

Membrane Materials Science

An Overview

DOUGLAS R. LLOYD

Department of Chemical Engineering, Separations Research Program, Center for Polymer Research, The University of Texas at Austin, Austin, TX 78712

Material science aspects of synthetic polymeric membranes are presented in this survey. The objective is to place each of the subsequent chapters of this volume into proper perspective. Therefore, frequent reference is made to the accompanying chapters and, where necessary, to alternative information sources. By way of introduction, this chapter considers in turn: material selection, material characterization and evaluation, membrane preparation, membrane characterization and membrane evaluation. Membrane module design and manufacture, transport phenomena and process performance are introduced in the discussion only as they pertain to membrane materials science. Following this introduction, the various chapters of this volume are previewed.

Membrane science is a phrase that encompasses a vast array of topics (1). The common thread that ties together the various aspects of membrane science is that each one deals to some extent with the study of permeation and permeable media. More specifically, the permeable medium or membrane is a phase between two phases. The role of the membrane may be either to change the composition of a solution on the basis of relative permeation rates (membrane separation processes), to physically or chemically modify the permeating species (ion-exchange membranes and biofunctional membranes), to conduct electric current, to prevent permeation (packaging and coating) or to regulate the rate of permeation (controlled release). Functionally, membranes may be either *passive* or *reactive* depending upon the membrane's ability to alter the chemical nature of the permeating species. Membranes can also be categorized as being either *neutral* or *charged* according to their ionic nature. Structurally, membranes can be categorized as being either *non-porous* (that is, membranes in which the membrane phase is continuous, such as dense polymeric films and liquid

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membranes) or *porous* to various extents (for example, porous polymeric films in which both the polymer matrix and the void spaces are continuous. Further categorization according to the porous structure of these co-continuous membranes is discussed below under the heading "Membrane Preparation"). The various chapters in this book discuss the materials science of synthetic polymeric membranes for separations, conductive membranes and reactive membranes.

Membrane performance is often measured by the ability of the membrane to prevent, regulate or facilitate permeation. The rate of permeation and the mechanism of transport depend upon the magnitude of the driving force, the size of the permeating molecule relative to the size of the available permanent or dynamic transport corridor and the chemical nature (dispersive, polar, ionic, etc.) of both the permeant and the polymeric membrane material.

Membrane science can arbitrarily be divided into seven intimately related categories: material selection, material characterization and evaluation, membrane preparation, membrane characterization and evaluation, transport phenomena, membrane module design and process performance. This chapter and those to follow emphasize the materials science aspects of synthetic polymeric membranes; that is, the selection, characterization and evaluation of membrane materials as well as the preparation, characterization and evaluation of membranes. Transport phenomena, membrane module design and process performance enter the discussion only as these topics pertain to materials science.

Material Selection. In designing a membrane, one must first determine the physicochemical nature of the permeants (gas, vapor, liquid, solid; dispersive, polar, ionic; reactive, inert; physical size and shape). The membrane scientist then has *two materials science controls* over permeation: *membrane material selection* and *membrane preparation procedures*. Membrane material selection allows control over the nature and magnitude of the permeant-membrane physicochemical interactions. Choice of membrane material also determines the packing density and segment mobility of the polymer chains which comprise the solid regions of the membrane. Membrane preparation procedures determine membrane morphology and the extent to which physical considerations, such as steric hindrance, influence the rate of permeation. Together, material selection and membrane preparation procedures influence the mechanism of transport, membrane stability and membrane performance.

In the past, membrane material selection for gas separations (2) and liquid separations has often followed either an Edisonian or a common sense approach. For example, almost every polymer that can be formed into a film has been characterized in terms of gas permeability (at least for a few common gases). In this volume, Chern et al. (3) and Lloyd and Meluch (4) discuss membrane material selection in terms of physicochemical interactions for gas mixture separations and liquid mixture separations, respectively. Hoehn (5) presents similar arguments for membrane material selection in general. In comparison to the wide variety of polymers investigated

for their gas transport properties, the number of polymers studied for their liquid transport properties is somewhat limited. However, a survey of recent literature and patents (4) indicates that an ever-increasing number of polymers, copolymers and blends are being considered as potential membrane materials for liquid mixture separations. It is interesting to compare the number of materials which have reached commercialization for liquid separations and gas separations. Lloyd and Meluch (4) list in excess of twenty-seven polymers, copolymers and blends currently being used for liquid separation membranes. However, only polysulfone and a variety of cellulose acetates and silicone based polymers have attained commercial success for gas mixture separations (6).

In addition to the guidelines suggested by Chern et al. (3) and by Lloyd and Meluch (4), Ward et al. (7) point out that biocompatibility and sterilizability need to be considered when selecting membrane materials for therapeutic applications.

Each of these chapters (3-7), plus the chapter by Cadotte (8), demonstrates that one can molecularly engineer polymer chemical structures to obtain membrane materials which theoretically can achieve the desired control over permeability. Alternatively, the ideas developed (3-5) can simply serve as criteria by which one can select, from a list of available polymers, those membrane materials with the greatest potential for achieving the desired control over permeability.

Material Characterization and Evaluation. Physicochemical considerations can be useful in membrane material selection. However, it would be beneficial if one could experimentally verify that the proper choice has been made prior to undertaking the often difficult tasks of membrane preparation and characterization. In addition, it is frequently beneficial to have fully characterized the polymer prior to forming the membrane.

