Membrane Science and Technology

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Membrane Science and Technology

Preface

This book provides a comprehensive introduction to membrane science and technology. It covers the methods, structures, properties, and applications of the membranes. This volume also includes such new techniques of membrane preparation as Langmuir–Blodgett, liquid crystalline, and plasma deposition.

One of our objectives is to review basic physicochemical understanding of membrane science and present the fundamental preparative methods. We hope that this feature will prove useful to those who are interested in membrane science and engineering and those who would like to extend their knowledge of polymer science.

Another objective of this book is to examine recent progress and provide basic information about current topics. We have tried to present new trends and anticipate potential applications in various fields of membrane technology. We cover as wide a range of relevant topics as possible and consider areas where future work should be concentrated. However, emphasis throughout the book is on principles and topics which are based on the related subject matter.

This book is made up of four parts. Part I introduces the physical and chemical fundamentals of membrane science. Part II provides all new methods of membrane preparation and an extended discussion of experimental technique based on wet as well as dry methods. Part III is concerned primarily with the practical application of chemical processing and engineering. Part IV in-

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cludes biomedical uses. Collaboration between workers in all these different disciplines is essential to make membrane science useful in industrial processes.

The preparation of this book was initiated by a kind suggestion of Dr. Maurits Dekker and has come to its completion mainly through the efforts of the contributors. We are indebted to Ms. Vickie Kearn and Ms. Lisa Honski of Marcel Dekker, Inc., for their helpful suggestions and discussions concerning the initial organization of this book.

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Part IV: Biomedical Use

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Physical Chemistry

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1
The Physical Chemistry of Membranes

Yoshiharu Tsujita Nagoya Institute of Technology, Nagoya, Japan

Membranology has developed progressively during the last two decades, and has been applied in various processes, such as reverse osmosis of desalination and water purification, electrodialysis in a chlorine–caustic cell, ultrafiltration, pervaporation, gas separation, hemodialysis, controlled release of drugs, genetic engineering, and so on. This development has stimulated polymer synthesists and polymer physical chemists to design membranes for an advanced level of performance. The fundamental understanding and technological improvement of membranes are major objectives in recent membrane science.

I. MEMBRANE STRUCTURES

A. Classification of Membranes

Many kinds of membrane are known, differing in structure and function. A comprehensive representation of the relationships between pore diameter, membrane separation process, and penetrant size is shown in Fig. 1. It is possible to classify membranes according to their structure. There are homogeneous and heterogeneous membranes as a means of classifying homogeneity of a membrane phase. The homogeneous membranes indicate a homogeneous membrane structure parallel and perpendicular to the membrane surface. A membrane such as poly(dimethylsiloxane) is typical of homogeneous membranes and is used for a gas separation process. On the other hand, heteroge-

