
2 Synthetic Membranes for Membrane Processes

2.1 Introduction

According to Wikipedia [1], a membrane is a thin, typically planar structure or material that separates two environments or phases and has a finite volume. It can be referred to as an interphase rather than an interface. Membranes selectively control mass transport between phases or environments. Again, according to Wikipedia, membranes can be divided into three groups: (1) biological membranes, (2) artificial membranes, and (3) theoretical membranes.

Biological membranes include:

1. Cell membranes and intracellular membranes
2. Mucous membranes
3. S-layer
4. Serous membranes and mesothelia that surround organs, including:
 - a) The peritoneum that lines the abdominal cavity
 - b) The pericardium that surrounds the heart
 - c) The pleura that surrounds the lungs
 - d) The periosteum that surrounds bone
 - e) The meninges that surround the brain (the dura mater, the arachnoid, and the pia mater)

Artificial membranes are used in:

1. Reverse osmosis
2. Filtration (microfiltration, ultrafiltration)
3. Pervaporation
4. Dialysis
5. Emulsion liquid membranes
6. Membrane-based solvent extraction
7. Membrane reactors
8. Gas permeation
9. Supported liquid membranes

This book is devoted to synthetic, or artificial, membranes. In particular, our focus will be on polymeric synthetic membranes, since most industrial membranes belong to this category. Before entering the main subject of this book, i.e., atomic force

microscopy, the current status of synthetic polymeric membranes is outlined. Thus, in the following pages, we will provide some information about the preparation of membranes, the properties of membranes, and their applications.

2.2 Membrane Preparation

Synthetic membranes are fabricated in two main geometries:

1. Flat sheet—utilized in the construction of flat sheet, disc, spirally wound, plate, and frame modules
2. Cylindrical—utilized in tubular and capillary, or hollow fiber, modules

Membranes can be prepared from both ceramic and polymeric materials. Ceramic materials have several advantages over polymeric materials, such as higher chemical and thermal stability. However, the market share of polymeric membranes is far greater than ceramic membranes as the polymeric materials are easier to process and less expensive. A handful of technical polymers are currently used as membrane materials for 95% of all practical applications [2]. Polymeric materials that are used to prepare separation membranes are mostly organic compounds. A number of different techniques are available to prepare synthetic membranes.

2.2.1 Membranes with Symmetric Structure

Although most of the practically useful membranes are asymmetric, as explained later, some of the membranes have symmetric structures. They are prepared in the following ways:

Track etching A sheet of polymeric film moves underneath a radiation source and is irradiated by high-energy particles. The spots that are subjected to bombardment of the particles are degraded or chemically altered during this process. Then, the film undergoes an etching process in an alkaline or hydrogen peroxide bath (depending on the material), where the polymer is etched along the path of high-energy particles.

Precipitation from the vapor phase A cast polymer solution that consists of polymer and solvent is brought into a nonsolvent vapor environment saturated with solvent vapor. The saturated solvent vapor suppresses the evaporation of solvent from the film; the nonsolvent molecules diffuse into the film causing polymer coagulation.

2.2.2 Membranes with Asymmetric Structure

Most membranes used in industries have an asymmetric structure. Figure 2.1 shows schematically a typical cross-sectional view of an asymmetric membrane [3]. It consists of two layers: the top one is a very thin dense layer (also called the top skin layer), and the bottom one is a porous sublayer. The top dense layer governs the performance (permeation properties) of the membrane; the porous sublayer only provides mechanical strength to the membrane. The membranes of symmetric structures do not possess a top dense layer. In the asymmetric membrane, when the material of the top

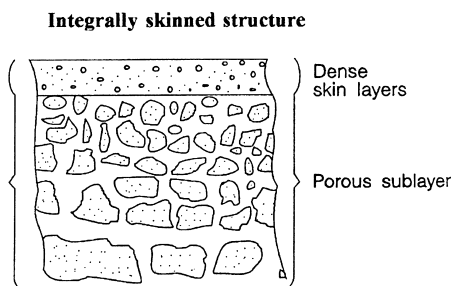


Fig. 2.1. Cross-sectional view of an asymmetric membrane. Reprinted from [3], with kind permission from the author

layer and porous sublayer are the same, the membrane is called an *integrally skinned* asymmetric membrane. On the other hand, if the polymer of the top skin layer is different from the polymer of the porous sublayer, the membrane is called a *composite* membrane. The advantage of the composite membrane over the integrally skinned asymmetric membrane is that the material for the top skin layer and the porous sublayer can be chosen separately to optimize the overall performance. There are various methods for the preparation of asymmetric membranes, which are described in the sections that follow.

