/clay nanocomposites: a review. *European Polymer Journal* **2009**, *45* (4), 967-984.
119. Choi, S.; Coronas, J.; Lai, Z.; Yust, D.; Onorato, F.; Tsapatsis, M., Fabrication and gas separation properties of polybenzimidazole (PBI)/nanoporous silicates hybrid membranes. *Journal of Membrane Science* **2008**, *316* (1), 145-152.
120. Galve, A.; Sieffert, D.; Vispe, E.; Téllez, C.; Coronas, J.; Staudt, C., Copolyimide mixed matrix membranes with oriented microporous titanosilicate JDF-L1 sheet particles. *Journal of membrane science* **2011**, *370* (1), 131-140.
121. Yu, J.; Sugiyama, K.; Zheng, S.; Qiu, S.; Chen, J.; Xu, R.; Sakamoto, Y.; Terasaki, O.; Hiraga, K.; Light, M., Al₁₆P₂₀O₈₀H_{4.4}C₆H₁₈N₂: A new microporous aluminophosphate containing intersecting 12- and 8-membered ring channels. *Chemistry of materials* **1998**, *10* (5), 1208-1211.
122. Jeong, H. K.; Krych, W.; Ramanan, H.; Nair, S.; Marand, E.; Tsapatsis, M., Fabrication of polymer/selective-flake nanocomposite membranes and their use in gas separation. *Chemistry of Materials* **2004**, *16* (20), 3838-3845.
123. Kim, W. G.; Nair, S., Membranes from nanoporous 1D and 2D materials: A review of opportunities, developments, and challenges. *Chemical Engineering Science* **2013**, *104*, 908-924.

124. Pavlidou, S.; Papaspyrides, C., A review on polymer-layered silicate nanocomposites. *Progress in polymer science* **2008**, *33* (12), 1119-1198.
125. Kim, W. G.; Lee, J. S.; Bucknall, D. G.; Koros, W. J.; Nair, S., Nanoporous layered silicate AMH-3/cellulose acetate nanocomposite membranes for gas separations. *Journal of membrane science* **2013**, *441*, 129-136.
126. Ulbricht, M., Advanced functional polymer membranes. *Polymer* **2006**, *47* (7), 2217-2262.
127. Tasselli, F.; Donato, L.; Drioli, E., Evaluation of molecularly imprinted membranes based on different acrylic copolymers. *Journal of Membrane Science* **2008**, *320* (1), 167-172.
128. Son, S. H.; Jegal, J., Chiral separation of D-, L-serine racemate using a molecularly imprinted polymer composite membrane. *Journal of applied polymer science* **2007**, *104* (3), 1866-1872.
129. Ul-Haq, N.; Park, J. K., Optical resolution of phenylalanine using D- Phe- imprinted poly (acrylic acid-co-acrylonitrile) membrane—Racemate solution concentration effect. *Polymer Composites* **2008**, *29* (9), 1006-1013.
130. Cristallini, C.; Ciardelli, G.; Barbani, N.; Giusti, P., Acrylonitrile-acrylic acid copolymer membrane imprinted with uric acid for clinical uses. *Macromolecular bioscience* **2004**, *4* (1), 31-38.
131. Li, L.; Yin, Z.; Li, F.; Xiang, T.; Chen, Y.; Zhao, C., Preparation and characterization of poly (acrylonitrile-acrylic acid-N-vinyl pyrrolidinone) terpolymer blended polyethersulfone membranes. *Journal of Membrane Science* **2010**, *349* (1), 56-64.
132. Ramamoorthy, M.; Ulbricht, M., Molecular imprinting of cellulose acetate-sulfonated polysulfone blend membranes for Rhodamine B by phase inversion technique. *Journal of membrane science* **2003**, *217* (1), 207-214.
133. Kalim, R.; Schomäcker, R.; Yüce, S.; Brüggemann, O., Catalysis of a β -elimination applying membranes with incorporated molecularly imprinted polymer particles. *Polymer Bulletin* **2005**, *55* (4), 287-297.
134. Silvestri, D.; Borrelli, C.; Giusti, P.; Cristallini, C.; Ciardelli, G., Polymeric devices containing imprinted nanospheres: a novel approach to improve recognition in water for clinical uses. *Analytica chimica acta* **2005**, *542* (1), 3-13.
