In Situ Modification of Microporous Membranes

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SYNOPSIS

Under proper conditions, *in situ* polymerizations of acrylic acid monomer solutions were performed within the microporous structures of a hydrophobic membrane, Celgard® 2500. Poly(acrylic acid) modified pores have been characterized to be permanently wettable by aqueous solutions, to be capable of gelling water to withstand increased transmembrane pressure gradients, and also to possess a higher transmembrane electrical resistance. In cases of less concentrated acrylic acid monomer solutions, a cross-linker was employed to facilitate polymer permanency within the infrastructure of the hydrophobic membranes. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There has been much interest in the literature regarding the use of immobilized liquid membranes (ILM).[1-8] Hydrophobic membranes are commonly used as supports for various modifications with the intent of creating different ILMs. By modifying the porous structures so that they become permanently hydrophilic, the applications of these membranes could be of increased interest in bioreactors, selective transports, gas separation, waste water purification, etc.

Many prior attempts to increase the utility of hydrophobic membranes by pore modification techniques have been described in the literature with mixed results. Possibly, the simplest of these measures involves treating the membranes with a surfactant[9] or impregnating them with a polymer solution and then evaporating the solvent.[10] However, with repeated uses, the surfactant or polymer tends to leach itself from the pores.

Some investigators have tried to graft compounds to a substrate by various chemical means. Miura[11] irradiated a hollow fiber microporous membrane of a polyolefin with ionizing radiation, reacted the membrane with vinyl acetate, and then hydrolyzed the membrane. Poly(vinyl alcohol) was then chem-

ically bonded to the membrane surface to give the membrane excellent hydrophilic properties. Ozari et al.[12] formed dynamic membranes by chemically modifying polypropylene membranes to include phosphoramide groups and then immersing them in 2% solutions of poly(acrylic acid). The resultant membrane seemed to be stable with respect to solvent flux and salt rejection.

An alternate method of achieving hydrophilic membranes involves formation of composite membranes. Fukuchi et al.[13] created a composite semipermeable membrane by cross-linking a thin film on to a porous support. They were able to achieve a hydrophilic membrane with high rejection and flux for a "long time" by coating a membrane with a solution containing a polyalkylenimine (or derivative thereof) and another compound selected from a group typified by piperazine, etc., letting it dry, and then adding a cross-linking agent having two or more functional groups capable of reacting with amino groups. Another composite membrane that is currently under investigation is the poly(vinyl alcohol) (PVA)-coated polyacrylonitrile (PAN) support membrane. These PVA–PAN membranes are being utilized for separations via vapor permeation and pervaporation methods.[5,7,8]

Thickening agents can also be used to stabilize liquid membranes by gelling the liquid in a microporous substrate. Thickening agents gel liquids by forming three-dimensional networks and can be of a high molecular weight polymer or a colloid with a high surface area. They exist for both water solutions

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and organic solvents. The gelling of liquid does not significantly affect the diffusion rate of small molecules or ions in the liquid. Since a thickened solution will not easily enter minute pores, it might be possible to dissolve the gelling agent in a solvent not thickened by the agent, load the pores, and then evaporate the solvent. This approach has been used by Verzwyvelt.[14] Neplenbroek et al.[4] recently presented their technique of increasing the stability of supported liquid membranes. By applying a homogeneous gel network in the pores of a support, they were able to achieve supported liquid membranes with increased mechanical stability against liquid displacement and long-term stability.

An alternate method would be to load the pores with a low-to-medium molecular weight polymer with a cross-linker for the polymer in question and then induce cross-linking *in situ*, as performed by Ding and Cussler who recently described a method in which hydrophobic pores are filled with gels of cross-linked PVA. Their procedure resulted in gel-filled fibers that could withstand transporous pressure differentials of at least 5 atmospheres without failure. The convection through the pores was stopped, but the overall mass transfer was unaltered. The gel-filled fiber walls provided excellent yield and purity, especially in the case of fractional extraction.[15]

A third way to introduce a thickening agent would be to load the pores with a monomer solution and perform the polymerization *in situ*. By proceeding in this fashion, a monomer in an appropriate solvent/initiator system would have the opportunity to polymerize in such a manner that the chains would interlace within a porous substrate. This chemical mesh work should render the polymer sessile within and around the porous struts. Hence, the hydrophobic membrane would possess permanently modified hydrophilic pores with characteristics akin to the polymer in question. This is the approach undertaken by the authors, which composes the topic of this paper.[16]

EXPERIMENTAL

Materials

Acrylic acid was chosen as a representative hydrophilic monomer for the potential advantage of its ionic character when part of a hydrophobic membrane and for its gelling capacity as a polymer. The monomer and its initiator, benzoyl peroxide, were both obtained from Aldrich. Trimethylolpropane

triacrylate (TMPTA) produced by the Celanese Chemical Co. was used as a multifunctional cross-linker in some of the reactions.