2.2.2.1 Phase Inversion Technique for Preparation of Integrally Skinned Asymmetric Membranes

Dry-wet phase inversion technique (Loeb-Sourirajan method) A number of methods can be used to achieve phase inversion. Among these, the dry-wet phase inversion technique and thermally induced phase separation (TIPS) are the most commonly used in membrane manufacturing. The dry-wet phase inversion technique, also called the *Loeb-Sourirajan* technique, was used by Loeb and Sourirajan in their development of the first cellulose acetate membrane for seawater desalination [4]. In this method, a polymer solution is prepared by mixing polymer and solvent (sometimes even nonsolvent). The solution is then cast on a suitable surface by a *doctor blade* to a precalculated thickness. After a partial evaporation of the solvent, the cast film is immersed in a nonsolvent medium called a *gelation bath*. Due to a sequence of two desolvation steps, i.e., evaporation of the solvent and solvent-nonsolvent exchange in the gelation bath, solidification of the polymer film takes place. It is desirable to choose a solvent of strong dissolving power with a high volatility. During the first step of desolvation by solvent evaporation, a thin skin layer of solid polymer is formed instantly at the top of the cast film due to the loss of solvent. In the solvent-nonsolvent exchange process that follows, the nonsolvent diffuses into the polymer solution film through the thin solid layer while the solvent diffuses out. The change in the composition of the polymer solution film during the solvent-nonsolvent exchange process, often called a composition path, is illustrated schematically in Fig. 2.2 (lines A, B, and C each represent a composition path).

The top skin layer can also be made porous by lowering the polymer concentration in the casting solution and the solvent evaporation period. This is called, hereafter, the porous skin layer. Asymmetric membranes can also be made in a tubular form using a casting bob assembly and a hollow fiber spinneret [5].

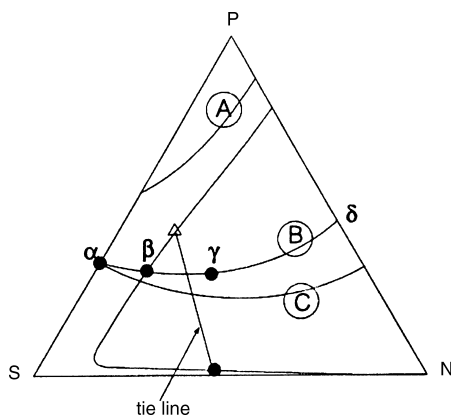


Fig. 2.2. Triangular diagram of polymer (P), solvent (S), and nonsolvent (N). Reprinted from [3], with kind permission from the author

Thermally induced phase separation method In this method, phase inversion is introduced by lowering the temperature of the polymer solution. A polymer is mixed with a substance that acts as a solvent at a high temperature and the polymer solution is cast into a film. When the solution is cooled, it enters into an immiscible region due to the loss of solvent power. Because the solvent is usually nonvolatile, it must be removed with a liquid that is miscible with the solvent but not miscible with the polymer.

2.2.2.2 Preparation of Composite Membranes

Dip coating An integrally skinned asymmetric membrane with a porous skin layer (called hereafter a substrate membrane) is prepared from a polymer solution by applying the dry-wet phase inversion method. The membrane is then dried according to the method described later, before it is dipped into a bath containing a dilute solution of another polymer. When the membrane is taken out of the bath, a thin layer of coating solution is deposited on the top of the substrate membrane. The solvent is then removed by evaporation, leaving a thin layer of the latter polymer on top of the substrate membrane.

Interfacial polymerization This method, developed by Cadotte and the coworkers of Film Tech in the 1970s, is currently most widely used to prepare high performance reverse osmosis and nanofiltration membranes [6]. A thin selective layer is deposited on top of a porous substrate membrane by interfacial *in situ* polycondensation. There are a number of modifications of this method primarily based on the choice of the monomers [7]. However, for simplicity, the polycondensation procedure is described by a pair of diamine and diacid chloride monomers.

