New Hydrophilic Polypropylene Membranes; Fabrication and Evaluation

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ABSTRACT: This article discusses a new method to prepare polypropylene membrane that has hydrophilic surfaces and asymmetric porous structure. This membrane is based on a newly developed hydroxylated polypropylene (PP–OH), which has a "brush-like" microstructure, high molecular weight, high melting point, and relatively high concentration of hydroxy groups. Under the leaching process conditions, various asymmetric hydrophilic PP/PP–OH membranes are prepared with controllable pore structures. The PP–OH polymer becomes the surface modifier of asymmetric PP membrane with flexible functional groups located on the membrane surfaces, including pore surfaces. This new hydrophilic PP/PP–OH membrane is useful in ultrafiltration, not only offering good selectivity and flux but also showing excellence in antifouling property. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 567–575, 1997

Key words: polypropylene membrane; hydrophilic; asymmetric; ultrafiltration; antifouling

INTRODUCTION

Many of the polymers used for commercially available synthetic membranes are hydrophobic polymers, such as polypropylene (PP), poly (ether imide), poly (vinylidene fluoride), and polysulfones. Among these hydrophobic polymers, polypropylene has been used extensively in filtration membrane applications because polypropylene is chemically stable and mechanically sturdy, and can be used at relatively high temperatures. However, in spite of its extensive uses, polypropylene is hydrophobic, i.e., nonwettable by water, and is impermeable to ions in an aqueous solution unless a positive pressure gradient is applied. Moreover, PP membranes, as well as other hydrophobic membranes prepared from other hydrophobic polymers, are characterized by a flux decline that is caused by fouling[1,2] due to solute adsorption and pore blocking.

It is generally accepted that the use of filtration membranes having hydrophilic surfaces can minimize fouling. The hydrophilic functional groups form hydrogen bonding with water and the wetted surface causes efficient diffusion of solutes. Accordingly, it would be very desirable to provide polypropylene filtration membranes with a hydrophilic surface covered with functional (polar) groups. A primary limitation of polypropylene in the membrane field is the difficulty of producing polypropylene with a hydrophilic surface. In the past, hydrophilization of polypropylene membranes has been performed by both chemical and physical modifications using posttreatment processes. Several approaches were reported by treating the polypropylene membranes with sulphonating agent,[3] plasma,[4] and grafting of hydrophilic monomers such as acrylamide[5] or acrylic ester[2] onto the macromolecules. A physical modi-

fication[6] of a polypropylene membrane involves wetting the membrane with a water-soluble polymer. Although there are several prior reports of treating polypropylene to render its surfaces hydrophilic, polypropylene has been one of the most resistant polymers to chemical modifications. The inert nature and crystallinity of polypropylene usually make it very difficult to chemically modify under mild reaction conditions. In many cases, the reaction involves serious side reactions, such as degradation and crosslinking.[7,8]

A variety of methods has also been developed for preparing polypropylene membranes with desirable morphological structure, including dense and symmetric and asymmetric porous membranes. The preparation of a nonoriented dense film comprised of a single phase blend of polypropylene and mineral oil was described by Salyer.[9] The methods for making porous polyolefin membrane were disclosed in many patents.[10,11] But a primary limitation of polypropylene in membrane field is the difficulty of achieving hydrophilic behavior, especially membranes containing hydroxy groups that have been suggested to be the prefered hydrophilic groups[12] on membrane surfaces.

In our previous article, we have systematically investigated a new functionalization chemistry based on the borane-containing polyolefins.[13–16] A broad range of functional polypropylene copolymers have been prepared with high molecular weight, high melting point, and controllable molecular composition and microstructure. The resulting functionalized polyolefins were proved to be effective compatibilizers to improve polyolefin blends[17,18] by forming small and uniform domain sizes and increasing the interaction between domains.