The microporous membrane chosen for modification was a commercially extruded sheet of isotactic polypropylene designated as Celgard® 2500. This film, manufactured by the Hoechst Celanese Corp., had an average thickness of 0.25 μm, a porosity of 45%, and average pore dimensions (w $\times$ l) of 0.04 $\times$ 0.4 μm, as obtained by scanning electron microscopy (SEM) studies. Another microporous film used for comparison studies was a cationic/nonionic surfactant coated Celgard 2500 commercially produced as Celgard 3501, also by the Hoechst Celanese Corp.

Procedures

To achieve permanent *in situ* polymerization, the solvent system that would yield the highest attainable molecular weight of poly(acrylic acid) had to be identified. This solvent system should possess the qualities of being able to wet out the hydrophobic membrane and also should not prevent, via chain termination, high molecular weight polymers from being attained. After performing *in vitro* studies, toluene with a benzoyl peroxide initiator was chosen as a viable system for the *in situ* polymerizations.

Monomer solutions of acrylic acid and benzoyl peroxide in toluene of various percentages were mixed together after first dissolving the initiator in a small amount of toluene. The solutions were purged with nitrogen to remove any dissolved oxygen that would act as an inhibitor. Celgard 2500 membranes of specific sizes (min. 1.5 $\times$ 3.5 in.) were wetted out with their respective monomer solution and quickly placed between two hydrophilic glass plates of a larger size that were subsequently clamped together. The glass plates were thoroughly cleaned prior to these experiments by placing them in a 50/50 acetone/H_2O boiling mixture for 10 min, after which they were ultrasonicated in a 50/50 HNO_3/H_2O for an additional 10 min. They were then rinsed with Millipore® water and allowed to dry. (For the 100 wt % acrylic acid monomer solution, Teflon-lined glass plates were necessary to prevent inseparable adhesion between the membrane and the surrounding glass.) The membrane confined between two glass plates was then placed in a nitrogen-purged oven at a temperature of 88–90°C. After 4 h, the membrane was released from the glass plates and allowed to dry at room temperature.

For acrylic acid monomer solutions of $\leq$ 60 wt %, TMPTA was utilized as a cross-linking agent. The procedure replicated the one described previously

Table I *In Situ* **Polymerization of Acrylic Acid within Celgard 2500**

Sample No.	Acrylic Acid Concn (%)	Initiator Concn (Mol % of Acrylic Acid)	Wettability After Rxn./Sonication
1	30	0.5	None/—
2	40	0.5	Complete/none
3	50	0.5	Complete/partial
4	60	0.5	Complete/complete
5	100	0.5	Complete/complete

with the addition of TMPTA in certain mol % to the monomer solution. The pore-modified membranes were then subjected to various modes of testing, further detailed in the next section.

RESULTS AND DISCUSSION

The gross morphology of Celgard 2500 is that of an extremely thin, white polypropylene film that is inherently unwettable by water. By subjecting these membranes to the procedures presented above, a complete, uniformly water wettable membrane was achieved with a 40 wt % acrylic acid monomer solution (Table I). However, after washing the modified membrane in a Bransonic 52 ultrasonic bath containing 50/50 EtOH/H_2O for 15 min and allowing it to dry, the membrane lost its wettability. The poly(acrylic acid) was deemed to be of a molecular weight insufficient to remain within the pores during agitation.

By increasing the concentrations of initial acrylic acid weight percentages, the desired permanency of the polymer was attained even after multiple 15 min sonications (Table I). The data implies that there must be a critical acrylic acid concentration between 50 and 60 wt % (assuming a 0.5 mol % initiator concentration) that would enable the polymer to achieve a molecular weight high enough to become entrapped. All solution-filled membranes are translucent. However, after evaporation of the toulene, only the higher monomer solutions ($\geq$ 60 wt %) produced permanently translucent modified membranes. This supports the hypothesis that the modification takes place all through the membrane pore structure and not only in the surface regions.