A diamine solution in water and a diacid chloride solution in hexane are prepared. A porous substrate membrane is then dipped into the aqueous solution of diamine. The pores at the top of the porous substrate membrane are filled with the aqueous solution in this process. The membrane is then immersed in the diacid chloride solution in hexane. Since water and hexane are not miscible, an interface is formed at the boundary of the two phases. Polycondensation of diamine and diacid chloride

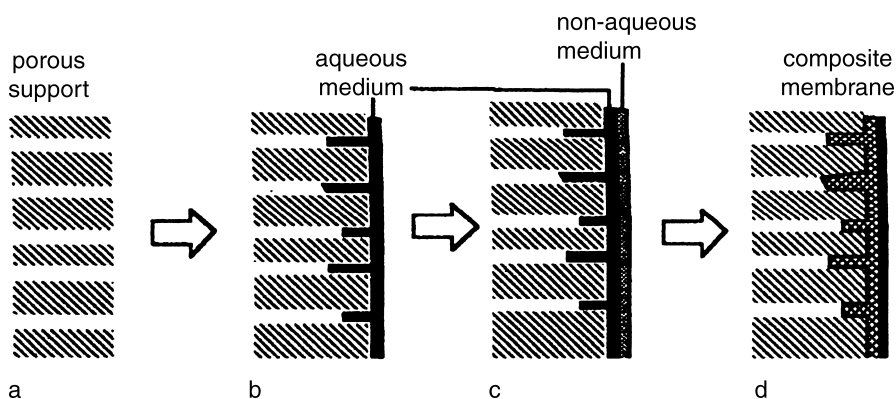


Fig. 2.3. Steps in the formation of a composite membrane via interfacial polymerization. Reprinted from [3], with kind permission from the author

takes place at the interface, resulting in a very thin layer of polyamide. The preparation of composite membranes by interfacial in situ polycondensation is schematically presented in Fig. 2.3.

2.2.2.3 Membrane Surface Modification

As mentioned above, the top skin layer governs the performance of a separation membrane. The surface deposition of contaminants from solutions or from gas mixtures is also affected by the surface properties of the membrane. This is particularly important when decline in the membrane flux with a prolonged operating period is observed, since it is often caused by the contaminant deposition. Hence, many attempts have been made to modify the membrane surface, aimed at prevention of contaminant deposition and maintenance of high flux. Several methods of surface modification are described below.

Chemical modification The surface of a membrane can be modified by chemical reactions. For example, when the surface of a polyamide composite membrane is brought into contact with a strong hydrofluoric acid solution, the top polyamide layer becomes slightly thinner by a chemical reaction with hydrofluoric acid. As a result, the flux increases considerably while the rejection of sodium chloride is unchanged or slightly increased [8].

Plasma polymerization When a vacuum is maintained inside a tubular reactor and a high frequency electric field is applied outside, a glow discharge is generated inside the reactor (Fig. 2.4). Plasma that consists of various ions, radicals, electrons, and molecules is formed in the glow discharge. When a porous substrate membrane is placed in the plasma, the surface of the membrane is subjected to various changes corresponding to the property of plasma. The substrate surface can be etched and/or chemically active sites can be introduced to the surface, and, upon contact with organic compounds, an irregular polymerization can occur at the substrate surface. This is called plasma polymerization [9].

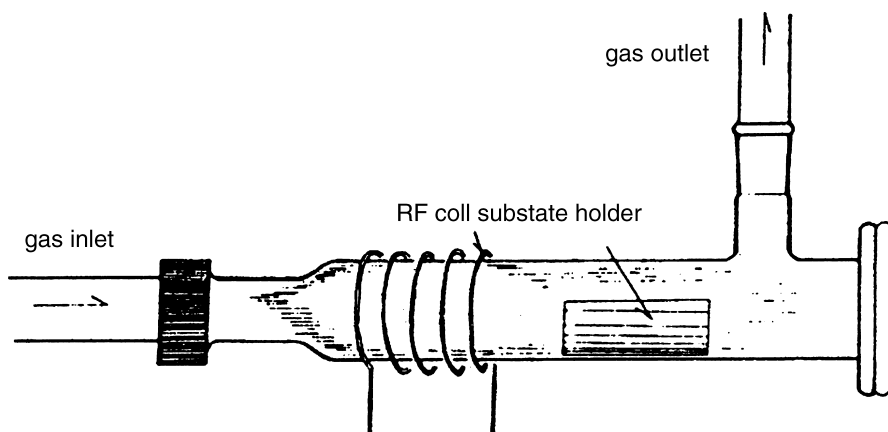


Fig. 2.4. Reactor for plasma treatment. Reprinted from [3], with kind permission from the author

Graft polymerization The surface of a porous substrate membrane is irradiated with γ -rays, which causes the generation of radicals on the membrane surface. Then, the membrane is immersed in a monomer solution. The graft polymerization of the monomers is initiated at the membrane surface. By choosing a very hydrophilic monomer, the hydrophilicity of the surface is increased considerably.