EXPERIMENTAL DETAILS

Materials and Instrumentation

The hydroxylated polypropylene (PP–OH) is prepared as described in the literature.[19]

PP, PEG, PVP, and xylene were purchased from commercial sources and used as received. Ultrafiltration rate was measured by the ultrafiltration cell (Amicon 8050), using aqueous solution of 2000 ppm with various solutes. Solute concentrations in the feed and product solutions were determined by means of refractometer (Waters R403). Scanning electron microscopy

was used to view the morphology of membranes with a Topcon International Scientific Instruments ISI-SX-40 using secondary electron imaging. Contact angle was determined by ten water points on each membrane surface. The measurement was carried directly on the sessile water drop with the help of the Rame Hart telescope goniometer. The sessile water drop have a diameter of at least 4 mm in order to eliminate the size influence on the contact angle. Tensile strength (MPa) was determined according to ASTM D 1708–84 using an Instron model 4201 lab top tester with a 1 KN load cell.

Preparation of PP–OH/PP Membranes

As a typical example in the preparation of membrane A-1, PP–OH (3 mol % of hydroxy group and $M_v = 183,000$ g/mol) was mixed with PP ($M_w = 230,000$ g/mol), hydrophilic additive (phenol), and xylene at 170°C with the weight ratio of 1 : 1 : 2 : 98. The mixture was then stirred at 170°C until a homogeneous solution was obtained. The solution was cast on the Teflon plate kept at 90°C and was spread with a casting bar equipped with a spacer. The solvent was allowed to evaporate completely at this temperature. The resulting film was then immersed in a bath of methanol (maintained at about 45°C) for 5 days to remove the phenol. The methanol bath was changed many times to facilitate the phenol extraction. The resulting PP/PP–OH membrane was stored in a distilled water bath before measuring its performance.

Similar procedures shown above were used in the preparation of sample A-2, except changing the additive to polyethylene glycol ($M_w = 1000$ g/mol). The homogeneous solution of PP–OH, PP, PEG, and xylene, with the weight ratio of 2 : 2 : 1 : 196 and at 170°C, was poured onto the preheated Teflon plate (at 90°C) and spread with a casting bar equipped with a spacer. After solvent preevaporation, the resulting film was immersed into a bath of frequently renewed hot water (80°C) for 5 days to remove PEG. The resulting PP/PP–OH membrane was also stored in a distilled water bath before measuring its performance. On the other hand, the preparation of sample A-3 involved two additives, PEG ($M_w = 1000$ g/mol), PVP ($M_w = 10,000$ g/mol). After mixing PP–OH, PP, PEG, PVP, and xylene with the weight ratio of 4 : 4 : 1 : 1 : 520 at 170°C, the similar film casting procedures were applied except the preevapora-

tion procedures. The thin film was allowed to preevaporate until the gel film was formed on the exposed surface. The solution with thin gel layer was then covered with a glass plate to provide a controlled, slow evaporation and cooling. After a completely gelled film was obtained, the film was dried at room temperature and ambient humidity. The resulting film was immersed into a bath of hot water (80°C) for 5 days to remove PEG and PVP. The hot water was exchanged for fresh one very often. The resultant film, now a membrane, was also stored in a distilled water bath before measuring its performance.

RESULTS AND DISCUSSION

The major object of this study is to develop a new hydrophilic polypropylene membrane that can provide not only good selectivity and flux but also excellent antifouling property in filtration applications. It is a further object of this study to develop a process for preparing asymmetric porous PP/PP–OH membranes with controllable pore structure. The membrane comprises polypropylene (PP) matrix and hydroxylated polypropylene (PP–OH) located on the surfaces of the membrane, including pores. In the ultrafiltration applications, it is desirable to have a dense skin layer with a uniform pore size (<1 μm). Away from the skin layer, the pore size sharply increases to relatively large size, up to 20 μm on the support surface.