To eliminate the necessity of using high weight percentages of monomer solutions, a multifunctional cross-linker was employed in conjunction with lower acrylic acid concentrations. As Table II indicates, any logical combination of TMPTA and benzoyl peroxide concentration with a 15 wt % monomer

solution would not allow enough *in situ* polymerization to achieve a wettable membrane. At 20 wt %, the only condition in which a completely wettable membrane could be achieved would be at 1 mol % (of acrylic acid) TMPTA with benzoyl peroxide at a concentration of 0.1 mol % (of all acrylate). This low concentration of initiator would allow for a slower rate of initiation. Thus, branched polymers with higher molecular weights would be formed that would lead to a more complete entanglement within the tortuous pores.

As far as the concentration of acrylic acid is concerned, a membrane could be completely wettable as long as the acrylic acid concentration in the monomer solution is $\geq$ 15–20 wt % with some amount of cross-linker. The amount of TMPTA in the monomer solution must be at least between 0.01 and 0.1 mol % of acrylic acid. As for the upper limit, there can be some desired results with a 5 mol % TMPTA, but at 10 mol %, any wettability of the membrane is lost after sonication. This higher concentration of TMPTA probably causes a cross-linking polymerization reaction that occurs too quickly to allow extended polymeric chains to form. The highly cross-linked polymers would not be extended enough to entangle in the pore structure and would be jostled from the pores upon sonication, thereby leaving an unwettable membrane.

The first method of characterization of the modified membranes involved the use of a Millipore pressure cell (cat. #XX4404700) to determine the stability/permanence of the modified internal pore structure. Selective membranes with an area equal to 45.6 cm^2 were placed in the pressure cell containing Millipore refined water and subjected to a pressure gradient of 50 psi, after which serial quantitative measurements of water flux were performed for each membrane. As Table III indicates, the Celgard 2500 allowed no water flux since it is a hydrophobic membrane. The Celgard 3501 allowed a flux of approximately 88 mL/h cm^2 for its first three trials. However, the flux declined with subsequent runs as

Table II *In Situ* **Polymerization of Acrylic Acid + Cross-linker within Celgard 2500**

Sample No.	Acrylic Acid (%)	Initiator (Mol % of All Acrylate)	Cross-linker (Mol % of Acrylic Acid)	Wettability After Rxn./Sonication
6	10	0.5	0.1	None/—
7	15	0.1	0.1	None/—
8	15	0.5	0.1	None/—
9	15	0.1	1.0	None/—
10	15	0.5	1.0	None/—
11	15	0.05	10.0	None/—
12	15	0.1	10.0	None/—
13	15	0.5	10.0	None/—
14	20	1.0	0.1	Partial/partial
15	20	0.5	0.1	Partial/partial
16	20	0.1	1.0	Complete/complete
17	20	0.5	1.0	Partial/partial
18	20	0.1	5.0	None/—
19	20	0.1	10.0	None/—
20	20	0.5	10.0	Partial/none
21	21	0.5	1.0	Partial/partial
22	23	0.5	1.0	Complete/complete
23	24	0.5	1.0	Complete/complete
24	25	0.5	0.01	Partial/none
25	25	0.1	0.1	Complete/complete
26	25	0.5	0.1	Complete/complete
27	25	0.5	1.0	Complete/complete
28	25	0.5	5.0	Complete/complete
29	30	0.5	0.01	Complete/none
30	30	0.1	0.1	Complete/complete
31	30	0.5	0.1	Complete/complete
32	30	0.1	1.0	Complete/complete
33	30	0.5	1.0	Complete/complete
34	30	0.5	5.0	Complete/complete
35	30	0.1	10.0	Partial/none
36	30	0.5	10.0	Complete/none
37	30	1.0	10.0	Complete/none
38	40	0.5	0.1	Complete/complete
39	50	0.5	0.1	Complete/complete
40	60	0.5	0.01	Complete/complete
41	60	0.5	0.1	Complete/complete

the surfactant was washed from the pores. The three representative pore-modified membranes also permitted water flux with samples #31 and #27 allowing the least amount. The higher concentrations of vinyl groups in these particular monomer solutions (30% acrylic acid and 1 mol % TMPTA, respectively) make them the most likely candidates to have the higher molecular weight polymeric chains. Therefore, the pores should be more completely filled with poly(acrylic acid), reducing the effective free cross section and also creating a greater swelling within the pores with subsequent decreased water flux. Sample #26 would allow the greatest amount of flux since it has the lowest concentration of vinyl groups in comparison to the other two membranes. More importantly, measurement of water flux through membrane #26 was relatively constant after 10 trials.