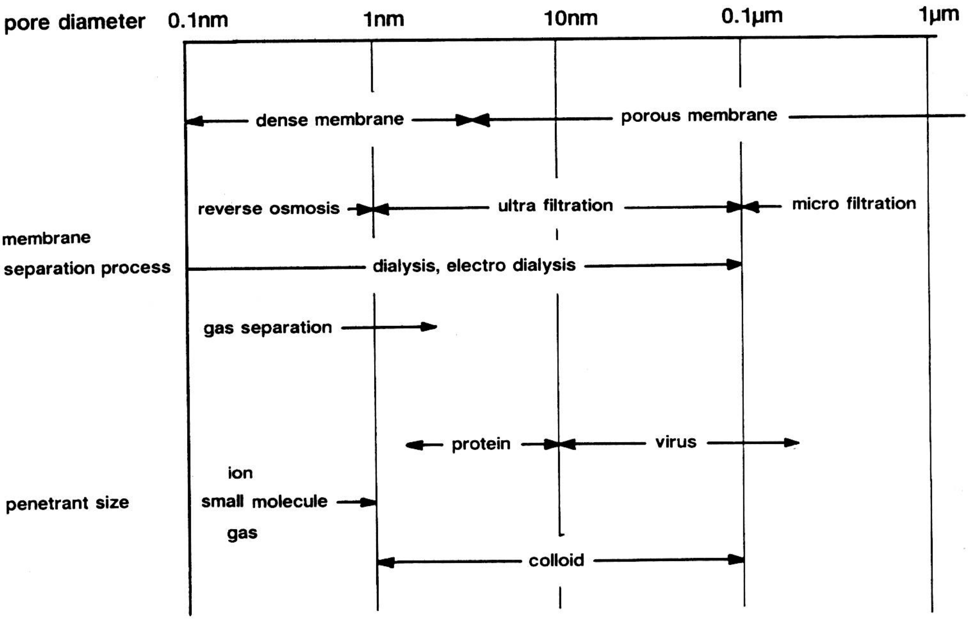


Fig. 1 Relationships between pore diameter, membrane separation process, and penetrant size.

neous membranes have a heterogeneous structure. The degree of heterogeneity is widely different in various membranes: for example, polymer blend membrane phase-separated at the polymer molecular level, composite membranes, laminated membranes, and porous membranes that are heterogeneous at the macroscopic level.

One can also classify membranes into symmetric and asymmetric membranes from the standpoint of the symmetry of membrane thickness. When a membrane structure shows symmetry perpendicular to the membrane surface, the membrane is said to be symmetric irrespective of heterogeneous porous membranes. The homogeneous membrane is also one of the symmetric membranes. Asymmetric membranes such as a membrane with a dense skin on a porous membrane are widely used for reverse osmosis and ultrafiltration processes driven under high pressure.

Membrane is utilized by the configuration of modules in large-scale membranology. It is necessary to set up effective membrane modules to establish high membrane performance. Many types of membrane modules are produced commercial [1,2]. Typical stacked plate and pleated cartridge systems are used for water purification with microfiltration membranes. Ultrafiltration modules of tubular (a), plate-and-frame (b), spiral-wound (c), and capillary membrane

(d) modules are depicted in Fig. 2 [1]. The tubular membrane module is prepared by direct casting on a porous stainless steeel or plastic tube. The advantages of this module system are easy adjustment of feed flow velocity and mechanical cleaning for membrane fouling. The plate-and-frame membrane module is composed of the membranes, porous membrane support materials, and spacers as shown in Fig. 2b and can provide a larger membrane area per unit volume than the tubular membrane module. The spiral-wound membrane module is in principle a plate-and-frame system rolled up as illustrated in Fig. 2c. This module has a very large membrane area per unit volume but suffers from severe membrane fouling. The capillary membrane module consists of a large number of capillaries with a diameter of 0.5 to 1.5 mm and can also provide a large membrane area per unit volume. The hollow-fiber membranes have an asymmetric structure in the radial direction: the dense skin membrane on the outside and the porous membrane on the inside. The diameter of the fiber is in the range 50 to 300 μm. Of the various membrane modules described above, the hollow-fiber membranes contain the largest membrane area per unit volume. The spiral-wound and hollow-fiber membrane module systems prevail today in the reverse osmosis separation process by which seawater can be desalinated. On the other hand, the tubular membrane module system is applied in the food and drug industry on a relatively small scale and the plate-and-frame membrane system is useful to the pharmaceutical and food industries because this membrane type is easy to exchange.

B. Fine Structure of Membranes

Membrane structure is very important for understanding the separation and permeation mechanism of a small molecule passing through polymer membranes. The membrane structure consists fundamentally of either a dense membrane or a porous membrane. Various types of membrane modules correspond basically to the configuration of these two membranes.

1. Dense Membranes

Dense membranes play an important role in the separation process of a small molecule, although the membranes are relatively thin. Amorphous dense membranes such as poly(dimethylsiloxane) and cellulose ester are usually prepared by either the compression molding of a molten state or the solvent cast of a polymer solution. The membrane structure of a dense membrane is considered to be a liquid (rubbery) state or a glassy state, depending on its glass transition temperature, except in the case of a crystalline dense membrane. A dynamic free volume in the liquid state and static frozen free volume (microvoid) in the glassy state are readily available for separation and permeation through the dense membrane, as will be described in detail later.