Hydroxylated Polypropylene

The preparation of PP–OH copolymer[19] involves Ziegler–Natta copolymerization of propylene and borene monomer, such as 5-hexenyl-9-BBN (BBN: borabicyclononane). Due to good

chemical stability of borane group to catalyst (catalyst poisoning[20,21] is usually the case in the polymerization of functional monomers using Ziegler–Natta catalysts) and good solubility of borane group in hydrocarbon solvent, the borane monomer behaves like a high α-olefin, such as 1-octene, and can be effectively incorporated into PP copolymer[22] with controllable concentration and high molecular weight. In turn, the borane groups in copolymer are easily converted to the corresponding hydroxy groups by suspending borane containing PP powder in NaOH/H_2O_2 aqueous solution at 40°C for 3 h. The effective interconversion in heterogeneous reaction condition is due to the high surface area of borane groups in the semicrystalline microstructure of the copolymers. The borane groups located in the flexible side chains may migrate to the surfaces or amorphous phases where the chemical reagents can be easily reached. Table I shows several PP–OH copolymers that are used in the membrane fabrications.

The molecular weight of PP–OH was determined by intrinsic viscosity, which was measured in cone/plate viscometer at 135°C in decalin solution. To enhance the solubility of polymers, the hydroxylated polymers were esterified with benzoyl chloride. The viscosity average molecular weights (M_v) were calculated using the Mark–Houwink equation.[23]

To be an effective surface modifier on the PP membrane, it is crucial to have the PP–OH copolymer, which can undergo cocrystallization with the PP homopolymer. In other words, the PP–OH copolymer must have high molecular weight and high crystallinity and melting point as isotactic PP. Due to the reactivity difference between propylene and borane monomer, the more reactive propylene was added by a step-wise fashion during the copolymerization. Such a process produced the PP–OH copolymer with a "brush-like" microstructure[22] as shown below:

F : —OH, —NH$_2$, —COOH
$n > 3$

Table I   The Summary of PP–OH Copolymers Prepared by the Copolymerization of α-Olefin (m_1) and Borane Monomer (m_2) with Continuous Reaction Process

Comonomers m_1/m_2 (Mol Ratio)	Reaction Temp/Time (°C/h)	Yield (%)	OH Groups in Copolymer (mol %)	Intrinsic Viscosity (η)	M_v (g/mol)	M_p (°C)
100/0	25/2	93	0	2.07	230,000	165
95/5	25/3	87	1.7	1.95	210,000	165
90/10	25/4	72	3	1.78	183,000	163
85/15	25/5	55	6	1.71	174,000	158

The consecutive sequence of propylene units preserves crystallinity and melting point of polypropylene segment. Therefore, the copolymer can form high crystallinity by itself, and can also effectively undergo cocrystallization[24,25] with isotactic polypropylene homopolymer. During the crystallization process, the mobile functional group located at the end of each side chain is expelled out from the crystalline phase to the amorphous phase and surfaces. In the porous PP/PP–OH membrane case, the functional groups will be located on the surfaces, including pore surfaces. The high surface area and mobility of functional groups offer many advantages to the membrane filtrations as will be discussed later.

PP/PP–OH Membrane

The preparation of asymmetric hydrophilic PP/PP–OH membranes involves a film casting and leaching process (discussed in the Experimental section). Several polar hydrophilic molecules, including phenol, polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), were used as the fugitive additives (pore forming agents). Figures 1–3 show the scanning electron microscopy (SEM) micrographs of three hydrophilic PP/PP–OH membranes (samples A-1 to A-3 in Table II), which are prepared by using the same PP and PP–OH polymers and different additives and preevaporation conditions. The film thickness is between 60 and 90 μm.

