

Formation of Pore-Filled Microfiltration Membranes Using a Combination of Modified Interfacial Polymerization and Grafting

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Received 23 July 2001; accepted 6 November 2001

ABSTRACT: A novel method of fabricating pore-filled membranes has been developed by coating a hydrophobic polyolefinic microfiltration membrane with polyethylenimine (PEI) to produce a chemically active surface. An evaporative coating technique was used to coat the internal surface of a polyolefinic membrane with PEI in chloroform (CHCl₃). The coated PEI was then crosslinked by naphthalene-1,4-disulfonyl chloride in carbon tetrachloride (CCl₄). The incorporation of the PEI coating changed the properties of the base membrane from hydrophobic to relatively hydrophilic; the nitrogens could be titrated, and the coating could not be washed out. 4,4'-Azo-bis(4-cyanovaleryl chloride), a heat-sensitive radical source, was incorporated into the coated membrane. The coated membrane, with incorporated azo compound, was heated to 75 °C in the presence of acrylic acid, 4-(vinylpyridine), or styrene to give the corresponding grafted, pore-filled membranes. The membranes exhibited hydraulic fluxes and pH valve effects consistent with molecular brushes grafted within the pores of the membranes. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 40: 242–250, 2002

Keywords: graft copolymers; hydrogels; crosslinking; coating; membranes

INTRODUCTION

A new class of ion-exchange membranes has been developed in our laboratories in which a controlled amount of a polyelectrolyte is anchored within the pores of a microfiltration membrane.¹ The microporous support in these membranes functions as a 'rigid' host or shell that constrains the polyelectrolyte, limits its swelling, and provides mechanical strength for the membrane. The hydrated polyelectrolytes swell to fill the pores of the membranes.

The properties of these membranes are very dependent on porosity and mechanical properties of the host microporous substrate, the degree of crosslinking of the gel-polymer, and the gel-polymer and water-volume fractions.² In the absence of crosslinking where polyelectrolyte chains are grafted to the wall of the pores to form molecular brushes, these membranes can exhibit remarkable sensitivity to changes in pH or ionic strength,^{1,3–13} temperature,¹⁴ or an external electric field^{15–17} with their permeability changing by several orders of magnitude. Valve effects with pore-grafted membranes have been extensively studied and modeled.^{18–24} The introduction of crosslinking into the polyelectrolyte reduces but does not eliminate this valve effect.²⁵

This article is concerned with the development of a flexible route to making this type of mem-

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 40, 242–250 (2002)
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DOI 10.1002/pola.10108

brane in which the pore-filling polymers are covalently bound to an adherent internal coating layer in the microporous host. Typically pore filling has been done by grafting a vinyl monomer to a surface using photochemical,²⁶ plasma-,²⁷ or chemical-activation²⁸ techniques. These routes can lead to the formation of homopolymer that has to be extracted from the membrane prior to its use or, in the case of plasma activation, the formation of asymmetric membranes. Moreover, there are limits as to the range of vinyl monomers that can be introduced by these routes.

In this work we describe a novel and effective route to the formation of pore-filled membranes. The membranes are made by first coating the internal surfaces of the polypropylene (PP) or polyethylene (PE) surface with a crosslinked polyamine. Radical initiators are then incorporated into the amine-rich surface, and the decomposition of these initiators, in the presence of vinyl monomers, results in a polymer that is chemically grafted to the coated layer of the microfiltration membrane. This route is flexible, and a range of molecular brushes can be grafted to the pore walls.

EXPERIMENTAL

Materials

The PE and PP microporous membranes, PE-2 and PP-2, respectively, were supplied by 3M Canada. Unless otherwise specified, the base PE-2 membrane was extracted with chloroform at room temperature for 15 min prior to use.

