Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kurihara, Masaru(1994) 'Molecular and Morphological Designs of High Performance Polymeric Membranes', Journal of Macromolecular Science, Part A, 31: 11, 1791 — 1805

To link to this Article: DOI: 10.1080/10601329408545882

URL: http://dx.doi.org/10.1080/10601329408545882

J.M.S.—PURE APPL. CHEM., A31(11), pp. 1791–1805 (1994)

MOLECULAR AND MORPHOLOGICAL DESIGNS OF HIGH PERFORMANCE POLYMERIC MEMBRANES

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ABSTRACT

Currently, membrane separation techniques, such as reverse osmosis and ultrafiltration, play an important role in industrial separation technology. To develop high performance polymeric membranes, it is essential to design the molecular and morphological structures of the membranes for their specific applications. In the reverse osmosis field, we have developed several kinds of composite membranes for specific uses. Applications include ultrapure water production, seawater desalination, softening and desalination of brackish water, and recovery of valuable substances. In the course of development, thin-film composite membrane materials and membrane morphology have been analyzed intensively and are becoming clearer. These results enable us to control membrane performance by an optimum combination of membrane materials and membrane morphology. The morphological structure and chemical structure of the composite membranes were designed to optimize the performance of both the ultrathin layer and the supporting substrate layer for each membrane's application. As ultrafiltration is expanding to various fields, requirements for membrane performance have become more severe, especially for 1) sharpness of molecular weight cutoff, 2) solvent and high temperature resistance, and 3) fouling resistance (low nonspecific protein adsorption). To satisfy these requirements, we have developed a new ultrafiltration membrane. Owing to the high resistivity and hydrophilicity of its chemical structure, the membrane shows excellent solvent and high temperature resistance as well as fouling resistance. In addition, sharp molecular cutoff was realized by controlling membrane morphology.

INTRODUCTION

Membrane separation methods, such as reverse osmosis and ultrafiltration, play an important role in industrial separation technology. Recently, membrane materials and membrane morphology have been analyzed intensively and are becoming clearer. It is becoming necessary to design molecular and morphological structures of membranes to develop high performance polymeric membranes.

In this paper we discuss the relationship between membrane designs and membrane performance, and focus on reverse osmosis membranes and ultrafiltration membranes recently developed by Toray.

REVERSE OSMOSIS MEMBRANES

Background

Among desalination technologies available today, reverse osmosis (RO) is usually the most economical process for a wide range of water salinity. Main applications include production of high purity water, desalination of seawater and brackish water for a drinking water supply, treatment of wastewater for environmental protection, and recovery of precious materials from industrial wastewater.

Thin film composite membranes have reached a major position among reverse osmosis membranes because of their outstanding membrane performance and durability [1]. In a typical thin film composite membrane, an ultrathin salt barrier layer covers the surface of a porous polysulfone substrate. This salt barrier layer is formed by an in-situ interfacial polymerization reaction or an in-situ crosslinking reaction at the surface of the water-soluble polymer layer. Figure 1 illustrates a typical structure of the thin film composite membrane Toray UTC-70.

The diversity of applications in an industrial market shapes the development of specialized membranes with the demands for unique performance characteristics. Such demands are represented by 1) high selectivity, 2) high water permeability, and 3) tolerance for oxidizing agents.

High selectivity is a major requirement in seawater desalination to gain potable water with a high recovery rate, and in ultrapure water production for the electronics industry to remove low molecular weight total organic carbon (TOC). High water permeability is necessary for low pressure, low running cost operation. Tolerance for oxidizing agents allows disinfection by chlorine, such that the membrane systems will operate dependably without biological fouling.

To satisfy these requirements, much research has been done on membrane materials, structure, and fabrication technology. The in-situ interfacial polycondensation method (Fig. 2) and in-situ crosslinking reaction at the surface of the water-soluble polymer layer method were developed to obtain high performance composite membranes [2-6]. With this method, crosslinked polyamide composite membranes, which meet the previously discussed requirements, have been pro-