135. Brooks, T. W.; Daffin, C. L., *Polymer Preprints* **1969**, *10*, 1174-1181.
136. Lee, J. S.; Hirao, A.; Nakahama, S., Polymerization of monomers containing functional silyl groups. 7. Porous membranes with controlled microstructures. *Macromolecules* **1989**, *22* (6), 2602-2606.
137. Ishizu, K.; Amemiya, M., Charge mosaic composite membranes constructed by phase growth. *Journal of membrane science* **1990**, *54* (1), 75-87.
138. Phillip, W. A.; Rzayev, J.; Hillmyer, M. A.; Cussler, E., Gas and water liquid transport through nanoporous block copolymer membranes. *Journal of Membrane Science* **2006**, *286* (1), 144-152.
139. Morkved, T.; Lu, M.; Urbas, A.; Ehrichs, E., Local control of microdomain orientation in diblock copolymer thin films with electric fields. *Science* **1996**, *273* (5277), 931.
140. Schmidt, K.; Schoberth, H. G.; Ruppel, M.; Zettl, H.; Hänsel, H.; Weiss, T. M.; Urban, V.; Krausch, G.; Böker, A., Reversible tuning of a block-copolymer nanostructure via electric fields. *Nature materials* **2008**, *7* (2), 142-145.
141. Peinemann, K. V.; Abetz, V.; Simon, P. F., Asymmetric superstructure formed in a block copolymer via phase separation. *Nature materials* **2007**, *6* (12), 992-996.
142. Ikkala, O.; ten Brinke, G., Functional materials based on self-assembly of polymeric supramolecules. *Science* **2002**, *295* (5564), 2407-2409.
143. Nunes, S. P., Block copolymer membranes for aqueous solution applications. *Macromolecules* **2016**, *49* (8), 2905-2916.

144. Nunes, S. P.; Car, A., From charge-mosaic to micelle self-assembly: block copolymer membranes in the last 40 years. *Industrial & Engineering Chemistry Research* **2012**, *52* (3), 993-1003.
145. Hilke, R.; Pradeep, N.; Madhavan, P.; Vainio, U.; Behzad, A. R.; Sougrat, R.; Nunes, S. P.; Peinemann, K. V., Block copolymer hollow fiber membranes with catalytic activity and pH-response. *ACS applied materials & interfaces* **2013**, *5* (15), 7001-7006.
146. Yu, H.; Qiu, X.; Nunes, S. P.; Peinemann, K. V., Biomimetic block copolymer particles with gated nanopores and ultrahigh protein sorption capacity. *Nature communications* **2014**, *5*.
147. Nunes, S. P.; Behzad, A. R.; Hooghan, B.; Sougrat, R.; Karunakaran, M.; Pradeep, N.; Vainio, U.; Peinemann, K. V., Switchable pH-responsive polymeric membranes prepared via block copolymer micelle assembly. *ACS nano* **2011**, *5* (5), 3516-3522.
148. Nunes, S. P.; Sougrat, R.; Hooghan, B.; Anjum, D. H.; Behzad, A. R.; Zhao, L.; Pradeep, N.; Pinnau, I.; Vainio, U.; Peinemann, K. V., Ultraporous films with uniform nanochannels by block copolymer micelles assembly. *Macromolecules* **2010**, *43* (19), 8079-8085.
149. Madhavan, P.; Sutisna, B.; Sougrat, R.; Nunes, S., Photoresponsive nanostructured membranes. *RSC Advances* **2016**, *6* (79), 75594-75601.
150. Yu, H.; Qiu, X.; Moreno, N.; Ma, Z.; Calo, V. M.; Nunes, S. P.; Peinemann, K. V., Self-assembled asymmetric block copolymer membranes: Bridging the gap from ultra- to nanofiltration. *Angewandte Chemie International Edition* **2015**, *54* (47), 13937-13941.
151. Madhavan, P.; Hong, P. Y.; Sougrat, R.; Nunes, S. P., Silver-enhanced block copolymer membranes with biocidal activity. *ACS applied materials & interfaces* **2014**, *6* (21), 18497-18501.
152. Lehn, J., Supramolecular chemistry - Concepts and properties. VCH, Weinheim, Germany: **1995**.
153. Barboiu, M.; Cerneaux, S.; van der Lee, A.; Vaughan, G., Ion-driven ATP pump by self-organized hybrid membrane materials. *Journal of the American Chemical Society* **2004**, *126* (11), 3545-3550.