Polyethylenimine [PEI, molecular weight: 25,000] and naphthalene disulfonic acid were obtained from Aldrich Chemical Co. Naphthalene disulfonyl chloride was prepared using reported procedures.²⁹

Equipment

IR spectra were obtained using a Bio-Rad (FTS-40) Fourier transform infrared spectroscopy machine. The membranes were compressed using a potassium bromide press to give translucent films for the IR examinations. An ISI, DS130 scanning electron microscope (SEM) was used, and the samples were gold or carbon [for energy dispersive X-ray (EDX) analyses] coated for examination.

Membrane-Coating Procedure

A weighed piece of the base PE2 membrane (typically 0.1 g, 35–40 cm²) was soaked in 50 mL of chloroform for 15 min and then air dried. The extracted membrane was immersed in 50 mL of solution of known concentration of PEI in chloroform for 15 min, removed from the solution, allowed to drain, and air dry. The weight gain of the coated membrane was determined.

The PEI-coated membrane was subsequently immersed in a solution of naphthalene disulfonyl chloride in dichloromethane or carbon tetrachloride, 50 mL, at 30 °C for 40 min. The membrane was washed in successive steps with methanol (MeOH), CHCl₃, a 1% solution of triethylamine (NEt₃) in CHCl₃, and finally CHCl₃ to remove unincorporated polymer; and hydrogen chloride (HCl) formed in the crosslinking reactions. The membranes were vacuum dried and then weighed.

The weight increase (W.I.) for both coated and crosslinked membranes is expressed as

$$\text{W.I.(\%)} = (W_c - W_n)/W_n \quad \text{or} \quad (W_x - W_n)/W_n, \quad (1)$$

where W_c and W_x refer to the weight of the coated and coated/crosslinked membranes, respectively, and W_n is the weight of the extracted nascent membrane. For each coating, three parallel experiments were conducted, and the values quoted are the mean of these results.

Incorporation of Azo Initiator

A solution of 4,4'-azobis(4-cyanovaleryl chloride) (0.05 g) in CHCl₃ (5 mL) was allowed to react with a coated membrane (48 cm²) at room temperature for 0.5–2 h. Following the reaction, the membrane was removed from the solution, allowed to drain, washed with more CHCl₃, and then dried. The mass gain was determined. The mass percentage increase is given by

$$\text{W.I.(\%)} = (W_a - W_c)/W_c \quad (2)$$

where W_a is the weight of the azo-incorporated membrane, and W_c is the weight of the coated membrane.

Graft Polymerizations

Membranes with incorporated azo compound were heated in a solution of a vinyl monomer (1 g)

Table I. Properties of Base Membranes

Membrane	Treatment	Relative Mass ^a	Relative Size	Thickness (μm)	Porosity (%)
PE-2	None	1	1	52 ± 2	82
PE-2	CHCl ₃ /2h	0.96	0.81	52 ± 3	82
PP-2	None	1	1	77 ± 2	68
PP-2	CHCl ₃ /2h	1	1	77 ± 2	68
PP-3	None	1	1	79	80

^a Relative to the nascent untreated membrane.

in CHCl₃ (9 mL) at 75 °C for 6–18 h in a nitrogen atmosphere. The resulting membranes were washed with MeOH, CHCl₃, 1% of NEt₃/CHCl₃, and CHCl₃; dried; and their masses determined. The graft yield (GY) was calculated as

$$\text{GY}(\%) = (W_g - W_a)/W_a \quad (3)$$

where W_g is the weight of the grafted membrane, and W_a is the weight of the azo-incorporated membrane.

Permeability Measurements

The pure water flux of each membrane was determined at 100 kPa using a stirred ultrafiltration cell. The stirring rate was 250–300 rpm. Deionized/carbon-filtered water was used unless otherwise specified. The flux values obtained were corrected to 25 °C.³⁰

RESULTS AND DISCUSSION

We have previously described an interfacial coating technology that allows the formation of dense, even, polyamide, polysulfonamide, or similar polymer coatings on the interior and exterior surfaces of microporous substrates.^{31,32} In this process a diamine, such as 1,8-octanediamine, is first evenly deposited onto the surfaces of the microporous support and then reacted with a diacid dichloride in a suitable solvent to form an adhering polymer layer. It was thought that by replacing the low molecular weight diamine with a polyamine and lightly crosslinking this should permit the formation of an adherent coating layer containing a large excess of amine groups that could then be used as a convenient platform for anchoring further materials.