The pressure cell was then used to determine the ability of the modified membranes to hold gelled liquid in its pores under various pressures. A 45 cm² membrane of sample #26 was placed in the pressure cell and then subjected to increasing transmembrane pressures. On the receiving end of the cell, a clear tube was attached while the other end of the tube was submerged in water to detect the point at which air passed through the membrane, i.e., the point at which the porous structure could no longer contain the gelled liquid. The measurements were performed

Table III Water Flux Measurements at 50 psi

Membrane	Flux (mL/h cm^2)
Celgard 2500	0.00
Celgard 3501	87.72
	87.72
	87.72
	81.58
	40.35
	9.21
Sample #26	0.076
	0.071
	0.064
	0.069
	0.068
	0.066
	0.057
	0.059
	0.056
	0.068
Sample #27	0.046
	0.045
	0.047
Sample #31	0.034
	0.026
	0.046
	0.046

using Millipore water with NaOH adjusted pH's equal to 7, 9, and 11. Celgard 3501 was used for comparison studies. As revealed in Table IV, the pore-modified membrane withstood 2–5× the transmembrane pressure gradients of the surfactant-treated membrane. Discrepancies in the data could be attributable to microscopic tears in the membranes or to experimental error including pressure leaks from the seals.

The capacity of the pore-modified membranes to withstand the increased transmembrane pressure gradients is probably due to the decreased mean pore size. As water enters the pores, the poly (acrylic acid) swells, leading to partial occlusion. The Young–Laplace equation relates the force holding a liquid within a cylindrical capillary to the contact angle, θ, the surface tension, γ, and the radius, R, of the pore:

$$\Delta P = 2\gamma \cos \theta / R$$

The pressure difference across the liquid membrane interface, ΔP, which is required to dislodge the liquid

membrane from the pore, is inversely proportional to the pore diameter.[6] Thus, since the mean pore size of the modified membrane should be smaller due to presence of the poly (acrylic acid) and its swelling, the resistance to transmembrane pressure should be increased, as is evident in Table IV. Also, by looking at each individual sample in conjunction with increasing pH, a trend of withstanding greater pressure gradients can be observed. This could be explained by the fact that totally ionized poly (acrylic acid) is known to be a better gelling agent.

Scanning electron microscopy was employed to examine the internal structure of the pores of certain modified membranes. Note in Figure 1 the standard array of pore structure in the control membrane. The pores are uniformly arranged and range from 0.02 to 0.75 μm in the long dimension and up to 0.1 μm in width.

The photomicrograph in Figure 2 represents a sample that had just been isolated from the polymerization reaction. The pore dimensions of this membrane are less uniform than those in the control. Some pores are stretched to become shorter in the long dimension and more round in shape secondary to welding of the pore struts. In this process of rearranging the internal structure, the poly (acrylic acid) has also filled in some pores to create smaller pores in previously existing larger ones. This creation of smaller pores lends support to the observation that the pore-modified membranes can withstand higher transmembrane pressure differences.

The membrane modified with 100 wt % acrylic acid is shown in Figure 3 after repeated sonications. The micrograph indicates that there is extensive filling of the pores with polymer to the point of near-complete occlusion.

Table IV Transmembrane Pressure Gradients

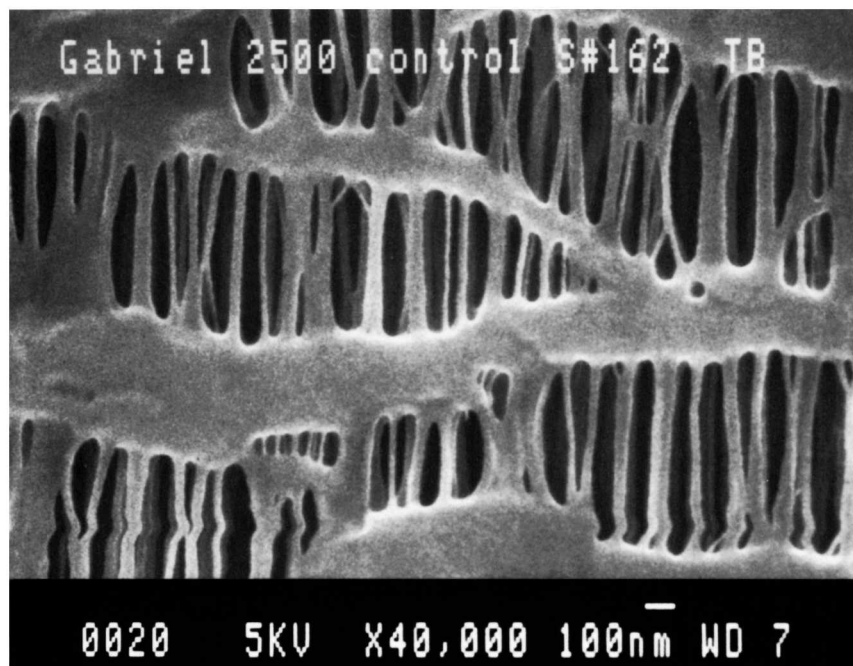|	Max. psi		
	pH 7	pH 9	pH 11
Sample #26	285	290	290+
	115	120	205
	85	7	70
	91	93	95
	128	129	0
	130	175	290
	85	85	116
Celgard 3501	61	72	72
	61	74	70
	62	71	71

Figure 1   SEM photomicrograph of Celgard 2500.