154. Barboiu, M., Constitutional hybrid materials—Toward selection of functions. *European Journal of Inorganic Chemistry* **2015**, *2015* (7), 1112-1125.
155. Sanchez, C.; Arribart, H.; Guille, M. M. G., Biomimetism and bioinspiration as tools for the design of innovative materials and systems. *Nature materials* **2005**, *4* (4), 277-288.
156. Toombes, G. E.; Mahajan, S.; Thomas, M.; Du, P.; Tate, M. W.; Gruner, S. M.; Wiesner, U., Hexagonally patterned lamellar morphology in ABC triblock copolymer/aluminosilicate nanocomposites. *Chemistry of Materials* **2008**, *20* (10), 3278-3287.
157. Simon, P. F.; Ulrich, R.; Spiess, H. W.; Wiesner, U., Block copolymer-ceramic hybrid materials from organically modified ceramic precursors. *Chemistry of materials* **2001**, *13* (10), 3464-3486.
158. Hoheisel, T. N.; Hur, K.; Wiesner, U. B., Block copolymer-nanoparticle hybrid self-assembly. *Progress in Polymer Science* **2015**, *40*, 3-32.
159. Jones, J. T.; Wood, C. D.; Dickinson, C.; Khimyak, Y. Z., Periodic mesoporous organosilicas with domain functionality: synthesis and advanced characterization. *Chemistry of Materials* **2008**, *20* (10), 3385-3397.
160. Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O., An ordered mesoporous organosilica hybrid material with a crystal-like wall structure. *Nature* **2002**, *416* (6878), 304-307.
161. Sanchez, C.; Boissiere, C.; Cassaignon, S.; Chaneac, C.; Durupthy, O.; Faustini, M.; Grosso, D.; Laberty-Robert, C.; Nicole, L.; Portehault, D., Molecular engineering of functional inorganic and hybrid materials. *Chemistry of Materials* **2013**, *26* (1), 221-238.
162. Jones, C. W., Zeolites go organic. *Science* **2003**, *300* (5618), 439-440.

163. Jirage, K. B.; Hulteen, J. C.; Martin, C. R., Nanotubule-based molecular-filtration membranes. *Science* **1997**, *278* (5338), 655-658.
164. Hollman, A. M.; Bhattacharyya, D., Pore assembled multilayers of charged polypeptides in microporous membranes for ion separation. *Langmuir* **2004**, *20* (13), 5418-5424.
165. Grainger, D.; Hägg, M. B., Evaluation of cellulose-derived carbon molecular sieve membranes for hydrogen separation from light hydrocarbons. *Journal of Membrane Science* **2007**, *306* (1), 307-317.
166. Steel, K. M.; Koros, W. J., Investigation of porosity of carbon materials and related effects on gas separation properties. *Carbon* **2003**, *41* (2), 253-266.
167. Su, B. L.; Vantomme, A.; Surahy, L.; Pirard, R.; Pirard, J. P., Hierarchical multimodal mesoporous carbon materials with parallel macrochannels. *Chemistry of materials* **2007**, *19* (13), 3325-3333.
168. Vu, D. Q.; Koros, W. J.; Miller, S. J., Effect of condensable impurity in CO₂/CH₄ gas feeds on performance of mixed matrix membranes using carbon molecular sieves. *Journal of Membrane Science* **2003**, *221* (1), 233-239.
169. Higuchi, A.; Yoshida, T.; Imizu, T.; Mizoguchi, K.; He, Z.; Pinnau, I.; Nagai, K.; Freeman, B. D., Gas permeation of fullerene- dispersed poly (1-trimethylsilyl-1-propyne) membranes. *Journal of Polymer Science Part B: Polymer Physics* **2000**, *38* (13), 1749-1755.
170. Sterescu, D. M.; Bolhuis-Versteeg, L.; van der Vegt, N. F.; Stamatialis, D. F.; Wessling, M., Novel gas separation membranes containing covalently bonded fullerenes. *Macromolecular rapid communications* **2004**, *25* (19), 1674-1678.
171. Reich, S.; Thomsen, C.; Maultzsch, J., *Carbon nanotubes: basic concepts and physical properties*. John Wiley & Sons: 2008.
172. Prehn, K.; Adelung, R.; Heinen, M.; Nunes, S. P.; Schulte, K., Catalytically active CNT-polymer-membrane assemblies: From synthesis to application. *Journal of Membrane Science* **2008**, *321* (1), 123-130.