In this context, *material characterization* refers to obtaining information related to the intrinsic properties of the polymer rather than structural or physical properties of the membrane which is to be subsequently formed from the polymer. It is often useful to characterize the polymer in terms of the following: molecular architecture or bulk properties (molecular weight characteristics, degree of branching, chemical functionality and, if necessary, copolymer or blend composition), polymer solution properties (polymer swellability, polymer solubility and solution viscosities), thermal properties (glass transition temperature and crystal melting temperature), chemical stability and, if appropriate, biocompatibility. Physical properties of the polymers, such as mechanical strength and extent of crystallization, often depend upon sample preparation procedures and are ultimately reflected in the properties of the membrane. As such, they are discussed below under the heading of Membrane Characterization and Evaluation.

Lloyd and Meluch (4) summarize several methods of evaluating potential membrane materials for liquid separations without actually preparing membranes. They point out that once a membrane or film has been formed, it is often difficult to distinguish the intrinsic properties of the polymer from the structural characteristics of the membrane, which are themselves dependent

upon preparation procedures. Therefore, they emphasize those methods which characterize membrane materials in terms of their physicochemical interactions with small molecules, without requiring the formation of membranes or dense films. Similar procedures (for example, inverse gas chromatography) can be used to characterize the physicochemical interactions which occur during gas and vapor transport.

Membrane Preparation. The ability of a membrane to regulate permeation lies not only in the selection of an appropriate membrane material, but also in the physical structure of the membrane. The physical structure and the physical properties of a membrane can be directly related to membrane preparation procedures.

Depending upon the membrane preparation procedure and based on information obtained from membrane characterization, membranes are often classified as having one of the following structures:

(i) *Non-porous, Dense or Homogeneous.* These membranes consist of closely packed polymer chains with a uniform, continuous packing density throughout the system. The void spaces between macromolecules, and thus the corridors for transport, are beyond the current level of optical and electron microscopic resolution. Transport through these interstitial spaces is often discussed in terms of dynamic free volume and energy requirements for polymer segmental motion. That is, the transport mechanism is considered to be one of dissolution in the "liquid" or "swollen" membrane phase and diffusion down the chemical potential gradient. The properties of dense films are often equated with the intrinsic properties of the bulk polymer. However, this comparison must be made with caution because chain packing, and thus transport properties, may be dependent upon thermal history or solution history during film preparation and upon the attainment of equilibrium prior to characterization. Dense films can be prepared by melt extrusion, compression molding or solution casting.

(ii) *Porous or Heterogeneous.* In contrast to the dense membranes in which the polymer forms essentially a continuous phase, porous membranes are comprised of co-continuous phases of polymer and interconnecting voids that serve as transport corridors. Depending on the size of the voids and the interactions which occur during transport, the mechanism of transport may be considered as one of convection, diffusion or a combination of these mechanisms. The size and distribution of these voids vary with membrane preparation procedure and are somewhat arbitrarily distinguished as *finely porous*, *microporous* and *macroporous*. Alternatively (9), the terms *ultragel* and *microgel* have been suggested to indicate membranes of different pore size; "ultra" indicating smaller pores (0.1–0.5 μm), "micro" indicating larger pores (1–2 μm). The exact pore size or range of pore sizes that are described by these various terms are poorly defined and differ from author to author. Porous membranes may be *symmetric* (that is, uniformly porous throughout the structure), *anisotropic* (that is, pore size varies continuously in one direction) or *skinned*. In this review, the terms *skinned* and *asymmetric* are used interchangeably to describe membranes which consists of a *thin, relatively dense layer* supported by a *porous support layer*. Symmetrically porous membranes often retain

solutes and suspended matter within the membrane structure; thus, the term depth filter is used to describe these membranes. On the other hand, highly anisotropic and skinned membranes reject solutes and suspended matter at the surface; thereby avoiding membrane clogging or blinding problems. Consequently, skinned, and to a lesser extent anisotropic, membranes have become the membranes of choice for liquid phase and gas phase separations.

Since permeation is inversely related to membrane thickness, the advantage of the skinned membrane over the homogeneous membrane lies in the extreme thinness of the skin (typically $< 1.0 \mu\text{m}$), and thus the ability to achieve high fluxes without any loss in selectivity. Whether the skin layer of a membrane is dense or finely porous often depends on the method of membrane preparation. Skin layers deposited from solution or plasma onto a porous support (8,10), especially those intended for gas separations, are probably homogeneous. Skin layers resulting from phase inversion processes (9,11,12) may be finely porous or dense, depending upon casting solution composition, casting conditions and post-formation thermal or chemical treatments. The presence or absence of pores, especially below the level of electron microscope resolution, continues to be a point of debate. Regardless of origin or structure, it is this skin which exerts the greatest influence over the permeation properties of the membrane. The skin and the porous support layer may be comprised of the same material and produced in one casting operation. In this case, the asymmetric membrane may be referred to as an *integrally-skinned microgel* or an *integrally-skinned ultragel* depending on the size of the pores in the support layer. Alternatively, the skin and the support may be comprised of different materials and produced in separate steps. These *nonintegrally-skinned* structures are referred to as *composite membranes* (8) or *dynamic membranes* (10) depending on the method by which and the time at which the skin is deposited on the support layer. Porous and asymmetric membranes are typically produced via a *phase inversion* process (9,11-13). The asymmetry and *porosity* (that is, *pore size*, *pore size distribution* and *pore volume*) of the final solidified gel are directly related to the structure of the metastable "solution" immediately prior to gelation (6,9,11-13).