The Base Membrane

The base membranes used in this work were PE and PP microporous membranes produced by a thermally induced phase-separation process.³³ The properties of the support membranes are listed in Table I. In the case of the PE membrane some mass loss (ca. 4%) and dimension changes were noted when it was treated with CHCl₃ (Table I). In all the work described, the PE membranes were extracted with CHCl₃ prior to coating attempts. No significant changes in the physical dimensions or weight of the PP membranes were observed with comparable treatments with CHCl₃.

Modified Interfacial Coating of the Membranes with Crosslinked PEI

A PEI of molecular weight 25,000 was used. PEI is a highly branched polymer with a reported degree of chain branching of 25, 50, and 25% for primary, secondary, and tertiary nitrogens, respectively.³⁴ The PEI was dissolved in CHCl₃ to form solutions of known composition. Samples of the base membranes were wetted with solutions of PEI dissolved in CHCl₃, allowed to drain, and the residual CHCl₃ evaporated. Substantial amounts of PEI could be 'coated' onto the base membranes using this method (Table II).

To anchor PEI, the coated membranes were treated with a solution of 1,5-naphthalene disulfonyl chloride crosslink to insolubilize the polyamine (Scheme 1).³⁵ The crosslinking was typically carried out at 20 °C with solutions of naphthalene disulfonyl chloride (NDSC) in methyl chloride (CH₂Cl₂) or CCl₄. Following the crosslinking, the membranes were washed with a series of solvents to remove unreacted PEI, NDSC, and HCl formed in the reaction. The membranes were subsequently dried and the mass gain mea-

Table II. Coating of Membranes with PEI/NDSC

Membrane	Base Material	PEI Concentration (wt %)	Mass Gain of PEI (%)	NDSC Concentration (wt %)	Mass Gain Crosslinked PEI (%)
1	PE-2	2	18 ± 3	0.002	12 ± 1
2	PE-2	2	18 ± 3	0.02	21 ± 2
3	PE-2	2	18 ± 3	0.1	20 ± 2
4	PE-2	3	32 ± 4	0.002	2 ± 1
5	PE-2	3	32 ± 4	0.02	28 ± 3
6	PE-2	3	32 ± 4	0.1	27 ± 2
7	PE-2	3	32 ± 4	0.4	18 ± 2
8	PE-2	4	42 ± 4	0.1	39 ± 2
9	PE-2	4	42 ± 4	0.4	23 ± 1
10	PP-2	2	20 ± 3	0.1	16
11	PP-2	3	34 ± 4	0.1	25
12	PP-3	3	34 ± 1	0.4	28 ± 6

sured. The results are listed in Table II as “mass-gain crosslinked PEI.”

The selection of solvent (CH_2Cl_2 or CCl_4) for NDSC was important. As previously described, this coating technology works well when the deposited diamine (polyamine) is relatively insoluble in the solvent containing the diacid chloride.³² Thus, although CH_2Cl_2 was a suitable solvent with higher concentrations of NDSC, at the low concentrations uneven coatings occurred with the formation of “blobs” of crosslinked PEI on the surface of the membranes. More even coatings were obtained when CCl_4 was used as the solvent.