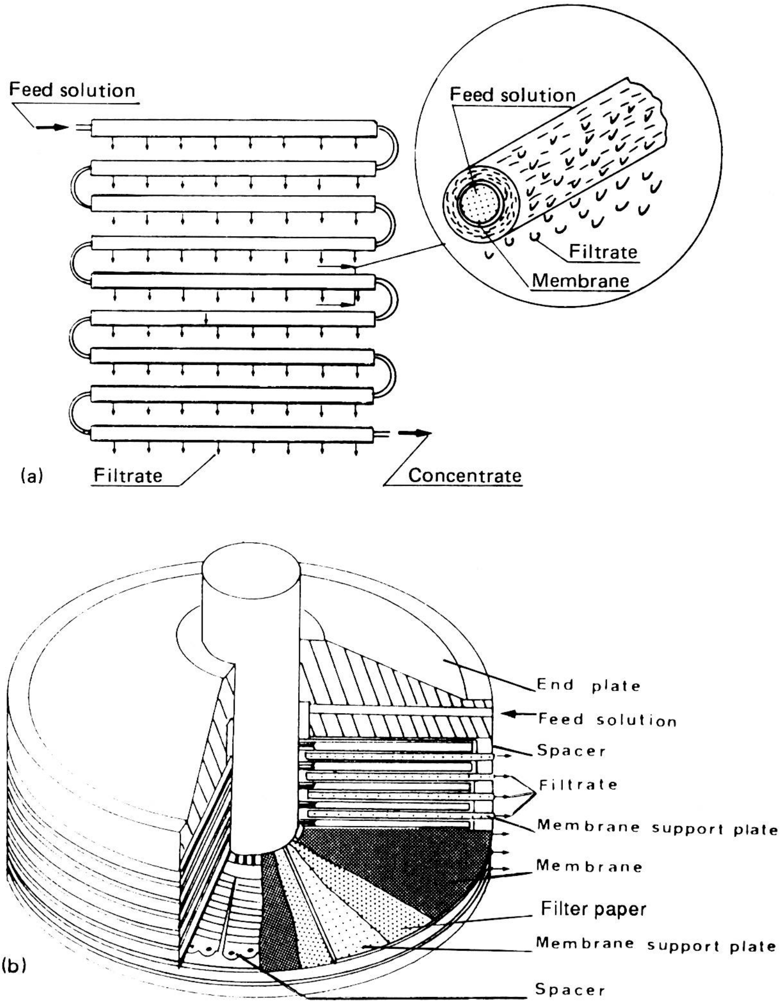
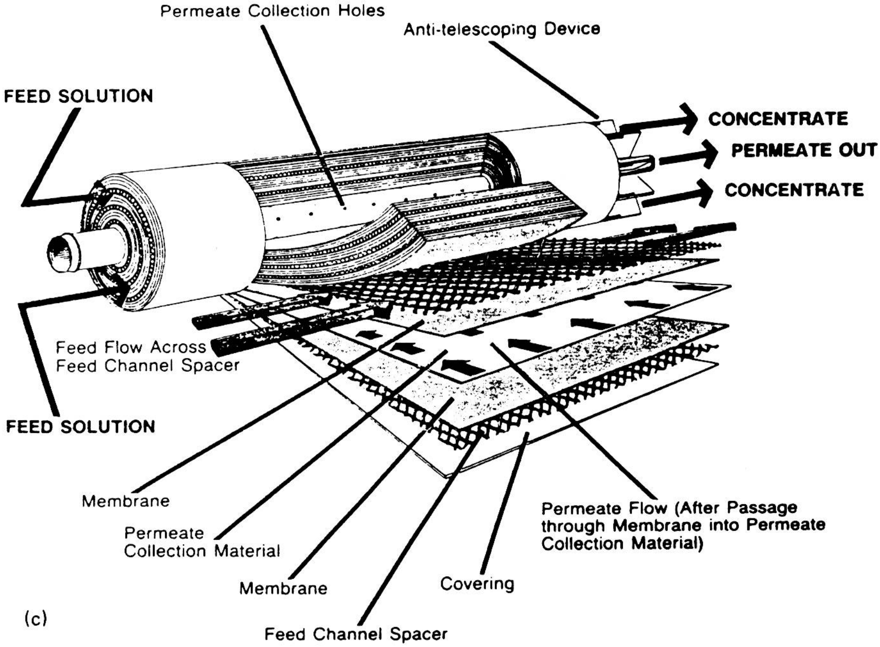
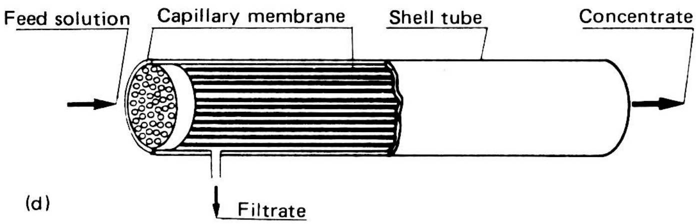