Often a post-formation treatment is used to improve membrane performance characteristics by physically or chemically modifying the membrane (6,9,11). One example of a physical modification is the thermal annealing of cellulose acetate membranes. The effect of this thermal treatment on the physical structure of the membrane is alternatively viewed as increasing the crystallinity or decreasing the porosity. Perhaps a combination of these effects occurs. In either case, the result is a decrease in flux and an increase in solute rejection with increasing temperature and duration of the thermal treatment. An example of a chemical modification is the sulfonation of hydrophobic membrane materials to increase hydrophilicity and thus increase water permeability (14). Usually these post-formation treatments are conducted prior to mounting the membrane in the membrane module. However, Grodzinsky and co-workers (15) have reported that the physical structure of a variety of charged polymeric membranes can be

temporarily and controllably altered after mounting the membrane in the module. By imposing an electric field on the membrane, the authors found that it is possible to modify the permeation rates of both charged and neutral species. Presumably the applied electric field causes the transport corridors to change in size due to electrostatic interactions within the membrane matrix.

When discussing membrane preparation, not only must the physical structure be considered, but one must also consider the membrane form or shape. In an effort to combat concentration polarization and membrane fouling and to maximize the membrane surface area per unit module volume, membranes are produced in the form of *flat sheets* (used either in plate-and-frame or spiral wound modules), supported and unsupported *tubes*, and *hollow fibers*. Although much of the technology associated with membrane development and membrane production is closely guarded as proprietary information, some of the details are beginning to appear in the literature (6,9-13,16-20).

Membrane Characterization and Evaluation. Following the selection, characterization and evaluation of the material and the preparation of the membrane, the next steps are to characterize the membrane in terms of physical properties and to evaluate the membrane in terms of performance.

In this context, *membrane characterization* refers to obtaining information about the physical structure of the membrane phase and characteristics of the bulk polymer. Pusch and Walch (21) have critically reviewed the commonly used techniques to investigate porous structure (pore size, pore size distribution, pore volume, anisotropy, etc.) and molecular structure (rubbery versus glassy, crystallinity, chain segment arrangement and mobility, etc.). Their list of methods for characterizing the porous structure includes microscopy, low-angle X-ray scattering, bubble point determination, mercury intrusion, fluid permeation measurements and molecular weight cut-off determinations. For characterizing the bulk polymer properties, Pusch and Walch list low-energy neutron scattering and diffraction, X-ray scattering and diffraction, infra-red absorption, nuclear magnetic resonance, thermomechanical analysis, differential thermoanalysis, differential scanning calorimetry, as well as gas permeation and sorption methods. For membranes that are used in an aqueous environment, the structure of the water within the membrane can be characterized via water sorption isotherms, nuclear magnetic resonance, infra-red absorption and by determining the heat capacity of the water within the membrane. These water-structure studies provide insight into the porous nature of the membrane and into the strength of the water-membrane interactions. In relating membrane structure to permeability, Pusch and Walch (21) make extensive use of an excellent collection of electron photomicrographs. In this volume Kyu (22) critically evaluates the techniques available for characterizing ion-exchange membranes in terms of polymer structure and functionality.

Frequently, only the properties of the skin layer of asymmetric membranes are of importance, because the skin layer is considered to play a dominant role in determining membrane

performance. In this volume, Smolders and Vugteveen (23) as well as Zeman and Tkacik (24) present a number of techniques for characterizing the porous structure of the skin layer of ultrafiltration membranes.

Membrane evaluation may refer to determining the ability of the membrane to achieve its desired function; for example, to separate the components of a mixture. Alternatively, membrane evaluation may refer to identifying a suitable application for an existing membrane. A survey of the literature reveals that there are few standard procedures for evaluating membrane performance. This lack of uniformity in evaluation procedures, plus the inability to confidently predict performance under a specific set of operating conditions on the basis of experiments conducted under different conditions, restricts comparisons of available membranes and performance data. Therefore, membrane performance must be evaluated for each application under the conditions of use. Depending on the specific membrane application, membrane evaluation might include measurements of flux, rejection or separation factor, ion-exchange capacity, membrane functionality or activity, membrane degradation (physical and chemical), membrane fouling, membrane compaction, release rates and barrier properties. These membrane properties are directly related to the choice of membrane material, the membrane preparation procedures and the final application conditions.

Overview of This Volume

The various chapters in this book address the topics of material selection, characterization and evaluation as well as membrane preparation, characterization and evaluation. At the expense of neglecting membranes for applications such as controlled release and impermeable barriers, this book focuses on synthetic membranes for separation processes as well as active membranes and conductive membranes. While many of the concepts developed herein can be extrapolated to other applications, the interested reader is referred elsewhere for specific details (for example, controlled release (25-30), coating and packaging barriers (31-33), contact lenses (34,35), devolatilization (36), ion-selective membrane electrodes (37-42) and membranes in electrochemical power sources (43)).

Membrane Material Selection and Evaluation. Chern et al. (3) and Lloyd and Meluch (4) propose possible approaches to the problem of selecting the appropriate membrane material to separate gas mixtures and liquid mixtures, respectively. Chern et al. discuss membrane permeation and separation in terms of thermodynamic solubility and kinetic mobility of the permeant gases in the polymer phase and how each of these is influenced by the molecular structure of the glassy polymeric membrane material. Correlations that apply in the absence of strong plasticization or swelling interactions between the penetrant gases and the membrane are discussed in terms of inherent polymer and penetrant properties to rationalize the solubility and mobility contributions to the permselection process. Advantages of focusing on "mobility

selection" rather than "solubility selection" are emphasized by these authors. They point out how the chemical nature of the polymer, and thus polymer segmental motion and packing, can be used to select membrane materials for gas mixture separations. The authors suggest that a loosely packed glassy polymer with sufficient cohesive energy and a rigid plasticization-resistant backbone is ideally suited to achieve both high flux and high selectivity. Structurally modified poly(aryl ethers), polyimides, polyamides, polycarbonates, polyesters and polyurethanes appear to be likely candidates to attain these goals. Chern et al. (3) suggest that modification of the above simple concepts are necessary when one or more of the permeants plasticizes the membrane material. The authors discuss these and other "environmental" considerations and the importance of evaluating the membranes under final useage conditions.