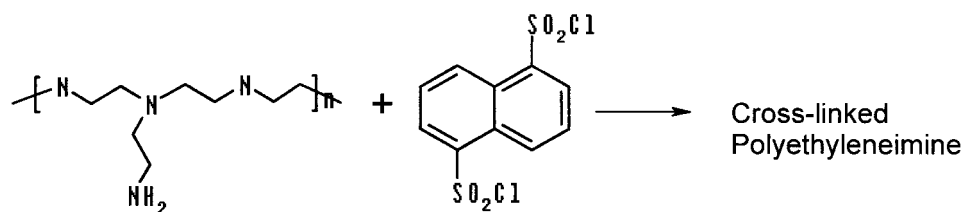
Examination of the data in Table II shows that the amount of anchored PEI depends both on the mass of PEI in the original coating as well as the concentration of NDSC in the contacting solution. At very low concentrations of NDSC most of the originally deposited PEI is not fixed and is lost either during the crosslinking process itself or in the subsequent washing steps, membranes 1 and 4. On the other hand, high concentrations of NDSC also do not help, and the yield of anchored PEI tends to be reduced under these conditions,

membranes 7 and 9. Comparable concentration effects on interfacial polymerization reactions have been previously observed.³⁵

Overall, the results in Table II indicate that it is possible to fix PEI to the microporous support. This process firmly anchors PEI within the microporous support membrane. For example, extraction of a coated/crosslinked membrane for 48 h in refluxing CHCl_3 did not cause any loss in mass.

Characterization of Coated Membranes

The coated membranes were examined using environmental SEM. Typical micrographs are shown in Figure 1 for membrane 7, containing 18 wt % of the NDSC crosslinked PEI. The two external surfaces of this membrane were indistinguishable by SEM. Comparison of SEM of one of these surfaces, Figure 1, with that of the starting base PE-2 membrane, Figure 2, clearly indicates that the coated membrane retains a microporous structure. There is no evidence for the formation of either a dense surface layer or any large discrete phases associated with the crosslinked PEI.

**Scheme 1**

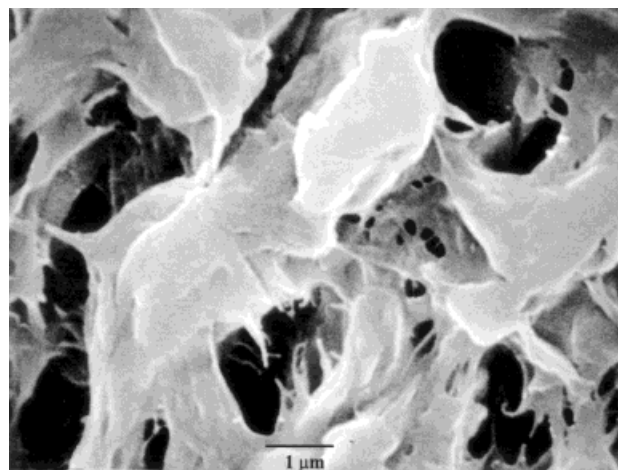


Figure 1. Environmental scanning electron micrograph of the surface of coated membrane 7 prior to treatment with azo initiator (magnification 10,000 \times).

Cross sections of this membrane were also examined by SEM, and again these showed little difference from cross sections of the starting membrane. The distribution of the crosslinked PEI in the membrane was probed by EDX analysis for sulfur. The sulfur is derived from the NDSC crosslinker and should be a good indicator of distribution of the coating formed in this process. The results of this sulfur analysis are depicted in Figure 3. There is a very even distribution of sulfur through the membrane indicating a uniform distribution of crosslinked PEI throughout the base PE microporous membrane.

Physical Properties of the Coated Membranes

No change in the thickness of the membranes was observed after coating (Table I). The coated mem-

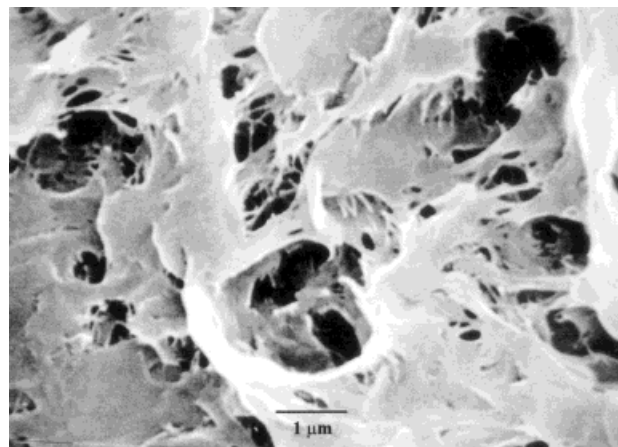


Figure 2. Environmental scanning electron micrographs of the surface of the polyethylene (PE-2) base membrane (magnification 10,000 \times).