Surface modification by surface modifying macromolecules (SMMs) In a polymer blend, thermodynamic incompatibility between polymers usually causes demixing of polymers. If the polymer is equilibrated in air, the polymer with the lowest surface energy (the hydrophobic polymer) will concentrate at the air interface and reduce the system's interfacial tension as a consequence. The preferential adsorption of a polymer of lower surface tension at the surface was confirmed by a number of researchers for the miscible blend of two different polymers. Based on this concept, surface modifying macromolecules as surface-active additives were synthesized and blended into polymer solutions of poly(ether sulfone) (PES). Depending on the hydrophobic [10, 11] or hydrophilic [12] nature of the SMMs, the membrane surface becomes either more hydrophobic or more hydrophilic than the base polymeric material.

2.2.3 Membrane Drying

The wet cellulose acetate membranes prepared for reverse osmosis purposes can be used for gas separation when they are dried. The water in the cellulose acetate membrane cannot be evaporated in air, however, since the asymmetric structure of the membrane will collapse. Instead, the multi-stage solvent exchange and evaporation method is applied. In this method, a water-miscible solvent such as ethanol first replaces the water in the membrane. Then, a second volatile solvent such as hexane replaces the first solvent. The second solvent is subsequently air-evaporated to obtain a dry membrane [13, 14]. The reason for replacing water with hexane is to reduce the capillary force inside the pore so that it will not collapse during the drying process.

2.3 Membranes for Separation Processes

2.3.1 Membranes for the Separation of Solutions and Solvent Mixtures

Membranes for the separation of solutions and liquid mixtures may be distinguished on the basis of pore sizes as reverse osmosis (RO, below 1 nm), ultrafiltration (UF, 2–100 nm), and microfiltration (MF, 100 nm to 2 μm), although this classification is very arbitrary. Pore sizes of nanofiltration (NF) membranes are between RO and UF membranes.

2.3.1.1 Reverse Osmosis Membranes

An RO membrane acts as a barrier to flow, allowing selective passage of a particular species (solvent) while other species (solutes) are retained partially or completely. Solute separation and permeate solvent (water in most cases) flux depend on the material selection, the preparation procedures, and the structure of the membrane barrier layer [5, 15]. Cellulose acetate (CA) is the material for the first generation reverse osmosis membrane. The announcement of CA membranes for sea water desalination by Loeb and Sourirajan in 1960 triggered the applications of membrane separation processes in many industrial sectors. CA membranes are prepared by the dry–wet phase inversion technique. Another polymeric material for RO is aromatic polyamide [16].

In aromatic polyamide polymers, aromatic rings are connected by an amide linkage, $-\text{CONH}-$. While the aromatic ring attached to $-\text{NH}-$ is metasubstituted, the ring attached to $-\text{CO}-$ is the mixture of meta- and parasubstitutions, which gives more flexibility to the polymeric material. Aromatic polyamide remains one of the most important materials for reverse osmosis membranes since the thin selective layer of composite membranes is aromatic polyamide synthesized by interfacial in situ polymerization.

2.3.1.2 Nanofiltration Membranes

Most NF membranes are negatively charged. In interfacial polycondensation, trimethylolpropane tri(2-hydroxyethyl) phosphate triacid chloride is often mixed with phthaloyl (diacid) chloride in the acidic component of the polycondensation reaction. Although most carboxylic groups are consumed to form amide linkage, a small portion of the carboxylic groups do not participate in the reaction, becoming the source of the electric charge. Since $-\text{COOH}$ becomes $-\text{COO}^-$ upon dissociation, the membranes are negatively charged. Because of the negative charge, anions are preferentially rejected by nanofiltration membranes.

Another method of preparing nanofiltration membranes is to dip-coat a thin layer of sulfonated poly(phenylene oxide) (SPPO) [17], sulfonated polysulfone (SPS) [18], or carboxylated polysulfone [19] on a porous substrate membrane. The sulfonic acid groups in SPPO and SPS also become negatively charged with $-\text{SO}_3^-$ groups upon dissociation. Sulfonic acid is a stronger acid than carboxylic acid.