In contrast to the separation of relatively inert gas mixtures, the separation of liquid mixtures is strongly influenced by both the effective size of the permeants and the chemical interactions which occur within the membrane phase. That is, both thermodynamic solubility or partitioning and kinetic mobility or transport are directly influenced by physical as well as chemical factors. Lloyd and Meluch (4) discuss membrane material selection in terms of the effective size of the permeants relative to each other and relative to the size of the membrane transport corridor. The transport corridor size is subsequently related to polymer molecular structure and membrane preparation procedures. In this sense, the discussion closely resembles that of Chern et al. (3). However, Lloyd and Meluch add the often more significant factor of chemical interactions near and within the membrane phase. The authors demonstrate the possibility of selecting an appropriate membrane material on the basis of the dispersive, polar and hydrogen-bonding character of both the available membrane materials and the solution components to be separated. Having selected an appropriate membrane material on this thermodynamic basis, membrane performance is ultimately related to the kinetics of transport through the physical structure of the membrane, which in turn is related to membrane preparation procedures. Lloyd and Meluch also discuss methods for characterizing and evaluating membrane materials prior to membrane formation.

Hoehn (5) reviews the development of aromatic polyamide (aramid), polyamide-hydrazide, polyhydrazide and polyimide membranes for liquid and gas phase separations. Hoehn discusses the structure-property relationships of these membranes in terms of polymer chemical composition (primary or Level I characteristics), in terms of steric effects resulting from chain packing and chain flexibility (secondary or Level II) and in terms of membrane morphology, such as asymmetry, anisotropy and skinning (Levels III and IV). It is Level I that Lloyd and Meluch (4) use to establish their material selection index on the basis of dispersive, polar and hydrogen bonding considerations. Structure Level II is beyond the level of detection via electron microscopy, and determines the size of the transport corridor in dense membranes and the skin layer of asymmetric membranes. As such, Hoehn's Structure Level II can be related to the corridor size parameter identified by Lloyd

and Meluch (4) and to the mobility selectivity discussed by Chern et al. (3). Levels I and II are intrinsic properties of the polymer; Levels III and IV represent physical structure characteristics on a microscopic level and are dependent upon membrane preparation procedures for integrally- and nonintegrally-skinned membranes, respectively. As such, Structure Level III relates to the chapters by Finken (6), Kesting (9), Strathmann (11), Kamide and Manabe (12), Hiatt et al. (13) and Cabasso (44), while Level IV relates to the chapters by Cadotte (8), Spencer (10), Cabasso (44) and Lee et al. (45).

Ward, Feldhoff and Klein (7) demonstrate that in addition to some demanding separation performance requirements (which are primarily attributable to membrane preparation procedures and transport mechanisms), therapeutic applications such as hemodialysis, hemofiltration and plasmapheresis impose some unique material selection restrictions. Specifically, one must consider protein adsorption, biocompatibility (that is, thrombogenicity, complement activation and toxicity) and the sterilizability of the membrane. In selecting a membrane material for any of these therapeutic liquid separations, the biocompatibility and sterilizability restrictions must be considered in addition to the guidelines established by Lloyd and Meluch (4). Thrombogenicity and complement activation are directly related to the physicochemical interactions between the polymer and the various components of blood. Toxicity is related to the chemical functionality of the polymer or any residual low molecular weight compounds in the polymer. Sterilizability is a function of both the thermal properties of the polymer, such as glass transition temperature and crystalline melting temperature, and the chemical stability of the polymer to ethylene oxide exposure and gamma irradiation. Additional requirements of optical clarity and biodegradability must also be taken into account in selecting membrane materials for other applications such as contact lenses and controlled release devices, respectively. Ward et al. review several membrane materials currently in use for therapeutic liquid separations and discuss their advantages and disadvantages for specific applications. The authors also point out that for continued growth in the use of membranes for therapeutic liquid separations a better understanding of blood-membrane physicochemical interactions is required. This knowledge would be of great value in predicting biocompatibility, and thus in selecting membrane materials. The authors also point out the need to refine membrane preparation procedures to more accurately control pore size and to produce membranes of narrow pore size distribution.

In the biomedical applications outlined by Ward et al. (7), more so than in any other separation application of synthetic polymeric membranes, the goal is to mimic natural membranes. Similarly, the development of liquid membranes and biofunctional membranes represent attempts by man to imitate nature. *Liquid membranes* were first proposed for liquid separation applications by Li (46-48). These liquid membranes were comprised of a thin liquid film stabilized by a surfactant in an emulsion-type mixture. While these membranes never attained widespread commercial success, the concept did lead to *immobilized or supported liquid membranes*. In

these membranes, the transport occurs in a stationary liquid phase which has been fixed within a porous membrane for purposes of stability. A variety of techniques have been used to support the liquid membrane phase including immobilization within porous inert "membranes" (for example, common filter paper, nitrocellulose filters, cellulose acetate films and hollow fibers, track-etched polycarbonate membranes, polytetrafluoroethylene membranes, polyvinyl chloride membranes and polypropylene membranes such as those discussed by Hiatt et al. (13)) as well as within ion-exchange membranes and between two relatively dense films in the form of a "sandwich." In any of these forms, the membranes can be used for either gas or liquid mixture separations.