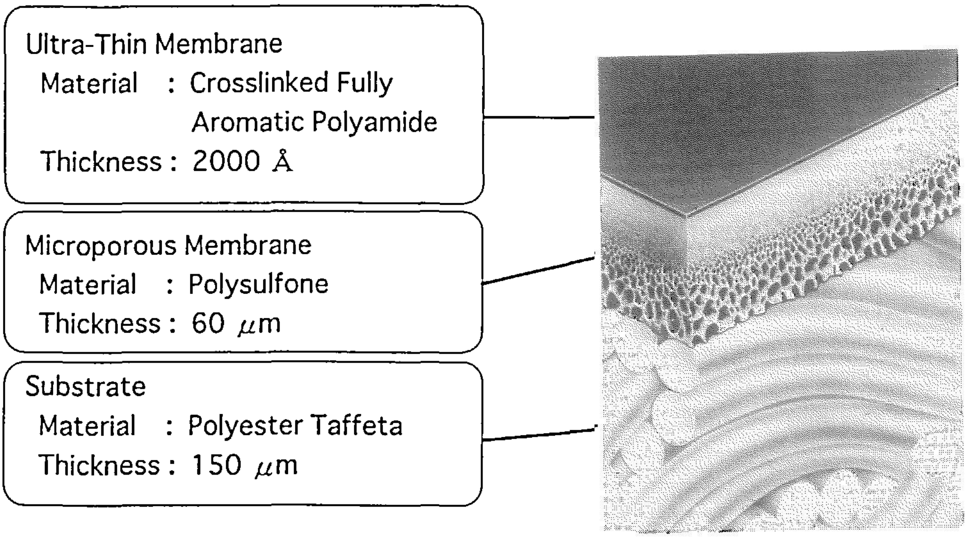

FIG. 1. Typical structure of the thin film composite membrane, Toray UTC-70.

duced commercially and have become one of the major reverse osmosis membrane types today.

Molecular Designs of Membrane Materials

Basically, membrane materials are required to have 1) proper hydrophilicity, 2) a rigid chemical structure (highly crosslinked), and 3) a chemically and thermally stable structure. Our assumptions to obtain a high performance membrane are as follows. Higher crosslinking density will be effective in the enhancement of solute

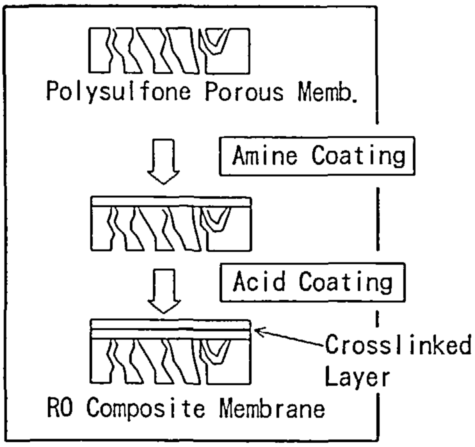

FIG. 2. In-situ interfacial polycondensation method.

rejection and the tolerance of oxidizing agents. High density of amide linkage will be effective for high water permeability.

To apply this assumption to crosslinked polyamide composite membranes, we synthesized several polyfunctional monomeric amines, such as tetraaminobenzanilide, triaminobenzanilide, tetraaminobiphenylether, tetraaminocarbazole, and 1,3,5-triaminobenzene, and evaluated them as a membrane component (Fig. 3). Among these polyamines, high purity 1,3,5-triaminobenzene (TAB) was found to be the most preferable polyamine to obtain a high performance reverse osmosis membrane [7, 8]. Because high purity TAB was not commercially available at that time, we developed a new synthesization method for it.

Various acid chlorides, which interfacially react with 1,3,5-triaminobenzene to produce an ultrathin layer, were also examined. Terephthaloyl chloride (TPC) gives superior salt rejection performance, and isophthaloyl chloride (IPC) gives superior water flux performance with preferable salt rejection. Although trimesoylchloride (TMC) was expected to form the highest crosslinking density, it did not give a high performance membrane, contrary to our expectations.

Finally, we selected TAB and *m*-phenylenediamine (MPD) as the polyamine, and TPC and TMC as the polyacylchloride. In consequence, we developed and commercialized UTC-70 [1, 7-10] (Fig. 4), a reverse osmosis membrane for ultrapure water production in the electronics industry. Moreover, we found that by changing the composition of these materials, we were able to design membrane performance.

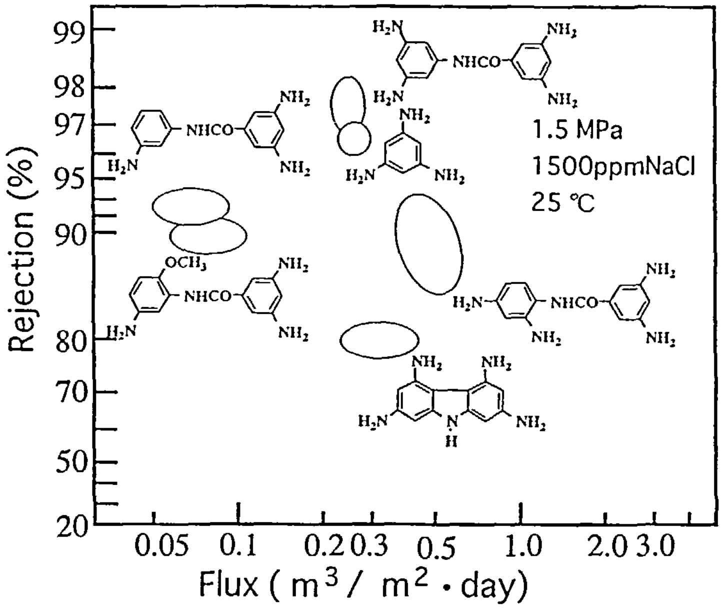

FIG. 3. Desalination performance of polyamide composite membranes from various polyamines.