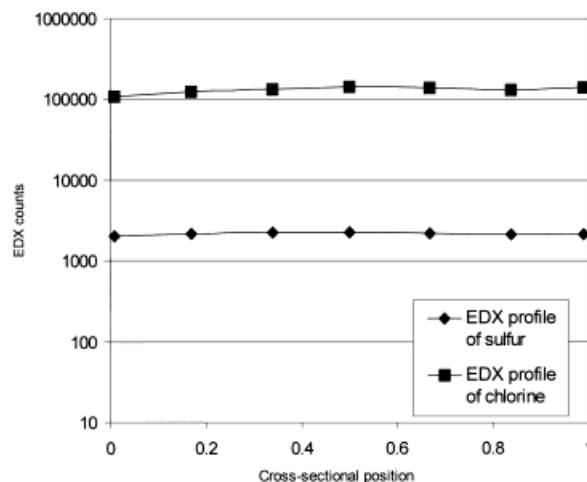
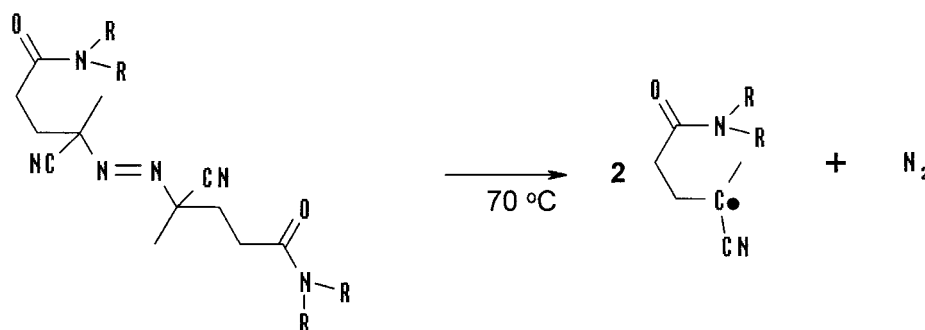


Figure 3. EDX analyses of cross sections of membrane 7 (sulfur profile) and membrane 11 with poly(*N*-methyl 4-vinylpyridinium) chloride grafted to coating (chlorine profile).

branes described in Table II were somewhat hydrophobic. To introduce water into the pores it was necessary to treat the membrane first with MeOH and then displace the MeOH with water. The water content of the membranes was determined. Within experimental error, the water content (porosity) of the coated membranes was the same as the starting PE and PP base materials.

The hydrophobic nature of the coated membranes would seem to indicate that the unreacted amine nitrogens of the coating layer are not accessible on the surface of the coatings. To probe this the ion-exchange capacities (IEC) of two of the membranes (#5 and 7) were determined. In the case of membrane 5 an IEC of 0.69 meq/g was found. On the basis of the previously mentioned mass gain and crosslinking ratio, membrane 5 has a total theoretical IEC of about 3 meq/g, meaning that less than 25% of the available amine nitrogens could be titrated with aqueous HCl. In contrast with membrane 5, no titratable nitrogen could be detected in the more heavily crosslinked membrane 7 (IEC < 0.05 meq/g). Clearly, under the conditions used in this coating process, dense layers are being formed that do not swell readily in water and allow N protonation to occur.