Way, Noble and Bateman (49) review the historical development of immobilized liquid membranes and propose a number of structural and chemical guidelines for the selection of support materials. Structural factors to be considered include membrane geometry (to maximize surface area per unit volume), membrane thickness ($<100\text{ }\mu\text{m}$), porosity ($>50\text{ volume }\%$), mean pore size ($<0.1\text{ }\mu\text{m}$), pore size distribution (narrow) and tortuosity. The amount of liquid membrane phase available for transport in a membrane module is proportional to membrane porosity, thickness and geometry. The length of the diffusion path, and therefore membrane productivity, is directly related to membrane thickness and tortuosity. The maximum operating pressure is directly related to the minimum pore size and the ability of the liquid phase to wet the polymeric support material. Chemically the support must be inert to all of the liquids which it encounters. Of course, final support selection also depends on the physical state of the mixture to be separated (liquid or gas), the chemical nature of the components to be separated (inert, ionic, polar, dispersive, etc.) as well as the operating conditions of the separation process (temperature and pressure). The discussions in this chapter by Way, Noble and Bateman should be applicable the development of *immobilized or supported gas membranes* (50).

Membrane Formation, Modification and Production. Kesting (9), Strathmann (11), Kamide and Manabe (12), Hiatt et al. (13) and Finken (6) all address the important subjects of membrane formation mechanisms and membrane production processes, including post formation treatments and modifications. In each chapter, the emphasis is on membrane preparation via a *phase inversion process*. To paraphrase Kesting (9), the phase inversion process is one in which a homogeneous polymer solution is converted or inverted into a three-dimensional macromolecular network or gel comprised of solid polymer regions and intervening voids. That is, a homogeneous solution *decomposes* into a two-phase system comprised of a solid, polymer-rich phase forming the rigid membrane structure and a liquid, polymer-poor phase forming the voids. The common thermodynamic feature of all phase inversion processes is that the free energy of mixing of the polymer system must be negative under certain conditions of temperature and composition. That is, the system must have a miscibility gap over a defined temperature and concentration range. The cause of the phase inversion or phase separation may be either a change in solution composition or a

change in solution temperature. Kesting distinguishes between a *dry* or *complete evaporation process*, a *wet* or *combined evaporation-diffusion process* and a *thermal process*. This distinction is based on the procedure used to achieve the phase inversion; that is, the cause of the precipitation and solidification of the polymer. Each of these variations of the phase inversion process, plus the closely related *polymer assisted phase inversion process*, is discussed in terms of the mechanism of membrane formation, membrane structural characteristics (*anisotropy* versus *asymmetry* or *skinning*, and structural irregularities) and membrane production considerations. Some of the topics discussed by Kesting in this comprehensive review are subsequently elaborated upon in greater detail elsewhere in this volume; for example, membrane formation mechanism (11,12), membrane production (11), thermal phase inversion (13) and composite or nonintegrally-skinned membranes (8,10).

Strathmann (11) explores further the details of the phase-inversion membrane formation mechanism and the influence of process variables. Concentrating on the wet phase inversion process, Strathmann discusses membrane formation by making use of three-component equilibrium phase diagrams. Recognizing that the phase-inversion process is actually a nonequilibrium process and thus difficult to describe in thermodynamic terms, Strathmann emphasizes the kinetic factors (diffusivities, driving forces, viscosity, etc.) which govern phase inversion. The major process variables considered are the choice of polymer and its concentration, the choice of solvent or solvent system, the choice of precipitant or precipitant system and the precipitation temperature. Extensive use is made of electron microscopy and optical microscopy in relating these membrane preparation process variables to membrane performance and the structure of the porous support layer. Strathmann demonstrates that through proper control of the process variables listed above the same membrane structure can be prepared from various polymers and that the same polymer can be used to prepare various membrane structures. The rate of precipitation is shown to have a direct influence on the structure of the porous support layer: slow precipitation produces a "sponge" structure; fast precipitation produces "finger-like" macrovoids. The rate of precipitation is related to the polymer concentration in the casting solution, the chemical similarity of the polymer-solvent, polymer-precipitant and solvent-precipitant pairs, the precipitant temperature, the diffusivities of the solvent and precipitant in the nascent membrane during gelation, the method of introducing the precipitant (vapor or liquid), the presence of additives in the precipitation medium and the resistance to solvent-precipitant exchange offered by any existing skin layer. Strathmann briefly discusses the effects of evaporation prior to precipitation and the effects of post-formation treatments such as annealing.

Relying heavily on their established expertise in the field of polymer solution thermodynamics, Kamide and Manabe (12) take a more detailed look at the mechanism of phase-separation which occurs during membrane formation. In this context, phase separation is the process which takes place during phase inversion. A theory is developed which allows for the prediction of pore characteristics

in a membrane cast from solution. According to this theory, provided that the initial polymer concentration is smaller than an established critical level, the phase-separation process yields a polymer-rich phase which becomes a small primary particle. Primary particles subsequently aggregate to form the larger secondary particles which eventually form the membrane pore walls. The authors point out that this nucleation-and-growth model differs from the spinodal decomposition model proposed by other authors. The theory developed by Kamide and Manabe allows them to model the primary-to-secondary particle growth process and to predict final pore size and pore size distribution. Experimental studies using electron microscopy to evaluate membrane structure were carried out to substantiate their predictions.