Fig. 2 Schematic representation of tubular membrane module (a), plate-and-frame membrane module (b), spiral-wound membrane module (c), and capillary membrane module (d).

Heterogeneous dense membranes have been the focus of special attention as a means of improving the multiseparation function. Kawatoh et al. [3] have reported a charged membrane with a phase-separated modulated structure where two polymer components form co-continuous phases through the membrane. The schematic representation of a unit cell of a modulated structure and the light micrograph of a polymer blend of chloromethyl polystyene/poly(acryl-



(c)

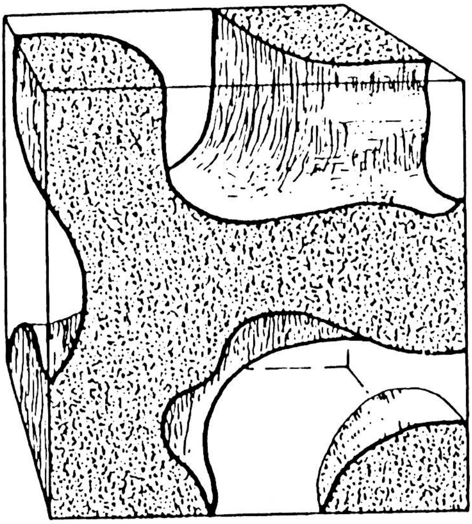


(d)

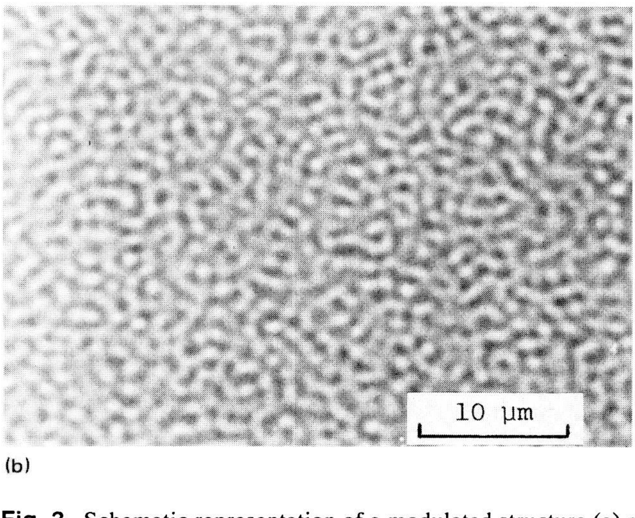
onitrile–co-styrene) are shown in Fig. 3a and b, respectively. Dense membranes with a modulated structure are to be developed further.

2. *Porous Membranes*

The porous membrane is also important in supporting the dense membrane. Therefore, the membrane has to resist the driving force, which is high-pressure driven for ultrafiltration and reverse osmosis separation, and must also not beprone to swellability caused by an aqueous solution. A part of the porous membrane of a polyether composite membrane that consists of a cross-linked polyether salt-rejecting barrier layer, a polysulfone supporting layer, and polyester fabric is shown in Fig. 4 [4]. One can see the porous membrane as a supporting layer of a thin dense layer with a thickness of 300 Å. Such a porous



(a)



(b)

Fig. 3 Schematic representation of a modulated structure (a) and light micrograph (b) of phase-separated modulated polymer blend of chloromethyl polystyrene/poly(acrylonitrile–co-styrene).

membrane is prepared by the precipitation of a polymer solution by a nonsolvent (phase inversion method) [5]. The formation of a pore is interpreted by the dissolution of good solvent in a polymer solution into a poor solvent. This im-

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