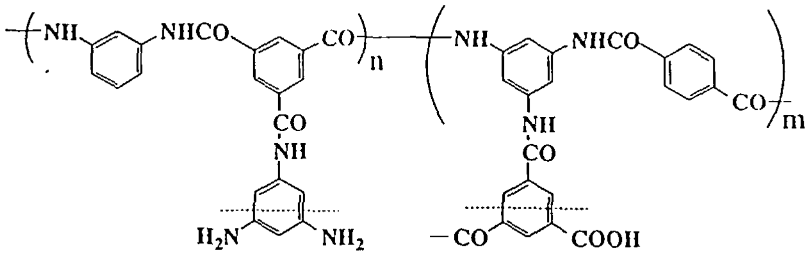

FIG. 4. Chemical structure of UTC-70.

Control of Performance in Membrane Fabrication

Based on UTC-70, Toray has now developed various types of composite reverse osmosis membranes suitable for a wide range of applications (Fig. 5). Performances of these membranes are controlled by changing the composition of the basic materials mentioned above, and also by changing the membrane fabrication.

A main process of membrane fabrication is an in-situ interfacial polycondensation reaction, i.e., an interfacial reaction between an aqueous solution of amines and an organic solution of acid chlorides. There are many factors in the process,

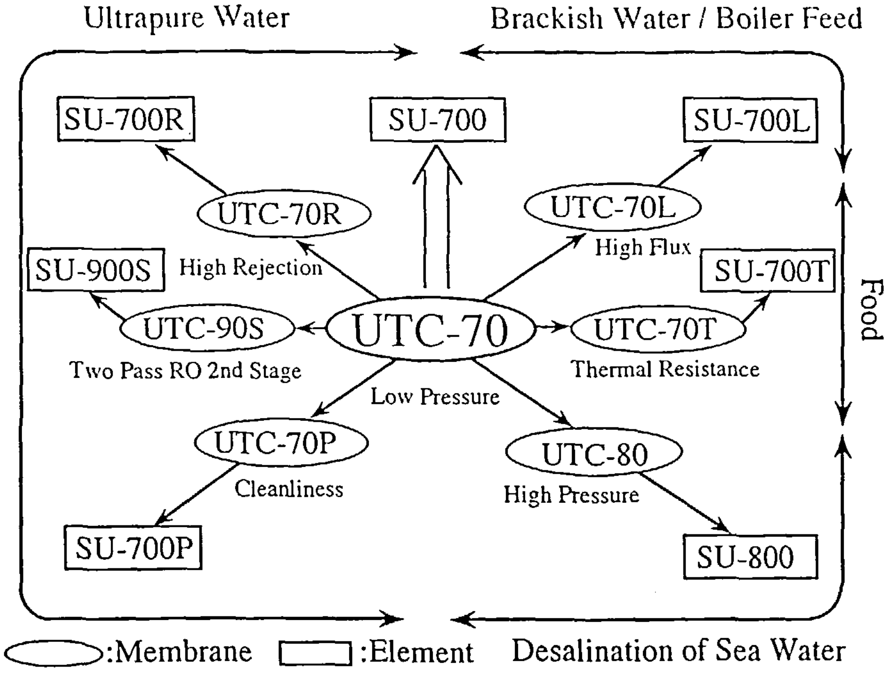

FIG. 5. Toray composite reverse osmosis membranes based on UTC-70.

e.g., diffusion rate of amines, membrane thickness, and surface charge related to end groups, that affect membrane performance (Fig. 6).

Another process of membrane fabrication is posttreatment. Posttreatment is the process that follows membrane formation via in-situ interfacial polycondensation. Various types of posttreatment, such as heat treatment, chemical treatment, etc., were investigated to change the chemical and physical characteristics of membranes.

The following sections discuss some examples of performance control involving in-situ interfacial polycondensation and posttreatments.

Improvement of Water Permeability (UTC-70L)

Based on our past experiments with various polyamide composite membranes, it was determined that the introduction of end acids is preferable to obtain better water permeability, and a decrease of end amines is preferable to obtain better tolerance of chloride. Using this approach, we tried to improve the water permeability of UTC-70. Our strategy for the introduction of end acids and the decrease of end amines is to improve the reactivity of acid chlorides by using a catalyst for in-situ interfacial polycondensation. As we had expected, we found that common catalysts for acylation worked effectively, and the water permeability of UTC-70 was increased without a severe decrease of membrane selectivity. This type of membrane is commercialized as UTC-70L, and membrane performance is shown in Fig. 7.