All the resulting membranes have an asymmetric porous structure, including a dense active surface (contacted to Teflon surface) and a highly porous support surface (opened to air). On the dense surface, the uniform pores are observed with the pore size varied from complete dense (in which pores cannot be observed by an scanning electron microscope) to < 1 μm. On the other hand, the pore size as high as 30 μm is observed on the support surface. In general, the pore size and density on surfaces are strongly determined by the processing conditions, the combination of additive (concentration and molecular weight), and preevaporation conditions. Pore structure in the membrane is the image of fugitive additives in the cast film. The additives diffuse from the surface contacted to Teflon to the surface opened to air during the preevaporation process. In sample A-1, the fugitive additive of phenol (low molecular weight and high diffusibility) produces sharp pore structure differences between two surfaces as shown in Figure 1. The small pore size and low

**Table II   A Summary of Preparation and Properties of PP/PP–OH Membranes**

	Preparation Conditions[a]				Physical Properties		Pore Size (μm)		
Sample	PP (g)	PP–OH (g)	Additive/(g)	Xylene (g)	Contact Angle[b]	Thickness (μm)	Dense Layer	Open Layer	Tensile Strength (Mpa)
A-1	4	4	phenol/8 g	392	79° + 5°	80	< 0.1	10–25	7.5
A-2	4	4	PEG/2 g PEG/1 g	392	79° + 1°	60	0.13–0.5	1–2	13.2
A-3	4	4	PVP/1 g	520	82° + 2°	90	0.5–1.5	2–8	4.8

[a] PP (M_v = 230,000 g/mol), PP–OH (3 mol % of hydroxy group and M_v = 183,000 g/mol). PEG (M_w = 1,000 g/mol) and PVP (M_w = 10,000 g/mol).
[b] The contact angle of dense skin layer.
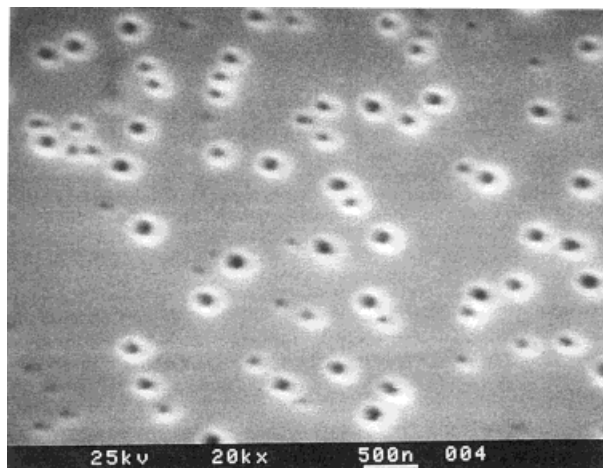
Surface contacted to Teflon
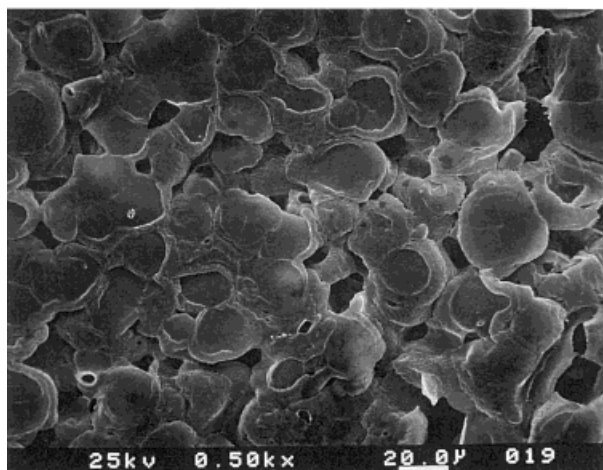
Surface exposed to air

Figure 1 SEM micrographs of A-1 asymmetric PP/PP−OH membrane (top) surface contacted to Teflon and (bottom) surface exposed to air.

pore density on the dense surface clearly indicate the fast diffusion of phenol away from Teflon surface during the preevaporation stage. The large pore size and high pore area on the support surface are due to high concentration of additive, which is removed during the leaching procedure. On the other hand, the higher molecular weight additive of polyethylene glycol in sample A-2 significantly reduces the rate of diffusion under the same processing conditions. Therefore, the difference of pore size and density between two surfaces is significantly reduced. In spite of the fact that only a quarter of the quantity of additive was used (vs. sample A-1), the density and size of pores on the dense surface increases. The effect of mem-

brane morphology by additive diffusion is even more apparent in sample A-3 (Fig. 3). With the use of higher molecular weight PVP, the pore size and density on both surfaces show little different.