2.3.1.3 Ultrafiltration Membranes

Ultrafiltration is primarily a size-exclusion-based, pressure-driven membrane separation process. UF membranes typically have pore sizes in the range of 2–500 nm and retain species in the molecular range from 3000 to 500 000 Da [20], while sol-

vent (water) passes through the membrane. UF membranes have a porous skin layer. The most important UF membrane properties are the membrane productivity (flux) and extent of separation (rejection of various feed components).

In contrast to the polymeric materials for reverse osmosis and nanofiltration membranes, for which the macromolecular structures have much to do with permeation properties such as salt rejection characteristics, the choice of membrane material for ultrafiltration does not depend on the material's influence on the permeation properties.

Membrane permeation properties are largely governed by the pore sizes and the pore size distributions of UF membranes. Rather, thermal, chemical, mechanical, and biological stability are considered of greater importance. Typical UF membrane materials are polysulfone (PS), poly(ether sulfone), poly(ether ether ketone) (PEEK), cellulose acetate and other cellulose esters, polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF), polyimide (PI), poly(etherimide) (PEI), and aliphatic polyamide (PA). All these polymers have a T_g higher than 145 °C except for cellulose esters. They are also stable chemically and mechanically, and their biodegradability is low. The membranes are made by the dry-wet phase inversion technique.

2.3.1.4 Microfiltration Membranes

Polymeric materials for MF membranes cover a very wide range, from relatively hydrophilic to very hydrophobic materials. Typical hydrophilic materials are polysulfone, poly(ether sulfone), cellulose (CE) and cellulose acetate, polyamide, polyimide, poly(etherimide) and polycarbonate (PC). Typical hydrophobic materials are polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE, Teflon) and poly(vinylidene fluoride).

Hydrophilic MF membranes can be made by the dry-wet phase inversion technique, which can also be used to make PVDF membranes. On the other hand, other hydrophobic microfiltration membranes are made by the thermally induced phase separation technique. In particular, semicrystalline PE, PP, and PTFE are stretched parallel to the direction of film extrusion so that the crystalline regions are aligned in the direction of stretch, while the noncrystalline region is ruptured, forming long and narrow pores. Hydrophobic membranes do not allow penetration of water into the pore until the transmembrane pressure drop reaches a threshold called the liquid entry pressure of water (LEP_w). These membranes can therefore be used for membrane distillation. The track-etching method is applied to make microfiltration membranes from PC.

An especially important characteristic of a microfiltration membrane is uniform pores with as many of them per unit area as possible, and with the thinnest possible layer where these pores are at their smallest. The use of MF membranes is the quantitative separation of suspended matter in the 0.1–10 µm size range from liquids and gases.

2.3.2 Membranes for Gas and Vapor Separation

The concept of separating gases with polymeric membranes is more than 100 years old, but the widespread use of gas separation membranes has occurred only within

the last 20–30 years. Separation is achieved because of differences in the relative transport rates of feed components. Components that diffuse more rapidly become enriched in the low pressure *permeate* stream, while the slower components are concentrated in the *retentate*, or residue, stream. The membrane process that separates components based on their relative rates of permeation distinguishes it from equilibrium processes such as distillation or extraction.

Gas and vapor separation membranes are classified into two categories. In the first, rubbery polymers such as silicone rubber, natural rubber, and poly(4-methyl-1-pentene) are used to take advantage of their high permeabilities, even though selectivities are rather moderate. Production of enriched oxygen for medical purposes is performed by this type of membrane with an oxygen/nitrogen selectivity of about two. Asymmetric membranes made from glassy polymers such as cellulose acetate and other cellulose derivatives, polycarbonate, aromatic polyamide, aromatic polyimides, and poly(phenylene oxide) (PPO) and its derivatives belong to the second category.