Improvement of Membrane Selectivity (UTC-70R)

To improve membrane selectivity, it is preferred that polyamide chains in the membrane be tightly packed. We found that a certain posttreatment, aimed at cleaving the hydrogen bonds of polyamides and reordering polymer chains, effec-

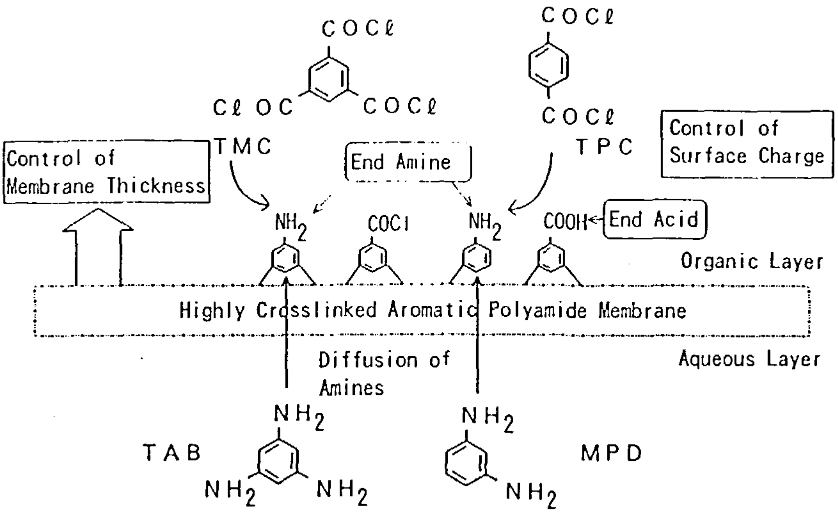

FIG. 6. Formation of a composite reverse osmosis membrane via in-situ interfacial polycondensation.

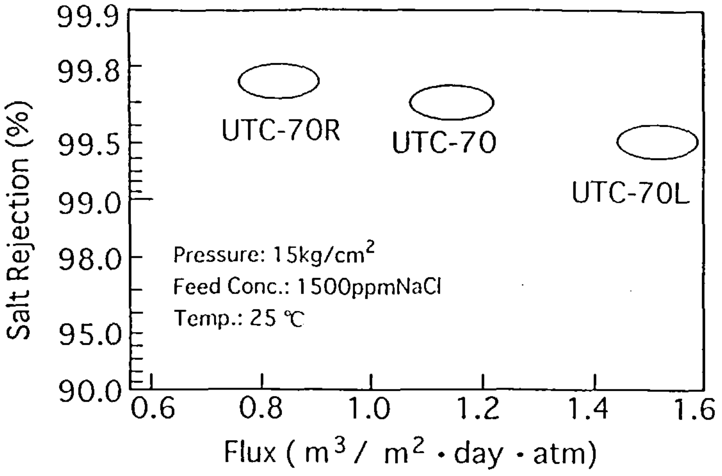

FIG. 7. Desalination performance of Toray low pressure membranes.

tively improved the membrane selectivity of UTC-70 (Fig. 8). This type of membrane is sold commercially as UTC-70R, and membrane performance is shown in Fig. 7.

Morphology of Thin Film Composite Membranes

In order to achieve practical fluxes with reverse osmosis membranes, the relatively dense surface of the membrane must be made as thin as possible. Thin film composite membranes are fabricated by depositing a thin and dense layer of polymer onto a microporous substrate. The usual methods used to form thin film

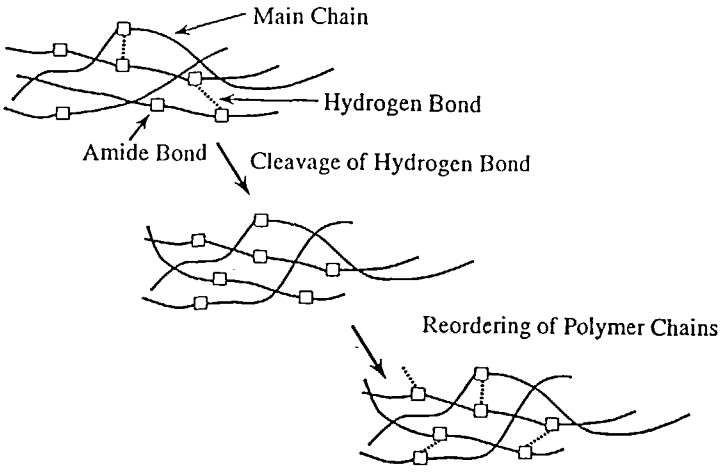

FIG. 8. Schematic illustration of posttreatment for cleavage of hydrogen bond and reordering.

composite membranes are 1) in-situ crosslinking reaction at the surface of the water-soluble polymer layer method and 2) in-situ interfacial polycondensation method.

The morphologies of thin film composite membranes depend on the materials used and the fabrication method.

1) In-Situ Crosslinking Reaction at the Surface of the Water-Soluble Polymer

An insoluble thin film was formed by a crosslinking reaction at the interface of the water-soluble polymer layer.