173. Zhang, D.; Shi, L.; Fang, J.; Dai, K., Influence of diameter of carbon nanotubes mounted in flow-through capacitors on removal of NaCl from salt water. *Journal of materials science* **2007**, *42* (7), 2471-2475.
174. Planeix, J.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P.; Dutartre, R.; Geneste, P.; Bernier, P.; Ajayan, P., Application of carbon nanotubes as supports in heterogeneous catalysis. *Journal of the American Chemical Society* **1994**, *116* (17), 7935-7936.
175. Hinds, B. J.; Chopra, N.; Rantell, T.; Andrews, R.; Gavalas, V.; Bachas, L. G., Aligned multiwalled carbon nanotube membranes. *Science* **2004**, *303* (5654), 62-65.
176. Skoulidas, A. I.; Ackerman, D. M.; Johnson, J. K.; Sholl, D. S., Rapid transport of gases in carbon nanotubes. *Physical Review Letters* **2002**, *89* (18), 185901.
177. Kim, S.; Jinschek, J. R.; Chen, H.; Sholl, D. S.; Marand, E., Scalable fabrication of carbon nanotube/polymer nanocomposite membranes for high flux gas transport. *Nano letters* **2007**, *7* (9), 2806-2811.
178. Hummer, G.; Rasaiah, J. C.; Noworyta, J. P., Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* **2001**, *414* (6860), 188-190.
179. Corry, B., Designing carbon nanotube membranes for efficient water desalination. *The Journal of Physical Chemistry B* **2008**, *112* (5), 1427-1434.
180. Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O., Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* **2006**, *312* (5776), 1034-1037.
181. Fornasiero, F.; Park, H. G.; Holt, J. K.; Stadermann, M.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O., Ion exclusion by sub-2-nm carbon nanotube pores. *Proceedings of the National Academy of Sciences* **2008**, *105* (45), 17250-17255.

182. Li, W.; Wang, X.; Chen, Z.; Waje, M.; Yan, Y., Carbon nanotube film by filtration as cathode catalyst support for proton-exchange membrane fuel cell. *Langmuir* **2005**, *21* (21), 9386-9389.
183. Nednoor, P.; Chopra, N.; Gavalas, V.; Bachas, L.; Hinds, B., Reversible biochemical switching of ionic transport through aligned carbon nanotube membranes. *Chemistry of materials* **2005**, *17* (14), 3595-3599.
184. Liu, Z.; Lin, X.; Lee, J. Y.; Zhang, W.; Han, M.; Gan, L. M., Preparation and characterization of platinum-based electrocatalysts on multiwalled carbon nanotubes for proton exchange membrane fuel cells. *Langmuir* **2002**, *18* (10), 4054-4060.
185. Mi, W.; Lin, Y.; Li, Y., Vertically aligned carbon nanotube membranes on macroporous alumina supports. *Journal of Membrane Science* **2007**, *304* (1), 1-7.
186. Yang, D.; Wang, S.; Zhang, Q.; Sellin, P.; Chen, G., Thermal and electrical transport in multi-walled carbon nanotubes. *Physics Letters A* **2004**, *329* (3), 207-213.
187. Wang, Z.; Ci, L.; Chen, L.; Nayak, S.; Ajayan, P. M.; Koratkar, N., Polarity-dependent electrochemically controlled transport of water through carbon nanotube membranes. *Nano letters* **2007**, *7* (3), 697-702.
188. Walz, T.; Smith, B. L.; Zeidel, M. L.; Engel, A.; Agre, P., Biologically active two-dimensional crystals of aquaporin CHIP. *Journal of Biological Chemistry* **1994**, *269* (3), 1583-1586.
189. Qiao, R.; Georgiadis, J.; Aluru, N., Differential ion transport induced electroosmosis and internal recirculation in heterogeneous osmosis membranes. *Nano letters* **2006**, *6* (5), 995-999.
190. Majumder, M.; Zhan, X.; Andrews, R.; Hinds, B. J., Voltage gated carbon nanotube membranes. *Langmuir* **2007**, *23* (16), 8624-8631.
191. Ionita, M.; Pandele, M. A.; Iovu, H., Sodium alginate/graphene oxide composite films with enhanced thermal and mechanical properties. *Carbohydrate polymers* **2013**, *94* (1), 339-344.
192. Li, X.; Ma, L.; Zhang, H.; Wang, S.; Jiang, Z.; Guo, R.; Wu, H.; Cao, X.; Yang, J.; Wang, B., Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO₂ separation. *Journal of Membrane Science* **2015**, *479*, 1-10.