The membrane in Figure 4 was one that lost its wettability after sonication. Inside the pore structure, there are what appears to be tiny aggregates of polymer adhering to the internal support. Since the cross-linker was present in such a high concen- tration (10 mol %) relative to the acrylic acid (30 wt %), the cross-linking polymerization reaction would have occurred with some considerable speed. Hence, the polymer would tend to form small aggregates and perhaps some low molecular weight
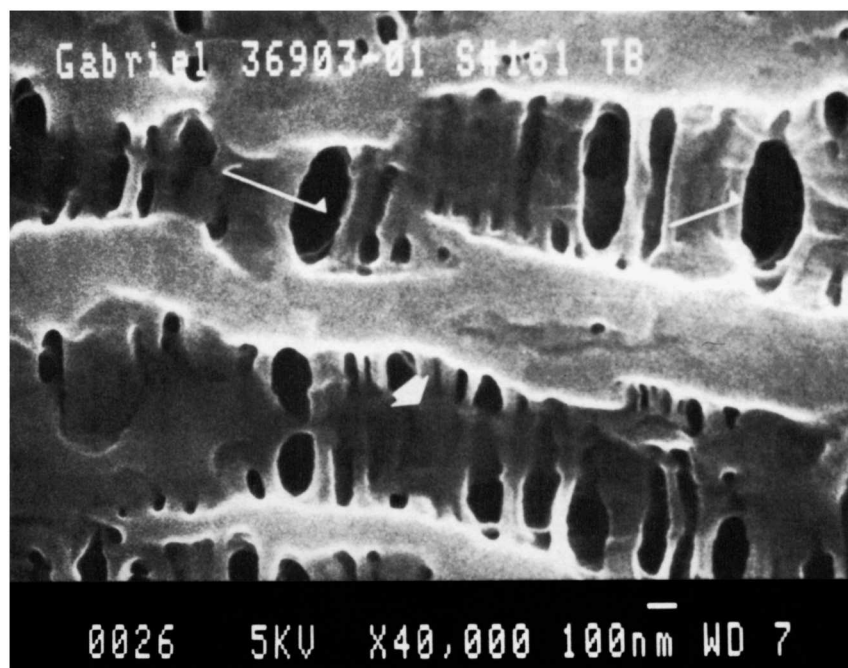
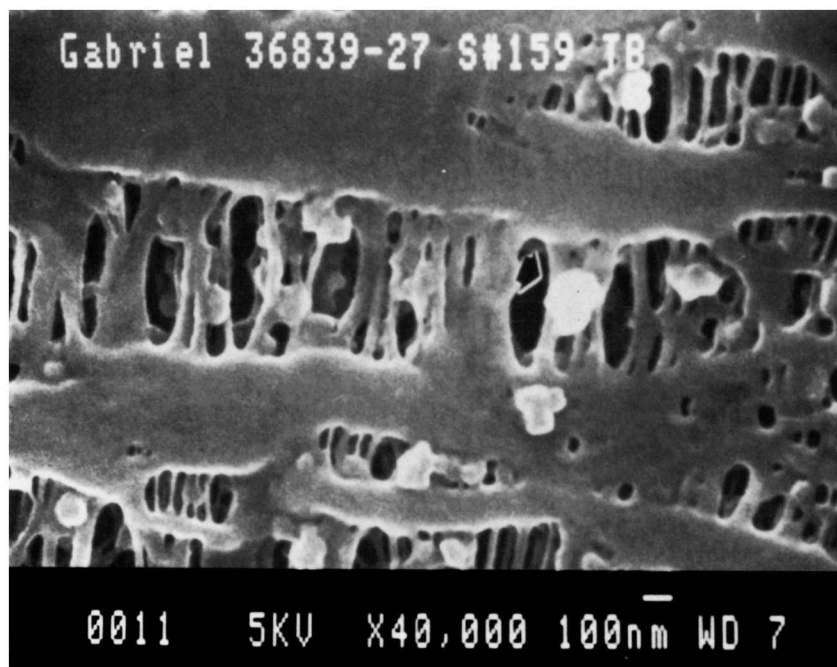**Figure 2**   SEM photomicrograph of pore-modified Celgard 2500 (Sample 25, Table II). Note the filling of pore structure (arrowhead) and distortion of pores (arrows).
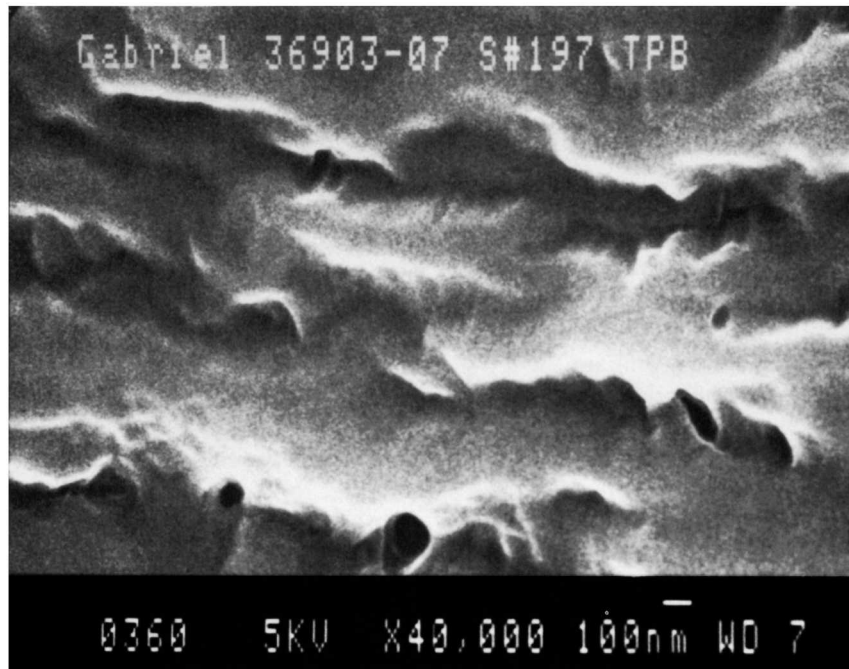
Figure 3 SEM photomicrograph of pore-modified Celgard 2500 (Sample 5, Table II). Note the absence of open pores.