The NS-100 membrane (North Star, USA) was fabricated by first dipping the microporous substrate in a water solution of polyethylenimine and reacting this polymer with a hexane solution of isophthaloyl chloride, followed by heat treatment. There are two types of reactions involved in the preparation of this membrane [4]. The mechanism of these reactions is shown in Fig. 9. Polyethylenimine contains primary, secondary, and tertiary amine groups. In the first step, the amine groups react rapidly with isophthaloyl chloride at the interface to produce a polyamide surface skin, while amine groups below the interface remain unchanged. In the next drying and heating process, internal crosslinking of polyethylenimine takes place with the elimination of ammonia between adjacent amine groups. These reactions produce a gel layer of crosslinked polyethylenimine under the crosslinked polyamide ultrathin layer. It is said that interfacial polyamide reactions occur primarily on the organic solvent side of the interface [3]. That is, the amine reactant migrates across the interface into the organic phase in order for reaction to occur. Since the high molecular weight and hydrophilic polyethylenimine is essentially insoluble in the organic phase, the resulting layer of the interface is extremely thin. The crosslinked polyethylenimine gel layer is necessary to support such a ultrathin layer.

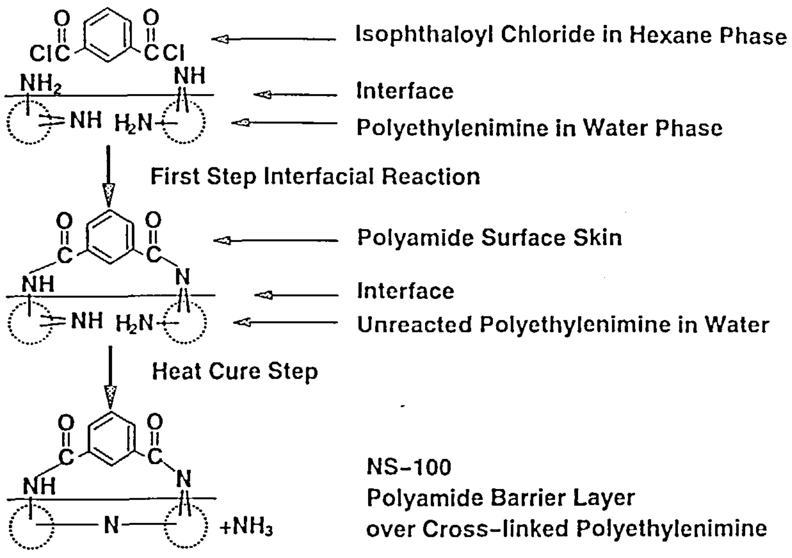

FIG. 9. A formation mechanism of NS-100 membrane.

The PA-300 membrane (UOP) is the same type of membrane. It uses polyetheramine as a water-soluble polymer and isophthaloyl chloride as a crosslinking agent [5]. Figure 10 shows an electron micrograph of the PA-300 membrane. The 0.01-μm ultrathin layer and the gel layer under the ultrathin layer can be seen clearly.

The thickness of the ultrathin layer fabricated by interfacial reaction using only polymeric amine is usually 0.01 μm. However, the thickness and membrane performance are easily controlled by using a mixture of polymeric and monomeric amines [6]. The mechanism of this interesting phenomenon is shown in Fig. 11. The water phase is a solution of polymeric and monomeric amines, and the upper organic phase is a solution of a crosslinking agent. The polymeric and monomeric amines diffuse to the organic phase and react with the crosslinking agent. The monomeric amine can easily diffuse across the ultrathin layer, so the resulting thickness of the ultrathin layer is greater than when only a polymeric amine is used. The thickness of the ultrathin layer is 0.03 μm when polymeric and monomeric amines are used compared to 0.01 μm when only a polymeric amine is used. Figure 12 shows an electron micrograph of such a membrane. The salt rejection of this membrane is in the 99.45–99.60% range. This rejection is greater than that of a membrane prepared from only a polymeric amine.

2) In-Situ Interfacial Polycondensation Type

Interfacial polycondensation on the microporous substrate to produce an ultrathin membrane layer is one application of the technique developed by P. W. Morgan [3].