The amine nitrogens in membrane 5 could be *N*-methylated on treatment with dimethyl sulfate in MeOH. Analysis for chlorine using neutron-activation analysis on a chloride-exchanged *N*-methylated membrane showed 40% of the amine nitrogens were reacted.



Scheme 2

Activation of the Coating Layer by Incorporation of a Radical Initiator

4,4'-Azobis(4-cyanovaleryl chloride) was selected as the radical initiator to be incorporated into the crosslinked PEI films. The incorporation of this azo compound onto hydroxy- and amino-containing surfaces and the subsequent decomposition (Scheme 2) in the presence of vinyl monomers to give surface-grafted polymers have been previously described.^{36,37} Smith³⁸ has shown that the diffusion of the two radicals out of the cage formed on decomposition of polymers containing azobis(4-cyanovaleramide) functionality in the backbone is dependent on the rigidity of the system in question.

Treatment of membrane 7 with 4,4'-azo-bis(4-cyanovaleryl chloride) in chloroform led to the incorporation of the azo functionality into the film. The reaction could be followed by an increase in weight of the coating layer (Table III). From the data in Table III, a mass increase of up to 5% could be achieved with a 2-h treatment. Evidence for the reaction of the diacid chloride with PEI was obtained by IR spectroscopy where the formation of bands at 1640 and 1567 cm^{-1} showed the presence of an amide carbonyl group and azo functionality, respectively. The absence of a band at about 1800 cm^{-1} attributable to the carbonyl

group of the starting azo diacid chloride indicates that no unreacted acid chloride groups remain after this treatment. A similar incorporation was observed with the PP-based membrane 11. Both membranes 7 and 12 had relatively heavily crosslinked coatings. Despite this heavy crosslinking, it was possible to incorporate a substantial amount of the azo compound.

Grafting of Polymers to the Coated Membranes

The thermally initiated decomposition of the azo-incorporated coating layer in the presence of various vinyl monomers was examined. Two coated membranes were used (membranes 7 and 12), each containing approximately 3% by weight of the azo initiator. Four different vinyl monomers were used, and grafting was carried out using thermal initiation of the system (70 °C). The degree of graft polymerization was determined by measuring the mass gain associated with the various membranes. IR spectra were obtained on compressed films to confirm the presence of the grafted polymer.

The results of the grafting experiments are given in Table IV. Graft polymerization takes place with each of the different monomers used. It is also apparent from these data that the choice of base membrane has little effect on the grafting process with very similar results being obtained with the PP- and PE-based materials.

The highest graft yield was obtained with acrylic acid as the monomer. We have previously found that poly(acrylic acid) (PAA) can be readily grafted within the pores of these base membranes using a photochemical-initiation procedure.^{2,39} Graft polymerization with the other monomers was less efficient, typically occurring with 30–50% graft yields.

The thicknesses, porosities (water contents), and ion-exchange capacities of the grafted mem-

Table III. Incorporation of Azo Initiator^a

Membrane	Reaction Time (min)	Mass Increase (%)
7	30	1.2
7	60	3
7	120	4.9
11	60	3.6

^a Membranes treated with 5 mL of 1% solution of 4,4'-azobis(4-cyanovaleryl chloride) in chloroform.

Table IV. Grafting onto Surface-Coated Membranes

Starting Membrane (wt % Azo Compound)	Vinyl Monomer	Solvent	Time (h)	Graft Yield (%)
11 (3.4)	Styrene	None	6	41
7 (2.9)	Acrylic acid	Dichloroethane	6	167
11 (3.4)	4-Vinylpyridine	<i>n</i> -BuOH/H ₂ O	18	28
7 (2.9)	4-Vinylpyridine	<i>n</i> -BuOH/H ₂ O	18	29
7 (2.9)	4-Vinylpyridine	Dichloroethane	6	47
7 (2.9)	4-Vinylpyridine/1% DVB	Dichloroethane	6	52

branes were determined (Table V). There was a small increase in the “dry” thickness of the membranes with grafted poly(4-vinylpyridine) (PVP) or PAA and a further small increase in thickness when these membranes were wet. These thickness changes parallel those observed with pore-filled membranes of this type produced by other methods.⁴⁰ In the case of the PVP-grafted membrane, there was a further, reversible increase in thickness when the membrane was treated with 1 M HCl to convert it to its protonated form. Comparable, reversible thickness changes of polvinylpyridine pore-filled membranes have been observed.²¹