chains. These chains would allow the membrane to initially wet out, but after sonication, they would be jostled from the pores.

A mercury porosimetry comparison study was performed between a sample of Celgard 3501 and sample #26 using an Autoscan 60 in conjunction with Quantachrome supplied software. By comparing the two in Table V, one can see that the modified membrane has a smaller pore volume and larger internal surface area.

Figure 4 SEM photomicrograph of pore-modified Celgard 2500 (Sample 26, Table II). Note the aggregates adhering to the pore structure (arrowhead).

Table V   Mercury Porosimetry (up to 6 kpsi)

Membrane	Volume (cc/g)	Surface Area (m²/g)
Celgard 3501	0.715	16.7
Sample #26	0.574	21.9

The smaller pore volume is a result of the poly-mer-filled spaces, whereas the larger surface area is due to increased number of smaller pores. This is evident in Figures 5 and 6, which compare the dV/dP vs. the radius for the control and modified membranes. The porosity is bimodally distributed in the modified membranes in the ranges of 2×10^2 to 1×10^3 and 2×10^3 to 1.7×10^4 Å. However, the control membrane contains a single distribution around 1.2×10^3 Å. Therefore, the modified membrane has pores that are both larger and smaller than those of the control, which is in agreement with the SEM studies.

To study the electrical resistance properties of the pore-modified membranes, representative samples were placed in an electrochemical cell in such a manner that they divided the cell into halves. A $1 M$ KCl electrolyte solution was placed on both sides of the membrane and a 40 mA direct current was

Table VI   Membrane Electrical Resistance

Membrane	Resistance (mΩ in.²)	
	pH 6.5	pH 9
Celgard 2500	44.6 ± 3.9	26.3 ± 18.6
	$n = 3$	$n = 3$
Celgard 3501	81.2 ± 38.5	34.5 ± 7.4
	$n = 10$	$n = 5$
Sample #26	209 ± 83	301 ± 122
	$n = 15$	$n = 12$

applied between two platinum wire electrodes. The voltage drop across the membrane was measured in both directions using standard calomel electrodes and the absolute measurements were averaged. After average voltage drops were corrected for the electrolyte resistance, the membrane resistances were calculated by multiplying the corrected voltages by the geometric membrane area (0.77 in.²) and dividing by the current. (It would be more correct to divide with the fraction of unfilled pore area.)