In reviewing phase inversion membrane preparation, Kesting (9) referred to the thermal phase inversion process as perhaps the most universally applicable method. Strathmann (11) refers to the process as the simplest procedure for obtaining microporous membranes. In this process, a homogeneous polymer solution at an elevated temperature is converted to a two-phase system by a decrease in temperature rather than by changing the solution composition. The resulting phase-separation process may be one of liquid-liquid separation followed by either polymer solidification or crystallization (13) or one of simultaneous polymer crystallization and solidification (51). The pore-forming latent solvent is subsequently extracted to produce a porous structure. Hiatt et al. (13) discuss the production of microporous membranes via thermally-induced liquid-liquid separation followed by polymer crystallization. They demonstrate that the pore structure of these membranes is dependent upon a number of controllable parameters including choice of polymer, polymer concentration, choice of pore-former and rate of solution cooling. The authors demonstrate the significance of these variables in preparing porous membranes of high molecular weight polypropylene and low molecular weight polyvinylidene fluoride. For example, polypropylene membranes cast from N,N-bis-(2-hydroxyethyl) tallow amine are shown to assume either an "open cell" structure or a "lacy" structure. In this case, a slow cooling induces a nucleation-and-growth mechanism to produce the macroporous open cell structure. A fast cooling induces spinodal decomposition to produce the microporous lacy structure which may even possess a skin layer. On the other hand, membranes made from polyvinylidene fluoride and carbitol acetate solutions produce either a structure of "polymer spheres" supported by a tight skin or a structure of "polymer leaves" stacked on a more open skin. The spherical structure results from either slow cooling or high polymer concentrations. The polymer leaf structure results from rapid cooling and low polymer concentrations. The membranes produced via thermal phase inversion have proven useful for controlled release, air filtration, plasmapheresis, depyrogenation and cross-flow microfiltration. They should also prove useful as liquid membrane supports.

Post-formation chemical, thermal and physical treatments are often used to modify the performance characteristics of membranes. Finken (6) presents recent results from his studies on thermal and physical modifications of integrally-skinned cellulosic blend

membranes for gas mixture separations. Freeze drying and the sublimation temperature were shown to influence membrane performance (flux and separation). Similarly, thermal annealing and the annealing temperature influence membrane performance. Finally, a proprietary solvent exchange and subsequent drying treatment was also shown to influence membrane performance.

In addition to the phase-inversion processes described by Kesting (9), Strathmann (11), Kamide and Manabe (12) and Hiatt et al. (13), a number of alternative membrane preparation processes exist. Of these alternative processes only two are presently used to produce commercial skinned membranes. Specifically, these nonintegrally-skinned membranes are referred to as *composite membranes* (8) and *dynamic membranes* (10) depending on the method of formation and the capability to replace or renew the skin layer. A major advantage of nonintegrally-skinned membranes is the ability to produce the skin layer from a polymer different than that used for the porous support. This is significant in that the two layers serve different purposes and thus have different requirements. The skin layer governs the separation and flux properties. Therefore, it should be chemically similar to the preferentially transported species (4) and the polymer molecules should be capable of close packing. On the other hand, the porous layer serves as a rigid, compaction-resistant support and should be chemically inert. In both composite and dynamic membranes, the skin layer is deposited on a porous support (usually polysulfone for composite membranes and stainless steel, carbon or ceramic for dynamic membranes). The porosity of the support layer can have a direct influence on the preparation and performance of these nonintegrally-skinned membranes. The number and frequency of the pores at the top of the porous support should be as great as possible to assure adequate binding of the skin to the support. The pore size should be as small as possible to minimize the distance between points of support for the deposited skin layer. In preparing composite membranes the skin layer is either laminated, dip-coated, polymerized from a plasma or interfacially polymerized from solution prior to membrane module fabrication (spiral wound or hollow fiber). On the other hand, the skin layer in a dynamic membrane is desposited in a pre-existing membrane module (usually tubular). Since the skin layer of dynamic membranes is stabilized by ionic cross-linking at best, it can be controllably removed and a new one deposited as desired.

Cadotte (8) presents a comprehensive review of the development of the composite membrane with emphasis on the pros and cons of the four preparation methods mentioned above and on the polymer chemistry involved. Cadotte points out that while each of the four methods continues to receive some attention, the interfacial polymerization method appears to be the most versatile. This method can be used to produce skin layers from polyamines, polyimines, polyurethanes, polyesters and other polymers. Elsewhere in this volume, Lee and co-workers (45) discuss the advantages and problems associated with using these composite membranes for ethanol-water separations via counter-current reverse osmosis. Also, Cabasso (44) discusses double-layer composite membranes.

Following a brief review of the development of dynamic membranes and an overview of the current state of the art, Spencer (10) discusses dynamic polyblend membranes. In particular, he looks at the influence that polymer selection and membrane preparation procedures have on membrane performance. Dynamic membranes composed of a poly(acrylic acid)/basic polyamine blend deposited on a ZOSS (hydrous zirconium oxide on stainless steel) ultrafiltration membrane are discussed. Their hyperfiltration or reverse osmosis properties are compared to the more traditional ZOPA (zirconium oxide plus poly(acrylic acid)) membrane.

Another non-integrally skinned membrane worthy of note is the coated membrane developed by the research group at Monsanto (52,53). The interesting points of distinction between the composite membranes discussed by Cadotte (8) and Monsanto's Prism membranes are the role of the skin and the role of the support layer. The skin layer of composite membranes as described by Cadotte controls flux and separation by serving as a semi-permeable barrier. The support layer acts primarily as a substrate for the skin; any influence that the support layer has on flux and separation is secondary. On the other hand, the coated skin layer in the Monsanto membrane is a highly permeable, relatively non-selective polymer used primarily to plug any defects in the already existing skin layer of the hollow fiber membrane. By imposing this additional resistance to pore flow, the coated skin forces the gases to permeate the polymer which comprises the hollow fiber. Consequently, the hollow fiber supporting the coated skin controls the flux and separation. The Monsanto membranes are discussed in this volume by Finken (6) and Kesting (9).