Table II summarizes the process conditions and physical properties of three PP/PP−OH membranes.

The PP/PP−OH membranes typically have a water permeability (discussed later) of about 7 to 25 L/m^{2}h. under a pressure of 2 kg/cm^2, and the contact angles on the surface of the membrane are about 80°. High percentage of hydroxy groups in the PP−OH copolymer must be located on the surfaces of the membrane, including the surface of pores. The same result was observed
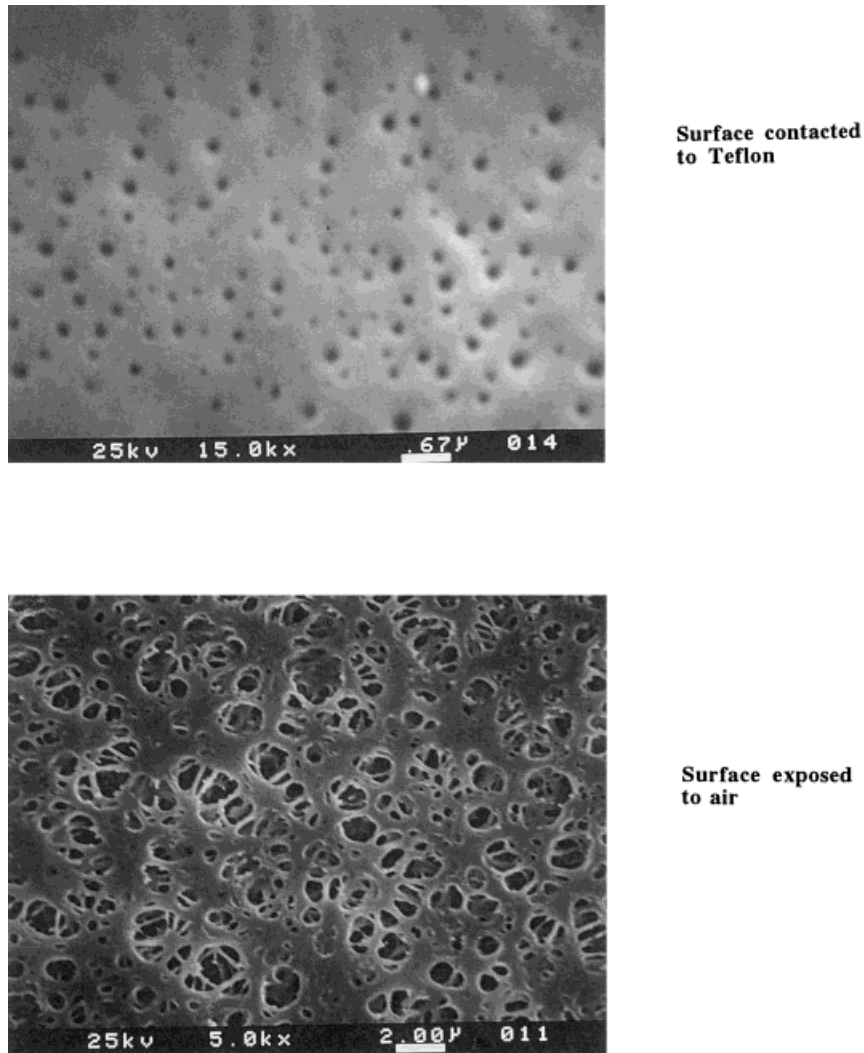
Surface contacted
to Teflon

Surface exposed
to air

Figure 2 SEM micrographs of A-1 asymmetric PP/PP–OH membrane (top) surface contacted to Teflon and (bottom) surface exposed to air.

in an independent study, by immersing PP/PP–OH membrane into $EtAlCl_2$ solution. It was found that most of —OH groups were reacted with $EtAlCl_2$ to form —O—$AlCl_2$ species[26] despite the heterogeneous condition. The control of hydroxy group location is obviously due to the chemical affinity between hydroxy group and fugitive additive. During the film casting, the PP–OH serves as the compatibilizer between PP and hydrophilic additive to produce a composite film with stable two-phase morphology containing a continuous phase and an uniform discrete spherical phase.