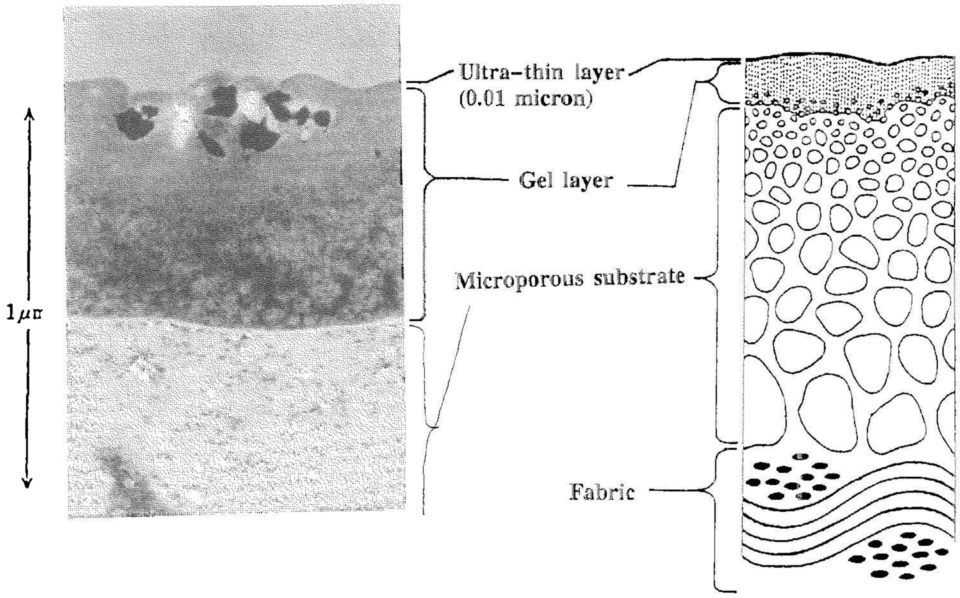

FIG. 10. Electron microphotograph and structure model of PA-300 membrane.

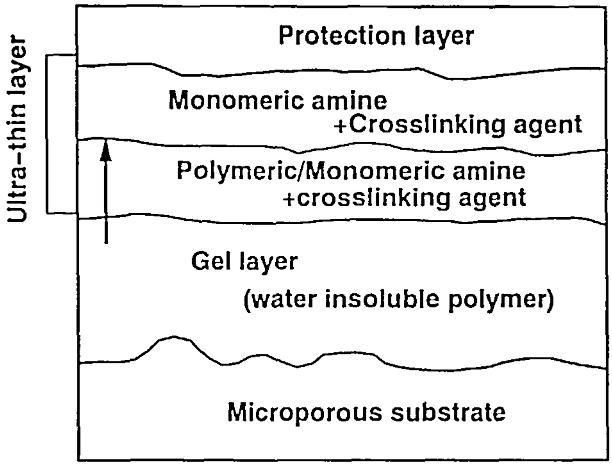

FIG. 11. Mechanism of interfacial polycondensation of polymeric/monomeric amine system.

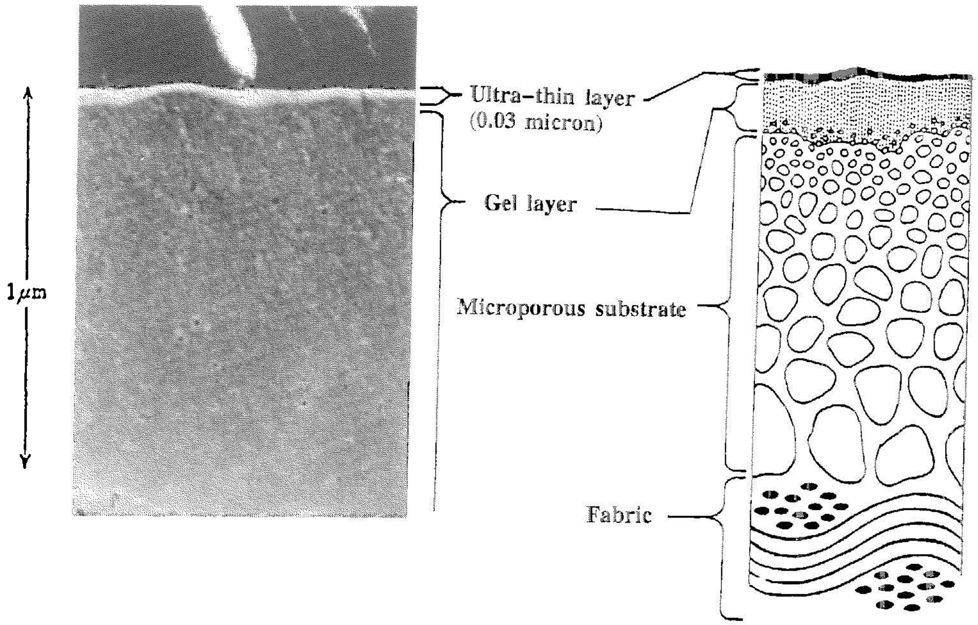

FIG. 12. Electron microphotograph and structure model of composite membrane formed by polymeric/monomeric amine system.

A microporous substrate is saturated in a water solution of monomeric amine. After draining the excess water solution, the substrate is contacted with organic solutions of amino reactive agents. An ultrathin layer is produced by interfacial polycondensation. This method seems like the membrane fabrication method of crosslinking a water-soluble polymer surface as described in Section 1. However, the morphological structures of these two types of membranes are different.

High performance reverse osmosis membranes, with high salt rejection and high water permeability, have been produced by many companies with this interfacial polycondensation method using an aromatic polyamine and an aromatic polyacylchloride. For example, a scanning electron micrograph of Toray's UTC-70 membrane [9] is shown in Fig. 13.