The search for alternative reverse osmosis membrane materials resulted in not only the emergence of new materials but also new membrane module designs and membrane preparation procedures. Specifically, workers at Dow (54-56) and DuPont (57,58) developed techniques for solution-spinning and melt-spinning hollow fiber membranes. In this volume, Hoehn (5) reviews the development of these membranes at DuPont. Cadotte (8) discusses the formation of composite hollow fiber membranes, including those developed at Albany International Research Company. Lee et al. (45) consider an interesting application of these membranes. Finken (6) and Kesting (9) present brief discussions of the coated hollow fiber membranes developed at Monsanto. Cabasso (44) provides a brief overview of four topics of current interest to those involved in the development of hollow fiber membranes. The topics referred to by Cabasso are: (i) methods of characterizing the development of morphology during wet-spinning, (ii) the use of double-layer composite membranes for gas separations, (iii) the characterization of stress-induced crystallization, and (iv) the use of ion-exchange hollow fibers for alcohol-water separations (a topic closely related to the chapter by Lee et al. (45)).

A number of procedures exist for preparing non-skinned membranes of either the symmetric or the anisotropic type (5,59). Finken (6) describes a procedure referred to as the Langmuir-Blodgett technique which was first used to produce extremely thin

dense films for gas separations by Ward and co-workers (60). Langmuir-Blodgett films have had only limited commercial success for separation processes; however, Aizawa (61) points out in this volume that these mono- and multilayer thin films have found extensive use for simulating natural or biological membranes. In his classic monograph on synthetic polymeric membranes (59), Kesting describes a number of other membrane preparation procedures and membrane structures. While many of these have never advanced beyond the level of laboratory curiosities, a few have attained commercial success. *Sintered* membranes, *nuclear track-etched* polycarbonate microfiltration membranes by Nuclepore Corp. (62), stretched polyolefin Celgard membranes by Celanese Corp. (63,64) and stretched polytetrafluoroethylene Gore-Tex membranes by W. L. Gore and Assoc., Inc. (65) have all proven to be commercially successful microfiltration and/or air filtration membranes. *Charged mosaic* membranes continue to be investigated for possible use in piezodialysis (66). *Ionotropic gels* in which the gel contains a resin or a resin precursor of one charge and the pores contain resin of the opposite charge (67) and *latex-polyelectrolytes* (68) appeared to hold the most promise as charged mosaic membranes; however, piezodialysis has never come to fruition as a method of desalination.

Membrane Characterization. Smolders and Vugteveen (23) and Zeman and Tkacik (24) discuss a number of methods for determining the physical characteristics of skinned ultrafiltration membranes. Smolders and Vugteveen (23) make use of a gas adsorption/desorption method, thermoporometry and selective permeation of aqueous dextran and aqueous polyethylene glycol solutions analyzed via liquid chromatography. Pore volume and pore size distribution are calculated from the hysteresis loop in the sorption/desorption studies. Cumulative and differential pore volumes are likewise obtained by observing the shift in melting or freezing temperature in thermograms for water in the pores. By comparing the molecular weight distribution of dextran and polyethylene glycol in the feed with that in the permeate, a fractional rejection curve is generated. When used in conjunction with the classical molecular weight cut-off curve, a more complete representation of membrane pore size is obtained. The authors use a combination of these techniques to characterize the skin layer of ultrafiltration membranes of various materials in terms of mean pore size (as small as 1.5 nm) and pore size distribution. Zeman and Tkacik (24) also make use of nitrogen sorption/desorption studies and the selective permeation or fractionation of aqueous dextran solutions to estimate the pore size characteristics of polysulfone ultrafiltration membranes. In addition, high resolution scanning electron microscopy, SEM, (90,100X magnification) is used to obtain a "visual" representation of the membrane structure. Analysis of the photomicrographs yielded pore size distributions that are adequately represented by log-normal functions and which show reasonable agreement between predicted and observed dextran rejection. The pore sizes estimated on the basis of gas sorption/desorption studies were significantly larger than those suggested in the SEM studies; therefore, the authors conclude that the sorption studies provide

information about the porous support layer rather than the skin layer. The techniques used by these authors, as well as those reviewed by Pusch and Walch (21), provide valuable insight into the mechanism of membrane formation and thus may assist membrane scientists in developing better membranes. However, many of these techniques do not characterize the membrane under the conditions of application; for example, the ultrafiltration membranes (23,24) are dried prior to gas sorption studies and microscopy. Therefore, caution must be exercised in interpreting the results of these characterization methods and relating them to membrane performance and transport mechanisms.

The transport corridors of some membranes are too small to be directly characterized by the techniques mentioned in the previous paragraph. Notably, the transport corridors of ion-exchange membranes and the skin layer of reverse osmosis and gas separation membranes are so small as to spark considerable controversy regarding the mechanism of transport in these membranes. Krause (69) proposes an *interpenetrating microphase model* for transport through ion-exchange membranes and the skin layer of reverse osmosis membranes. In this model, the membrane consists of two co-continuous, interpenetrating microphases—a feature confirmed by Kyu (22). Water, ions and the principle hydrogen-bonding groups of organic permeants are transported through a water-swollen, hydrophilic microphase. Small organic molecules without major hydrogen-bonding groups and the hydrophobic portions of other molecules permeate the hydrophobic microphase. Partition coefficients and diffusivities for a number of organic solutes in cellulose acetate membranes are correlated using the solubility parameters of only the hydrophobic portions of both the membrane polymer and the organic permeant.