The size and density of discrete domains are directly proportional to the concentration of hydrophilic additives. At the interface, the PP segments in the PP–OH copolymer must cocrystallize[25] with the PP homopolymer in the continuous phase and the hydroxy groups may form hydrogen bonding with hydrophilic additives in the discrete phase. During the leaching process, the high crystalline (high melting point) PP phase maintains dimension stability and becomes a reticular structure, whereas the discrete phase of additive is dissolved in water (or methanol) to produce pores. The OH groups in PP–OH copolymer therefore become free and are exactly located at the surface of pores.

Filtration Study

The resulting asymmetric PP/PP–OH membranes are evaluated in the filtration studies, separating
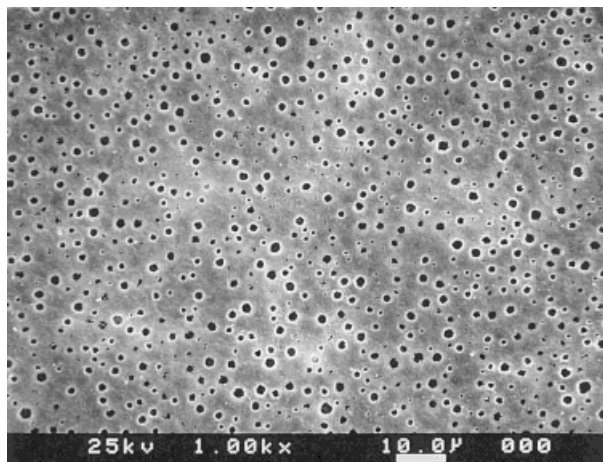
Surface contacted
to Teflon
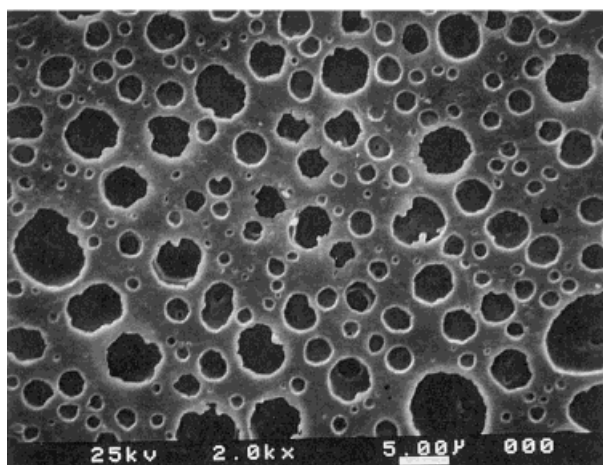
Surface exposed
to air

Figure 3 SEM micrographs of A-1 asymmetric PP/PP–OH membrane (top) surface contacted to Teflon and (bottom) surface exposed to air.

substances in a variety of filtration processes, including microfiltration, ultrafiltration, and dialysis processes. The performance of membrane can be illustrated by measuring solute permeability coefficient, % rejection, and stability in long-term use. The solute permeability coefficient (P) $(cm^3 \cdot cm/cm^2 \cdot s)$ can be calculated by following equation.

$$P = \frac{-d}{A(1/V_1 + 1/V_2)t}$$
$$\times \ln\left[(1 + V_1/V_2)\frac{C_t}{C_o} - \frac{V_1}{V_2}\right]$$

where V_1, V_2, A, d, C_o, and C_t are volumes of the

concentrated and dilute component, membrane area, thickness, and concentrations of the concentrated component at times o and t, respectively. Water permeability $(liter/m^2 \cdot h \cdot atm)$ determines the filtration rate through the membrane per unit area and time under pressure. The rejection (%) is calculated by following equation.