These asymmetric membranes are made by the dry–wet phase inversion technique. Membranes must be dried before being used. Solvent exchange is necessary to dry cellulose acetate membranes. These membranes take advantage of the high selectivity of glassy polymers. The selective dense layer at the top of the membrane must be very thin so that a high flux can be achieved. They are used in a wide range of industrial gas separation processes such as hydrogen recovery from various chemical syntheses, sour gas removal from natural gas and production of nitrogen-enriched air. For the asymmetric membranes to be effective in gas separation, the thin selective layer at the top of the membrane should be perfect. This requirement is more stringent in gas separation membranes than liquid separation membranes since defective pores cannot be automatically closed when the surface is in contact with dry gas. In contrast, defective pores of RO and pervaporation (PV) membranes can be closed by the swelling of the top skin layer when it is brought into contact with feed liquid.

Since it is difficult to make a selective skin layer defect-free, a method was proposed by Henis and Tripodi to seal defective pores. Their method was applied to asymmetric polysulfone membranes, which led to the production of the commercial Prism membrane [21].

According to the method, a relatively thick silicone rubber layer is coated on a thin selective layer of an asymmetric polysulfone membrane. The thickness of silicone rubber is about 1 μm while the effective thickness of the selective polysulfone layer is one tenth of 1 μm . While being coated, silicone rubber penetrates into the pores to plug them. Thus, feed gas is not allowed to leak through the defective pores. The selectivity of the membrane approaches that of the defect-free polysulfone layer. Moreover, since the permeabilities of silicone rubber for gases are orders of magnitudes higher than those of polysulfone, the permeation rate is not affected very much even when a relatively thick silicone rubber layer is coated.

Membranes for vapor removal from air have a structure similar to the Prism membrane, but they are prepared on a different principle [22]. Aromatic poly(etherimide) is used to produce a porous substrate membrane by the dry–wet phase inversion method. This polymer was chosen over polysulfone/poly(ether sul-

fone) due to the higher durability of poly(etherimide) to organic vapors. Unlike an asymmetric polysulfone substrate for the Prism membrane, the top layer of the asymmetric poly(etherimide) membrane has a large number of pores, the size of which is equivalent to those of ultrafiltration membranes. When a layer of silicone rubber is coated on the top layer of the porous substrate membrane, the silicone rubber layer will govern the selectivity, and the porous support will provide only mechanical strength to the composite membrane. Since the permeabilities of water and organic vapors through the silicone rubber layer are much greater than those of oxygen and nitrogen, these membranes are effective in dehumidification of air and removal of organic vapors from air.

2.3.3 Membranes for Pervaporation and Membrane Distillation

Pervaporation and membrane distillation (MD) are distinguished from the above membrane separation processes since phase change, from liquid to vapor, takes place in the process.

2.3.3.1 Pervaporation

Pervaporation is characterized by the imposition of a barrier (membrane) layer between a liquid and a vaporous phase, with a mass transfer occurring selectively across the barrier to the vapor side. Separation occurs with the efficacy of the separation effect being determined by the physiochemical structure of the membrane.

Pervaporation membranes were developed for the dehydration of ethanol and other organic solvents. Therefore, the dense selective layer is made of polyvinyl alcohol that is one of the most hydrophilic materials. Water is preferentially sorbed to polyvinyl alcohol and also preferentially transported. To suppress the excessive swelling of polymer in water, polyvinyl alcohol is partially cross-linked by dialdehydes such as glutaraldehyde [23].

The dense polyvinyl alcohol layer is supported by a porous PAN substrate membrane. Polyelectrolyte material [24] and chitosan [25], a natural product, are also potentially useful for dehydration by pervaporation. Silicone rubber membranes developed for the removal of organic vapors from air can also be used for the removal of volatile organic compounds (VOCs) from water by pervaporation [23]. Because of the high hydrophobic nature of silicone rubber, VOCs are preferentially sorbed and transported through the membrane.

2.3.3.2 Membrane Distillation

Membrane distillation is similar to pervaporation since phase change is involved in the process. When feed liquid (usually water) is in contact with a nonwetted porous hydrophobic membrane, water does not enter into the pores because the feed liquid is maintained below a threshold pressure, the liquid penetration pressure of water. Only water vapor permeates through the pores from the feed to the permeate side. The driving force is the vapor pressure drop from the feed to the permeate side, since the permeate temperature is maintained below the feed temperature. Commercial hydrophobic membranes made of polypropylene, poly(vinylidene fluoride) and poly-

Synthetic Polymeric Membranes
Characterization by Atomic Force Microscopy
Khulbe, K.C.; Feng, C.Y.; Matsuura, T.
2008, XVIII, 198 p. 146 illus., Hardcover
ISBN: 978-3-540-73993-7