193. Wang, Z.; Yu, H.; Xia, J.; Zhang, F.; Li, F.; Xia, Y.; Li, Y., Novel GO-blended PVDF ultrafiltration membranes. *Desalination* **2012**, *299*, 50-54.
194. Johnson, J.; Koros, W. J., Utilization of nanoplatelets in organic-inorganic hybrid separation materials: separation advantages and formation challenges. *Journal of the Taiwan Institute of Chemical Engineers* **2009**, *40* (3), 268-275.
195. Gras, S. L.; Mahmud, T.; Rosengarten, G.; Mitchell, A.; Kalantar-zadeh, K., Intelligent control of surface hydrophobicity. *ChemPhysChem* **2007**, *8* (14), 2036-2050.
196. Heskins, M.; Guillet, J. E., Solution properties of poly (N-isopropylacrylamide). *Journal of Macromolecular Science—Chemistry* **1968**, *2* (8), 1441-1455.
197. Lue, S. J.; Hsu, J. J.; Wei, T. C., Drug permeation modeling through the thermo-sensitive membranes of poly (N-isopropylacrylamide) brushes grafted onto micro-porous films. *Journal of Membrane Science* **2008**, *321* (2), 146-154.
198. Chilkoti, A.; Dreher, M. R.; Meyer, D. E.; Raucher, D., Targeted drug delivery by thermally responsive polymers. *Advanced drug delivery reviews* **2002**, *54* (5), 613-630.
199. Pişkin, E., Molecularly designed water soluble, intelligent, nanosize polymeric carriers. *International journal of pharmaceuticals* **2004**, *277* (1), 105-118.
200. Kim, H. K.; Park, T. G., Synthesis and characterization of thermally reversible bioconjugates composed of α -chymotrypsin and poly (N-isopropylacrylamide-co-acrylamido-2-deoxy-D-glucose). *Enzyme and microbial technology* **1999**, *25* (1), 31-37.

201. Kikuchi, A.; Okano, T., Nanostructured designs of biomedical materials: applications of cell sheet engineering to functional regenerative tissues and organs. *Journal of Controlled Release* **2005**, *101* (1), 69-84.
202. Chen, Y. C.; Xie, R.; Chu, L. Y., Stimuli-responsive gating membranes responding to temperature, pH, salt concentration and anion species. *Journal of membrane science* **2013**, *442*, 206-215.
203. Ying, L.; Kang, E.; Neoh, K., Synthesis and characterization of poly (N-isopropylacrylamide)-graft-poly (vinylidene fluoride) copolymers and temperature-sensitive membranes. *Langmuir* **2002**, *18* (16), 6416-6423.
204. Ying, L.; Kang, E.; Neoh, K.; Kato, K.; Iwata, H., Drug permeation through temperature-sensitive membranes prepared from poly (vinylidene fluoride) with grafted poly (N-isopropylacrylamide) chains. *Journal of membrane science* **2004**, *243* (1), 253-262.
205. Wang, W.; Tian, X.; Feng, Y.; Cao, B.; Yang, W.; Zhang, L., Thermally on-off switching membranes prepared by pore-filling poly (N-isopropylacrylamide) hydrogels. *Industrial & Engineering Chemistry Research* **2009**, *49* (4), 1684-1690.
206. Adrus, N.; Ulbricht, M., Novel hydrogel pore-filled composite membranes with tunable and temperature-responsive size-selectivity. *Journal of Materials Chemistry* **2012**, *22* (7), 3088-3098.
207. Spohr, R.; Reber, N.; Wolf, A.; Alder, G. M.; Ang, V.; Bashford, C. L.; Pasternak, C. A.; Omichi, H.; Yoshida, M., Thermal control of drug release by a responsive ion track membrane observed by radio tracer flow dialysis. *Journal of controlled release* **1998**, *50* (1), 1-11.
208. Temtem, M.; Pompeu, D.; Barroso, T.; Fernandes, J.; Simões, P. C.; Casimiro, T.; do Rego, A. M. B.; Aguiar-Ricardo, A., Development and characterization of a thermoresponsive polysulfone membrane using an environmental friendly technology. *Green Chemistry* **2009**, *11* (5), 638-645.