Rejection (%)

$$= \left[1 - \frac{\text{Permeate solute concentration}}{\text{Retentate solute concentration}}\right] \times 100$$

Molecular weight cutoff is the molecular weight

Table III   The Ultrafiltration Results of PP/PP–OH Membranes

Solute	Molecular Weight (g/mol)	Flux (l/m²·h)			Rejection (%)		
		A-1	A-2	A-3	A-1	A-2	A-3
Water	18	7.5	8.9	23.2	0	0	0
PEG	200	6.2	6.7	22.4	0	0	0
PEG	600	5.3	6.2	21.3	8	5	0
PEG	1,000	3.8	5.2	20.3	40	42	0
PEG	7,500	2.1	2.0	19.2	91	89	5
PEG	20,000	1.7	1.2	12.2	96	95	97
Dextran	10,000	1.8	1.9	12.8	89	87	68
Dextran	40,000	1.5	1.6	8.7	95	93	95
Dextran	75,000	1.1	1.0	6.5	98	97	98

(M_w) at which at least 90% of a solute of that M_w is retained by membrane.

Table III shows the ultrafiltration results of A-1, A-2, and A-3 samples for three solutes, including water, polyethylene glycol, and dextran with various molecular weight. The examination is performed at 25°C with the pressure of 2 kg/cm², and the concentration of solute is about 2000 ppm in water.

Only a single membrane is used in each set of evaluation study. In addition, each evaluation is carried out for a long period time without significant changes in rejection (%) and flux. In fact, the used membrane is reexamined by SEM measurement after completing the evaluation studies. No detectable changes in membrane morphology, including pore size and shape, is observed. The significant improvement in antifouling property is clearly attributed to the hydroxy groups located on the surfaces of PP/PP–OH membrane.

Overall, all PP/PP–OH membranes show good selectivities. The rejection molecular weight is correlated to the pore size on the dense layer; the larger the size, the larger the rejection molecular weight. The sharp selectivity is clearly shown in Figure 4.

For A-1 and A-2 membranes, the rejection molecular weight is about 7500 g/mol for PEG and 10,000 g/mol for Dextran. For A-3 membrane, the rejection molecular weight increases to 20,000 g/mol for PEG and about 40,000 g/mol for Dextran. As expected, the flux is strongly related to the pore size in the dense layer. In general, the relatively high flux is observed in each PP/PP–OH membranes, including sample A-1 with highly dense layer. In addition to the macroscale structural factors, such as pore structure and thickness, some microscale (molecular) factors may

also influence mass transfer rates. The flexible hydroxy groups located at the end of each side chain in PP–OH polymer may provide advantages, such as thermodynamic transitions related with macromolecular relaxation phenomena,[27] in transporting hydrophilic mass through the pore structures.

CONCLUSION

New type hydrophilic polypropylene PP/PP–OH membranes have been developed, which not only offer high flux and high retention of substances in the separation process but also significantly
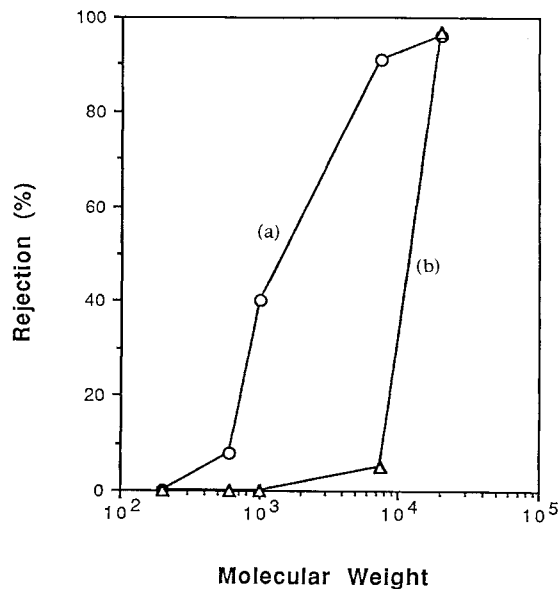