Way et al. (49) point out that *ion-exchange membranes* or *ionomeric membranes* can be used as support materials for immobilized liquid membranes. Of course, these membranes have a variety of other applications which capitalize on their ability to exchange either cations or anions (70,71). Ion-exchange membranes are highly swollen gels carrying either a fixed positive charge (anion exchange membrane) or a fixed negative charge (cation exchange membrane). These membranes can be prepared by dispersing a conventional ion-exchange resin within a polymer matrix, by casting a film from an ionomeric polymer or by chemically modifying an existing non-ionic polymer film. The most common fixed anions in cation-exchange membranes are sulfonic and, to a lesser extent, carboxylic. Phosphoric, phosphinic and selenic groups have also been used. Anion-exchange membranes have been made with fixed quaternary ammonium, quaternary phosphonium and tertiary sulfonium groups. Since the basic groups are not entirely stable, most of the advances in ion-exchange membranes have been in the development of cation-exchange membranes. The performance of these membranes depends on the nature and density of the fixed ionic groups as well as the mechanical and chemical stability of the polymer matrix. Kyu (22) summarizes the properties and structure of perhaps the most important class of ion-exchange membranes; that is, perfluorinated ion-exchange membranes. A review of the properties and structure of earlier ion-exchange membranes can be found

elsewhere (72). Kyu demonstrates how the structure of these membranes can be investigated through the use of wide-angle and low-angle scattering studies as well as spectroscopic and microscopic studies. Physical and ion-exchange properties are characterized via stress relaxation, dielectric relaxation and dynamic mechanical studies. Because each of these methods of investigation probe a different aspect of the membrane, Kyu suggests that a variety of these techniques must be combined to obtain a satisfactory representation of the membrane and its capabilities.

Membrane for Specific Applications. Lee and co-authors (45) discuss the selection and development of membranes for separating ethanol and water. A process design referred to as countercurrent reverse osmosis, CCRO, was used to investigate the problems of high osmotic pressures associated with concentrated alcohol solutions. Because of the high alcohol concentrations that result and the CCRO mode of operation, not only does the choice of membrane material become critical (that is, Structure Levels I and II defined by Hoehn), but so does the asymmetric structure of the membrane (Structure Levels III and IV). In CCRO, a portion of the concentrated feed is circulated to mix with the permeate on the low pressure side of the membrane. To attain good mixing of these two solutions and to facilitate the diffusion of the alcohol to the low pressure side of the membrane skin, the porous support layer must have an open structure. For this purpose, thin film composite membranes proved to be best. Lee and co-workers report that composite membranes in which the skin layer is formed via the polymerization of a monomeric amine perform better than composite membranes in which the skin is formed by *in situ* cross-linking of prepolymer (8). Presumably the later technique for composite membrane preparation produces a gel which hinders diffusion within the porous sublayer. These workers also concluded that the hollow fiber membrane conformation is preferred because it facilitates circulation on the low pressure side.

Wagener (73) discusses electrically conductive membranes or *electromembranes*. The purpose of these membranes is to achieve control over permeation of charged species by presenting an electric potential barrier. Thus, separation is to be accomplished on the basis of electrochemical interactions rather than or in addition to on a size distinction basis. These membranes differ from ion-exchange membranes in that no ions are exchanged during permeation. An additional application for electromembranes is in the area of membranes for chemical communication, as discussed in this volume by Aizawa (61). Wagener describes alternative methods for the preparation of electromembranes by utilizing the porous membranes described by Hiatt et al. (13) and polyacetylene chemistry followed by an iodine or a NOPF₆ doping. Wagener demonstrates that the amount and type of dopant as well as the choice of polymer from which the porous membrane is made each play a role in determining the conductive properties of the electromembrane. Polymers which do not contain active hydrogens were found to make the best porous support materials. For example, polyethylene and polyvinylidene fluoride served as useful porous substrates while nylon-6 failed to

yield suitable electromembranes. This is apparently due to the influence that the membrane material has during the acetylene polymerization, rather than any effect the porous polymer might have during transport.¹ Electromembranes with conductivities in the range 10^{-2} to 10^1 ohm cm^{-1} were produced.

Closing out this volume, Aizawa (61) presents a comprehensive review of *biofunctional synthetic membranes*. These membranes represent another attempt by man to mimic natural or biological membranes. In this case not only are chemical compounds separated but they are often chemically modified while being transported in the membrane. Aizawa notes that the original attempts to mimic biological membranes resulted in the incorporation of biologically active molecules in planar bilayer lipid membranes and liposomes; both of which are liquid membranes. As mentioned above in discussing the chapter by Way et al. (49), these relatively weak, noncovalent assemblies were not stable and found limited practical use. More recently techniques have been developed to permit the immobilization of biologically active molecules within synthetic polymeric membranes. The most common techniques of immobilization are covalent bonding to the support matrix and entrapment within the pores of the support matrix. Aizawa reviews three classifications of biofunctional synthetic membranes: biocatalytic, energy-transducing and information-transducing. Under each of these three headings, he discusses historical development, the molecular mechanism that occurs in the biological membrane which the synthetic membrane is trying to mimic, the methodology of membrane preparation and current trends in the research and development of these membranes.

Summary

In preparing this volume of the ACS Symposium Series, the editor and the authors have concentrated their efforts on the materials science of synthetic membranes. In doing so, it was necessary to limit discussions of other, equally important, aspects of membrane science. Specifically, we have focused on synthetic polymers serving as either membranes or membrane supports. Readers with an interest in the materials science of inorganic membranes (metallic, ceramic and glass (74) as well as precipitation (75) membranes), gas membranes (50) and natural biological membranes (76) are referred to the literature. Readers with an interest in transport modelling, process design and optimization, membrane applications and the economics of membrane processes are referred to the literature cited in this overview and elsewhere in this volume. Each chapter of this volume is designed to present the state of the art at the time of final manuscript preparation (early 1984), to provide an appreciation of the materials science of synthetic membranes and to encourage further developments in these areas. An understanding of the concepts presented herein can facilitate the selection of better membrane materials, the preparation of better membranes, the modelling of membrane transport and the improvement of membrane separation processes.

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