The morphological difference between this interfacial polycondensation membrane and the crosslinking of polymer surface membrane is the formation of protuberances at the membrane surface. Since this monomer can diffuse through the ultrathin layer, the polycondensation reaction is continued, and the resulting ultrathin layer becomes thicker.

ULTRAFILTRATION MEMBRANES

Background

Following A. S. Michaels' success in making an artificial ultrafiltration membrane [11], various kinds of membranes have been developed and investigated.

Recently, due to the development of biotechnology, there has been an increasing need for the separation of proteins and peptide drugs from biological broths. However, many ultrafiltration membranes have been troubled by membrane fouling, which reduces membrane performance during operation. In the pharmaceutical

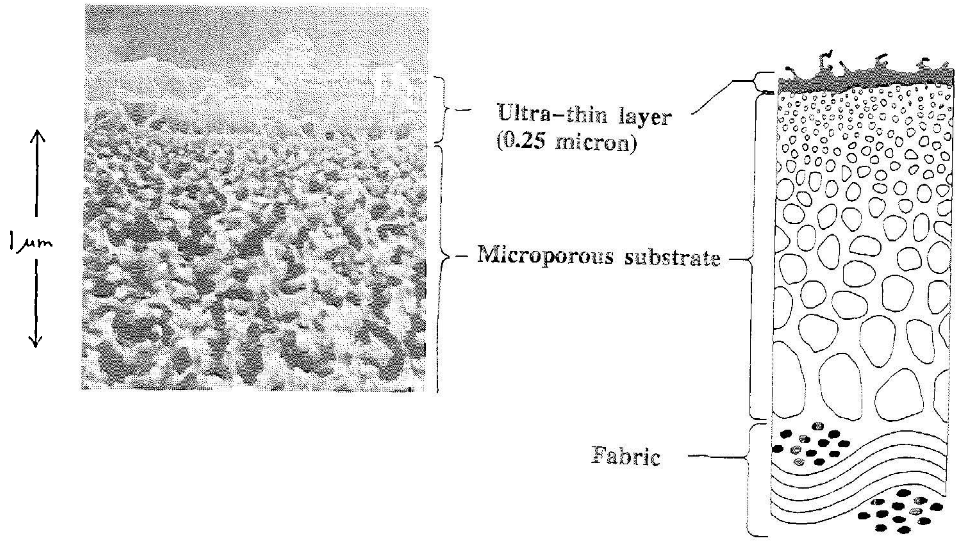

FIG. 13. Electron microphotograph and structure model of UTC-70 membrane.

and food industries, ultrafiltration membranes are required to have high temperature resistance and solvent resistance, which allows them to be used in nonaqueous systems. Therefore, new ultrafiltration membranes are required to have superior performance as represented by 1) sharpness of molecular weight cutoff, 2) solvent and high temperature resistance, and 3) fouling resistance (low nonspecific solute adsorption).

Design of High Resistant Ultrafiltration Membrane

In the case of ultrafiltration membranes, the durability of the membrane is due to the membrane material. Therefore, selection of membrane material is the most important aspect in the design of highly resistant ultrafiltration membranes. Figure 14 shows a comparison of engineering plastics which have been investigated for ultrafiltration membranes with solvent and high temperature resistance. It is extremely difficult to find materials which satisfy both excellent resistivity and excellent processibility. Polyimide is the only material commercialized as a resistant ultrafiltration membrane.

To satisfy the requirements of resistivity and processibility, our strategy is as shown in Fig. 15.

In some solvents, polyphenyrene sulfide sulfone (PPSS) has a processibility similar to that of polysulfone, which is currently widely used for ultrafiltration membranes. Therefore, an ultrafiltration membrane of PPSS was formed using a procedure similar to the conventional one. After formation, the membrane was treated with an oxidizer to convert PPSS to polyphenyrene sulfone (PPSO) which

	Processibility	Sharpness of Molecular Weight Cutoff	Solvent Resistance	Heat Resistance
PPS	poor	poor	excellent	excellent
PTFE	poor	poor	excellent	excellent
PEEK	poor	poor	excellent	excellent
Polyimide	good	good	excellent	excellent

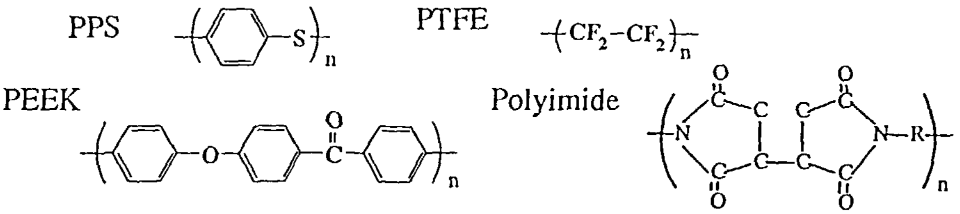

FIG. 14. Comparison of membrane materials for high resistance UF membrane.