Figure 4 Ultrafiltration studies for (a) A-1 membrane and (b) A-3 membrane.

improve fouling property. The preparation of new membrane involves a newly developed functionalized polypropylene (PP–OH) that is a very effective surface modifier for polypropylene. In PP/PP–OH membrane, the PP–OH polymer provides the hydrophilic surfaces of membranes, including the surfaces of pores. With the film casting-leaching process and the choice of hydrophilic additive, procedures to prepare asymmetric PP/PP–OH membranes with controllable pore size and hydrophilic surfaces have been demonstrated.

REFERENCES

1. M. Mulder, *Basic Principles of Membrane Technology,* Kluwer Academic Publishers, London, 1990

2. S. Hiroyuki, M. Masahiro, T. Ryozo, T. Toshikazu, T. Kazumi, and F. Fumiaki, U.S. Pat. 5,480,953.

3. K. Matsuda and M. Kohno, U.S. Pat. 4, 409, 339.

4. Y. J. Wang, C. H. Chen, M. L. Yeh, G. H. Hsiue, and B. C. Yu, *J. Membr. Sci.,* **53,** 275 (1990).

5. M. Toshio, H. Okihiko, O. Makoto, and S. Yukio, U.S. Pat. 5,186,835.

6. K. Jun, H. Takayuki, T. Hiroshi, and K. Kenji, Eur. Pat. Appl. EP 498,414 (1992).

7. G. Ruggeri, M. Aglietto, A. Petragnani, and F. Ciardelli, *Eur. Polym. J.,* **19,** 863 (1983).

8. R. M. Ho, A. C. Su, C. H. Wu, and S. I. Chen, *Polymer,* **34,** 3264 (1993).

9. I. O. Salyer, U.S. Pat. 3,201,364.

10. Y. Doi, M. Kohno, and K. Yoshitake, U.S. Pat. 4,190,707.

11. G. H. Shipman, U.S. Pat. 4,539,256.

12. H. J. Chun, J. J. Kim, S. H. Lee, U. Y. Kim, and K. Y. Kim, *Polym. J.,* **22,** 477 (1990).

13. T. C. Chung, U.S. Pat. 4,734,472.

14. T. C. Chung, U.S. Pat. 4,812,529.

15. T. C. Chung, *Trends Polym. Sci.,* **3,** 191 (1995).

16. T. C. Chung, D. Rhubright, and G. J. Jiang, *Macromolecules,* **26,** 3467 (1993).

17. T. C. Chung, G. J. Jiang, and D. Rhubright, U.S. Pat. 5,286,800.

18. T. C. Chung and D. Rhubright *Macromolecules,* **27,** 1313 (1994).

19. T. C. Chung and D. Rhubright, *Macromolecules,* **24,** 970 (1991).

20. K. J. Clark and W. G. City, U.S. Pat. 3,492,277.

21. M. D. Purgett and O. Vogl, *J. Polym. Sci., Part A: Polym. Chem.,* **26,** 677 (1988).

22. T. C. Chung and D. Rhubright, *Macromolecules,* **26,** 3019 (1993).

23. J. B. Kinsinger and R. E. Higher, *J. Phys. Chem.,* **63,** 2002 (1959).

24. W. Chinsirikul, T. C. Chung, and I. Harrison, *J. Thermoplast. Compos. Mater.,* **6,** 18 (1993).

25. S. H. Lee, C. L. Li, and T. C. Chung, *Polymer,* **35,** 2980 (1994).

26. T. C. Chung and A. Kumar, *Polym. Bull.,* **28,** 123 (1992).

27. N. A. Pappas and H. J. Moynihan, *J. Appl. Polym. Sci.,* **30,** 2589 (1985).