The ion-exchange capacities of the PVP- and PAA-grafted membranes were determined (Table V). As compared with the starting coated membrane 7, each of the grafted membranes had a readily measurable IEC. In the case of the PVP- and PAA-grafted membranes the measured IEC was close to 70% of the calculated value on the basis of mass gain associated with grafting. The high measured IECs of these membranes as compared with their estimated values indicate that the incorporated vinyl polymers are readily accessible to aqueous acid or base. This supports the suggestion that grafting has occurred on the coated surfaces (interior/exterior) of the microporous membrane rather than bulk polymerization in the coating layer.

Characterization of the Grafted Membranes

The morphology of the grafted membranes was examined using SEM with samples prepared by freeze-substitution. Micrographs of a coated PP membrane 11 and the same membrane functionalized with the azo initiator and grafted with PVP 11-PVP (28%) are shown in Figures 4 and 5, respectively. The coated membrane 11, Figure 4, retains the microporous structure of the base PP membranes. The PP-based membranes typically appear to be more open and with a better defined fibril/nodule structure than the PE membranes (cf. Fig. 2).

It is difficult to detect differences between the micrographs of the grafted membranes and that of the coated membrane (Fig. 4). There is no evidence for the formation of a discrete separate phase of PVP; the grafted polymer appears to be homogeneously distributed in the membrane. We have previously noted the difficulty of detecting grafted PVP in these microporous membranes using SEM because the grafted polymer appeared to collapse back on the walls of the base membrane under the conditions used for SEM.

To confirm that grafting had occurred, elemental profiles were obtained for cross sections of these membranes using EDX analysis (Fig. 3). In the case of the PVP-grafted membrane it was treated with dimethyl sulfate to form the quaternary salt. The resulting membrane was exchanged with chloride,

Table V. Properties of Grafted Membranes

Membrane	Ion-Exchange Capacity (meq/g)		Thickness (μ m)			Water Content (%)
	Measured	Calculated	Dry	Wet (pH 5.5)	Wet (pH < 2)	
7	< 0.05	—	53	55	—	72
7-PVP (29%)	1.43	2.02	61	64	78	68
7-PA (62%)	3.81	5.3	58	64	—	69

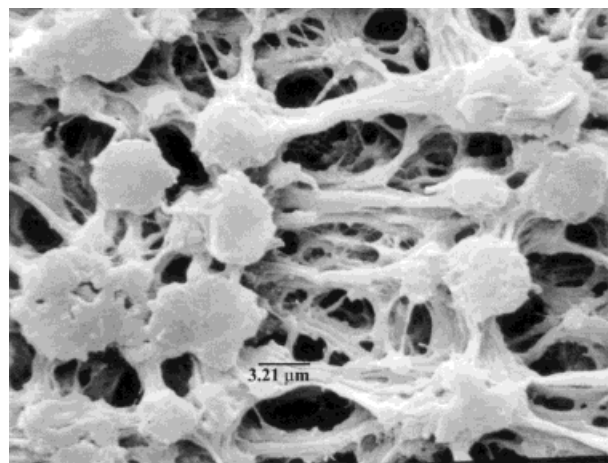


Figure 4. Environmental scanning electron micrograph of the surface of coated membrane 11 prior to grafting reactions (magnification 3120 \times).