209. Hsu, C. C.; Wu, C. S.; Liu, Y. L., Multiple stimuli-responsive poly (vinylidene fluoride) (PVDF) membrane exhibiting high efficiency of membrane clean in protein separation. *Journal of Membrane Science* **2014**, *450*, 257-264.
210. Guo, H.; Ulbricht, M., Preparation of thermo-responsive polypropylene membranes via surface entrapment of poly (N-isopropylacrylamide)-containing macromolecules. *Journal of Membrane Science* **2011**, *372* (1), 331-339.
211. Zhuang, M.; Liu, T.; Song, K.; Ge, D.; Li, X., Thermo-responsive poly (N-isopropylacrylamide)-grafted hollow fiber membranes for osteoblasts culture and non-invasive harvest. *Materials Science and Engineering: C* **2015**, *55*, 410-419.
212. Ou, R.; Wei, J.; Jiang, L.; Simon, G. P.; Wang, H., Robust thermoresponsive polymer composite membrane with switchable superhydrophilicity and superhydrophobicity for efficient oil-water separation. *Environmental science & technology* **2016**, *50* (2), 906-914.
213. Chen, Y. C.; Xie, R.; Yang, M.; Li, P. F.; Zhu, X. L.; Chu, L. Y., Gating characteristics of thermo-responsive membranes with grafted linear and crosslinked poly (N-isopropylacrylamide) gates. *Chemical engineering & technology* **2009**, *32* (4), 622-631.
214. Li, P. F.; Xie, R.; Jiang, J. C.; Meng, T.; Yang, M.; Ju, X. J.; Yang, L.; Chu, L. Y., Thermo-responsive gating membranes with controllable length and density of poly (N-isopropylacrylamide) chains grafted by ATRP method. *Journal of Membrane Science* **2009**, *337* (1), 310-317.
215. Hernández-Guerrero, M.; Min, E.; Barner-Kowollik, C.; Müller, A. H.; Stenzel, M. H., Grafting thermoresponsive polymers onto honeycomb structured porous films using the RAFT process. *Journal of Materials Chemistry* **2008**, *18* (39), 4718-4730.
216. Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D., Super-hydrophobic surfaces: from natural to artificial. *Advanced materials* **2002**, *14* (24), 1857-1860.

217. Lau, K. K.; Bico, J.; Teo, K. B.; Chhowalla, M.; Amaratunga, G. A.; Milne, W. I.; McKinley, G. H.; Gleason, K. K., Superhydrophobic carbon nanotube forests. *Nano letters* **2003**, *3* (12), 1701-1705.
218. Verplanck, N.; Galopin, E.; Camart, J.-C.; Thomy, V.; Coffinier, Y.; Boukherroub, R., Reversible electrowetting on superhydrophobic silicon nanowires. *Nano letters* **2007**, *7* (3), 813-817.
219. Sondag-Huethorst, J.; Fokkink, L., Potential-dependent wetting of electroactive ferrocene-terminated alkanethiolate monolayers on gold. *Langmuir* **1994**, *10* (11), 4380-4387.
220. Aydogan, N.; Gallardo, B. S.; Abbott, N. L., A molecular-thermodynamic model for Gibbs monolayers formed from redox-active surfactants at the surfaces of aqueous solutions: redox-induced changes in surface tension. *Langmuir* **1999**, *15* (3), 722-730.
221. Gallardo, B. S.; Abbott, N. L., Active control of interfacial properties: a comparison of dimeric and monomeric ferrocenyl surfactants at the surface of aqueous solutions. *Langmuir* **1997**, *13* (2), 203-208.
222. Gallardo, B. S.; Gupta, V. K.; Eagerton, F. D.; Jong, L. I.; Craig, V. S.; Shah, R. R.; Abbott, N. L., Electrochemical principles for active control of liquids on submillimeter scales. *Science* **1999**, *283* (5398), 57-60.
223. Gallardo, B. S.; Metcalfe, K. L.; Abbott, N. L., Ferrocenyl surfactants at the surface of water: principles for active control of interfacial properties. *Langmuir* **1996**, *12* (17), 4116-4124.
224. Riskin, M.; Basnar, B.; Chegel, V. I.; Katz, E.; Willner, I.; Shi, F.; Zhang, X., Switchable surface properties through the electrochemical or biocatalytic generation of Ag⁰ nanoclusters on monolayer-functionalized electrodes. *Journal of the American Chemical Society* **2006**, *128* (4), 1253-1260.