The data in Table VI indicate an increased resistance in sample #26. This is expected since the modified membrane has a decreased internal volume
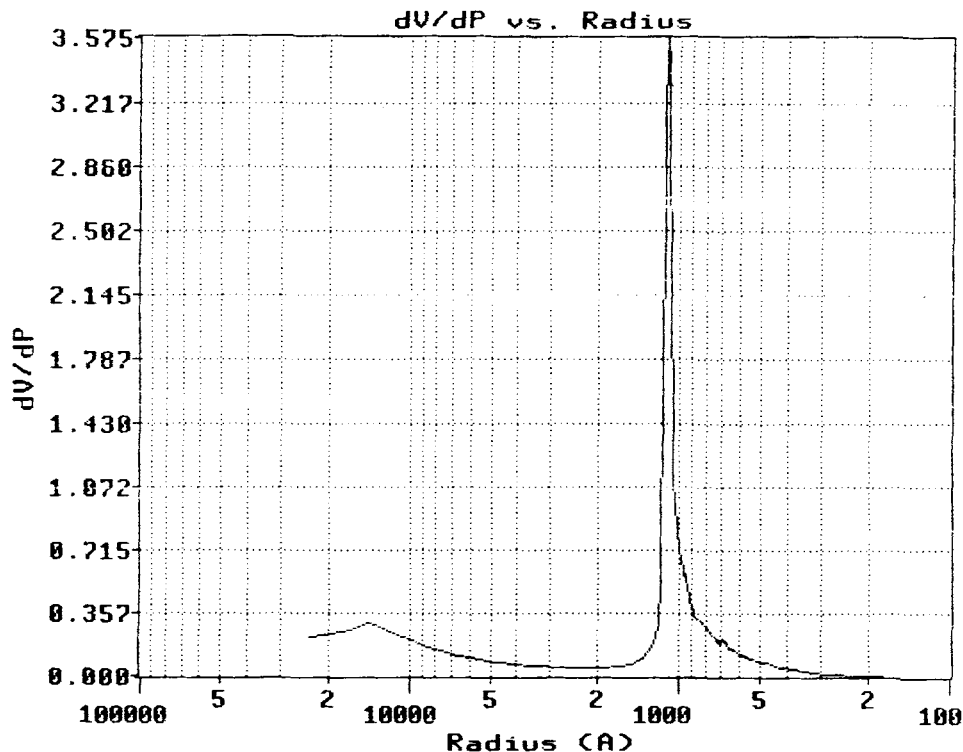
Figure 5   Mercury porosimetry: dV/dP vs. radius for Celgard 3501.
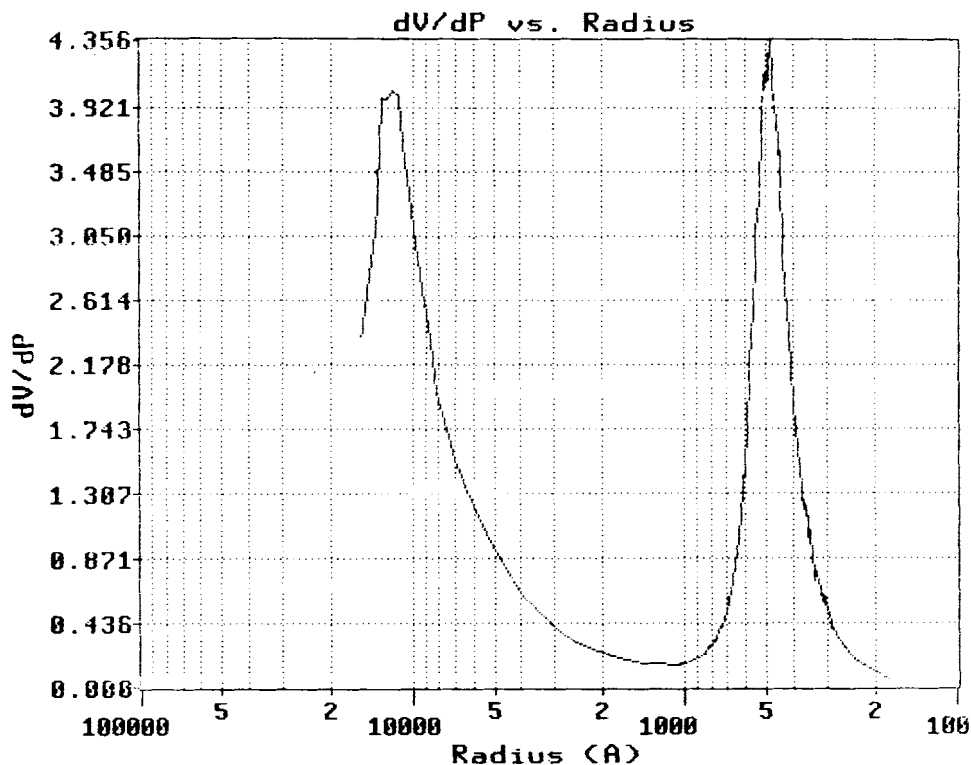
Figure 6   Mercury porosimetry: dV/dP vs. radius for modified Celgard 2500 (Sample 26, Table II).