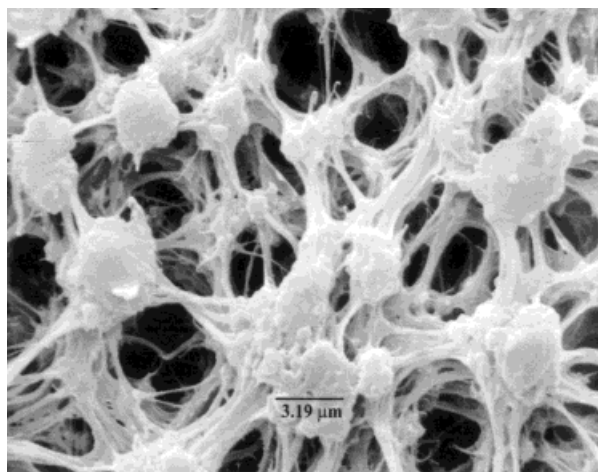


Figure 5. Environmental scanning electron micrograph of the surface of membrane 11-PVP grafted with poly(4-vinylpyridine) (magnification 3130 \times).

and a chlorine profile was obtained. In Figure 3, these membranes show a reasonably even distribution of the incorporated polyelectrolyte throughout the membrane cross section. In other words, the grafted polymers are incorporated into the pores of the host, base membrane.

Permeability Measurements

As a final characterization step, the water fluxes of several of these membranes were determined (Table VI). Each of the treatments outlined in this article results in a change of the water flux. Thus, the fluxes observed with the starting base membrane, extracted with CHCl_3 , the coated membrane 7, and the incorporation of the azo compound into the membrane are all very similar, differing by less than a factor of 2. Thermal decomposition of the azo compound in the absence of

any vinyl monomer was carried out as a control, and, again, this only caused a small reduction in permeability. In each case these membranes can be regarded as being microporous.

The fluxes of the grafted membranes show considerable differences from those of the base and coated membranes described previously. First, the pure water fluxes of membranes 7-PVP (29%) and 7-PAA (62%) were significantly lower than that of coated membrane 7. Second, these same two membranes exhibited substantial pH valve effects with changes in pH. In the case of 7-PVP (29%) at pHs less than 2, the flux of membrane is reduced by a factor of almost 300 as compared with that measured at a pH of 5. This reversible valve effect arises from protonation of the pyridine nitrogen atoms and the resulting swelling of the grafted polymer. In our previous work using photoanchoring methods, we have shown that the

Table VI. Pure Water Fluxes of Membranes Measured at 100 kPa and 25 $^{\circ}\text{C}$

Membrane	Pure Water Flux ^a ($\text{kg}/\text{m}^2\text{s}$)	Flux ($\text{kg}/\text{m}^2\text{s}$) (pH < 2)	Flux ($\text{kg}/\text{m}^2\text{s}$) (pH > 11)
PE-2	1.46	—	—
PE-2 extracted	2.98	—	—
7	2.14	—	—
7 (Azo treated)	2.26	—	—
7 (Azo heated)	1.29	—	—
7-PVP (29%)	0.32	0.0011	—
7-PAA (62%)	0.0011	0.012	0.00035

^a Flux obtained at the normal water pH of about 5.5.

incorporation of about 30% of PVP is sufficient to exhibit a valve effect of this range.^{1,3} Indeed the similarity of the results obtained here using this coating/grafting route with photochemically produced membranes fully confirms the effectiveness of this route to produce pore-filled membranes.

A smaller valve effect is observed with 7-PAA (62%). As expected, in this case the valve is reversed as compared with that exhibited by 7-PVP (29%) as PAA is ionized at higher pH values. The valve range observed is comparable to results obtained in our laboratory with other PAA-incorporated membranes.

CONCLUSIONS

The work described in this article has shown that it is possible to form pore-filled ion-exchange membranes using a process that involves coating the surfaces of a microporous membrane with a substrate containing a radical initiator. Using this method, we have been able to graft a variety of polyelectrolytes within the pores of microporous-based membranes.

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council, Canada (NSERC) and the donation of base membranes by 3M Canada.

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