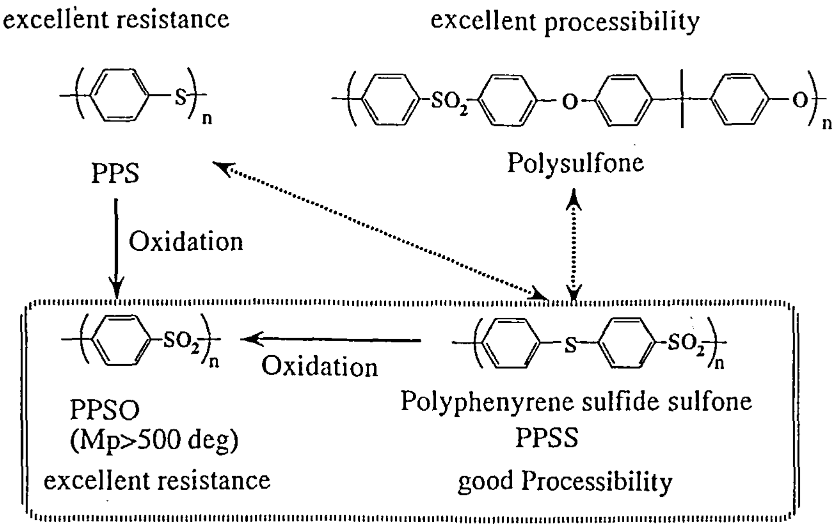

FIG. 15. Strategy for development of high resistance UF membrane.

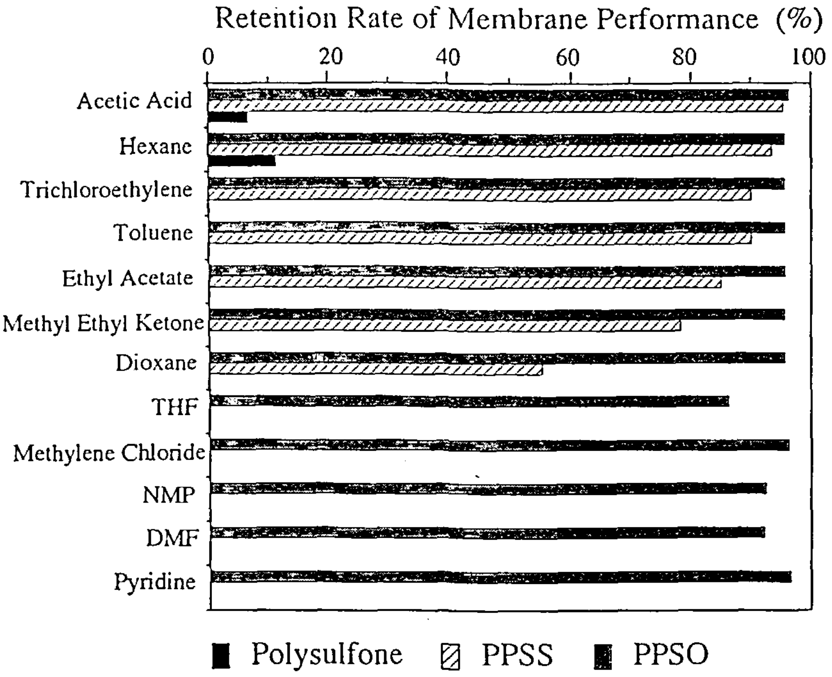

FIG. 16. Solvent resistance of PPSS and PPSO membranes.

exhibits excellent solvent and high temperature resistance. The resulting PPSO membrane has unique characteristics: 1) controllability and sharpness of molecular cut-off similar to polysulfone, 2) excellent solvent and high temperature resistance (Fig. 16), and 3) low nonspecific solute adsorption owing to the hydrophilic character of the PPSO chemical structure [1].

CONCLUSION

As applications of membrane separation technology expand, various requirements for membrane performance arise. Therefore, it is important to control membrane performance and specialize it for each application.

In reverse osmosis membranes we introduced high amide linkages into the polyamide membrane in order to realize better salt rejection and better water flux. A crosslinked, fully aromatic polyamide membrane from 1,3,5-triaminobenzene was found to have excellent separation performance and durability. Based on UTC-70, a fully aromatic polyamide membrane from 1,3,5-triaminobenzene produced by Toray, various types of membranes have been developed to satisfy different requirements for a wide range of applications. In such membranes, controlling membrane performance is accomplished through composition of the membrane materials, control of the polycondensation reaction, physical treatment, and chemical treatment. These aspects are closely linked to the chemical and physical structures of the membranes.

In ultrafiltration membranes, solvent and heat resistance requirements are the most frequent demands in expanding their application. Owing to the excellent processibility of PPSS polymer and its high resistance after oxidation, the PPSO membrane we developed shows the excellent performance needed to satisfy such demands.

Finally, we point out that the design of the chemical and physical structures of high performance polymeric membranes is accomplished on the basis of detailed analyses of membrane materials and membrane morphology, and on a better understanding of membrane performance.

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