and, therefore, a lower cross-sectional pore area that would limit the diffusion of ions through the pores. Also, at pH 6.5, there would be a number of ionized carboxylic acid groups (pK ~ 4.5) that would retard passage of negatively charged chloride ions. At pH 9, the resistance of the modified membranes increased slightly due to an increase in the number of ionized carboxylic acid groups. Slight variations within the sample data could be attributed to inherent experimental errors or possibly small variations within the samples themselves.

CONCLUSIONS

A good solvent system for polymerizing acrylic acid *in situ* within the pores of Celgard 2500 has been shown to be toluene with a benzoyl peroxide initiator. This system yields a high molecular weight polymer that is necessary for long-term stability within the pores.

With a reaction time of 4 h and an initiator concentration of 0.5 mol %, an acrylic acid concentration of at least 50–60 wt % is needed to create polymeric chains of a length required for permanency within the pores after sonication. It might be possible that a slightly lower concentration of acrylic

acid may achieve the same desired effect if the initiator concentration is also lowered.

In situ polymerization of acrylic acid within the pores of Celgard can be achieved with a lower concentration of monomer if a cross-linker such as trimethylolpropane triacrylate (TMPTA), is employed. The lowest concentration of acrylic acid that can be used in the presence of TMPTA to achieve a uniformly permanent water-wettable membrane must be greater than 15 wt %. The lowest concentration proven experimentally to yield this type of membrane was 20 wt % acrylic acid with a 0.1 mol % (of all acrylate) initiator and 1 mol % (of acrylic acid) TMPTA. At higher concentrations of acrylic acid (25–30 wt %), the concentration of cross-linker could range anywhere between > 0.01–0.1 mol % and < 5–10 mol %, with 0.1 and 5 mol % being the lowest and highest concentrations, respectively, proven to achieve the desired results. As for the initiator concentration, both 0.1 and 0.5 mol % (of all acrylate) were proven to achieve a wettable membrane when used in conjunction with a viable cross-linker concentration and an acrylic acid concentration ≥ 25 wt %.

Acrylic acid pore-modified membranes can be characterized in several ways. The membranes used for characterization purposes were mostly those

made from a monomer solution of 25 wt % acrylic acid, 0.5 mol % initiator, and 0.1 mol % TMPTA, but the same general characteristics should apply to the other membranes with some minor variations.

The pore-modified membranes have been shown to be permanently hydrophilic with a capability of water flux. The effective water flux is somewhat dependent upon the degree of polymerization that has occurred within the pores. Therefore, a monomer solution that would be expected to yield higher molecular weight polymeric chains will create a membrane with a lower potential for water flux.

When swelled with a liquid gel, pore-modified membranes can withstand greater transmembrane pressures than can a surfactant-treated control (Celgard 3501). These pressures can be as little as 2X or perhaps even as much as 5X the pressure withstood by the control membranes.

SEM and mercury porosimetry studies show that the internal pore structure of the modified membrane has been modified in such a way that there are a greater number of smaller and larger pores than that of the control. The modified membrane also has a greater internal surface area, although a smaller cross-sectional area. There can be some physical variations in the modified membrane attributable to laboratory experimental procedures.

The electrical resistance of the modified membrane is higher than the resistance of the control Celgard membranes. This can be attributed mainly to the smaller unfilled conducting area in these membranes.

The solvent system used in these experiments allowed for an easy, practical way to define the parameters governing the theory of in situ polymerization in the laboratory without the use of more sophisticated equipment. In situ polymerization creating permanent hydrophilicity within Celgard membranes should also be achievable via the use of a water-solvent system. Through the use of instruments capable of controlling humidity, temperature programming, and other atmospheric conditions, it is likely that acrylic acid could polymerize to a high molecular weight in situ. Also, the acrylic acid was only used as a representative hydrophilic monomer.

Other monomers also have the potential for in situ polymerization, thus creating new membranes with possibly different characteristics as those presented here.

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