225. Tajima, K.; Huxur, T.; Imai, Y.; Motoyama, I.; Nakamura, A.; Koshinuma, M., Surface activities of ferrocene surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1995**, *94* (2), 243-251.
226. Balzani, V.; Credi, A.; Silvi, S.; Venturi, M., Artificial nanomachines based on interlocked molecular species: recent advances. *Chemical Society Reviews* **2006**, *35* (11), 1135-1149.
227. Chen, H.; Palmese, G. R.; Elabd, Y. A., Electrosensitive permeability of membranes with oriented polyelectrolyte nanodomains. *Macromolecules* **2007**, *40* (4), 781-782.
228. Chuo, T. W.; Wei, T. C.; Chang, Y.; Liu, Y. L., Electrically driven biofouling release of a poly (tetrafluoroethylene) membrane modified with an electrically induced reversibly cross-linked polymer. *ACS applied materials & interfaces* **2013**, *5* (20), 9918-9925.
229. Lahann, J.; Mitragotri, S.; Tran, T. N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R., A reversibly switching surface. *Science* **2003**, *299* (5605), 371-374.
230. Ichimura, K.; Oh, S. K.; Nakagawa, M., Light-driven motion of liquids on a photoresponsive surface. *Science* **2000**, *288* (5471), 1624-1626.
231. Abbott, S.; Ralston, J.; Reynolds, G.; Hayes, R., Reversible wettability of photoresponsive pyrimidine-coated surfaces. *Langmuir* **1999**, *15* (26), 8923-8928.
232. Budyka, M. F., Diarylethylene photoisomerization and photocyclization mechanisms. *Russian Chemical Reviews* **2012**, *81* (6), 477-493.
233. He, D.; Susanto, H.; Ulbricht, M., Photo-irradiation for preparation, modification and stimulation of polymeric membranes. *Progress in Polymer Science* **2009**, *34* (1), 62-98.
234. Bunker, B.; Kim, B.; Houston, J.; Rosario, R.; Garcia, A.; Hayes, M.; Gust, D.; Picraux, S., Direct observation of photo switching in tethered spiropyrans using the interfacial force microscope. *Nano Letters* **2003**, *3* (12), 1723-1727.
235. Uda, R. M.; Matsui, T.; Oue, M.; Kimura, K., Membrane potential photoresponse of crowned malachite green derivatives affording perfect photoswitching of metal ion

- complexation. *Journal of inclusion phenomena and macrocyclic chemistry* **2005**, *51* (1-2), 111-117.
236. Vlassioulk, I.; Park, C. D.; Vail, S. A.; Gust, D.; Smirnov, S., Control of nanopore wetting by a photochromic spiropyran: a light-controlled valve and electrical switch. *Nano letters* **2006**, *6* (5), 1013-1017.
237. Oosaki, S.; Hayasaki, H.; Sakurai, Y.; Yajima, S.; Kimura, K., Photocontrol of ion-sensor performances in neutral-carrier-type ion sensors based on liquid-crystalline membranes. *Chemical communications* **2005**, (41), 5226-5227.
238. Nicoletta, F. P.; Cupelli, D.; Formoso, P.; De Filpo, G.; Colella, V.; Gugliuzza, A., Light responsive polymer membranes: a review. *Membranes* **2012**, *2* (1), 134-197.
239. Hendri, J.; Hiroki, A.; Maekawa, Y.; Yoshida, M.; Katakai, R., Permeability control of metal ions using temperature- and pH-sensitive gel membranes. *Radiation Physics and Chemistry* **2001**, *60* (6), 617-624.
240. Park, H. W.; Jin, H. S.; Yang, S. Y.; Kim, J. D., Tunable phase transition behaviors of pH-sensitive polyaspartamides having various cationic pendant groups. *Colloid and Polymer Science* **2009**, *287* (8), 919-926.
241. Park, Y. S.; Ito, Y.; Imanishi, Y., pH-controlled gating of a porous glass filter by surface grafting of polyelectrolyte brushes. *Chemistry of materials* **1997**, *9* (12), 2755-2758.
242. Peters, A. M.; Lammertink, R. G.; Wessling, M., Comparing flat and micro-patterned surfaces: Gas permeation and tensile stress measurements. *Journal of Membrane Science* **2008**, *320* (1), 173-178.
243. Ariga, K.; Hill, J. P.; Ji, Q., Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application. *Physical Chemistry Chemical Physics* **2007**, *9* (19), 2319-2340.