New Porous Perfluoropolyether Membranes

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ABSTRACT: A new family of porous fluorinated membranes was developed from perfluoropolyethers (PFPEs). The PFFE–dimethacrylate **(3)** was dispersed in isopropanol to form a clear homogeneous solution, which after UV curing in polypropylene molds formed a porous polymer disk. A series of 10 polymers was prepared with ratios of isopropanol to PFPE ranging from 1.3:1 to 0.2:1. The water content of the membranes after hydration varied from 56 to 7% (w/w) and was directly proportional to the percentage of isopropanol used in the polymerization. However, the tensile elastic modulus, which ranged from 0.17 to 15 MPa, was inversely proportional to the water content. The high water content membranes [52 and 46% (w/w)] had a similar permeability to glucose, inulin, and albumin, while the membranes with lower water contents of 37 and 25% displayed progressively lower permeability. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1756–1763, 2001

Key words: perfluouropolyether; membrane; porosity

INTRODUCTION

Porous polymers or membranes maintain an important industrial role in the field of liquid-separation technology. With pore sizes ranging from the nanometer to micron scale, membranes are utilized in applications as diverse as water purification and effluent treatment, food, dairy, and beverage processing, and the recovery of enzymes and fermentation products from bioreactors.[1–3] An increasingly important application of membrane technology is in the field of biomaterials. While applications such as dialysis membranes4 and, to a lesser extent, vascular grafts[5] are well established, the area of drug delivery continues to grow rapidly.[6] More recent developments such as the encapsulation of islet cells for the treatment of diabetes[7] and keratoprosthetic implants for the partial restoration of vision[8] remain in the embryonic stages of clinical evaluation. A common feature of these therapies is the need for the controlled diffusion of molecules through the medical device either as a primary function, such as the delivery of insulin to treat diabetes, or as a secondary function, such as maintaining the nutrient flux through the implant to sustain healthy tissue while the primary role of the implant is being performed. In the case of vascular grafts and keratoprosthetic implants, the porosity serves the additional function of allowing integration of the surrounding tissue into

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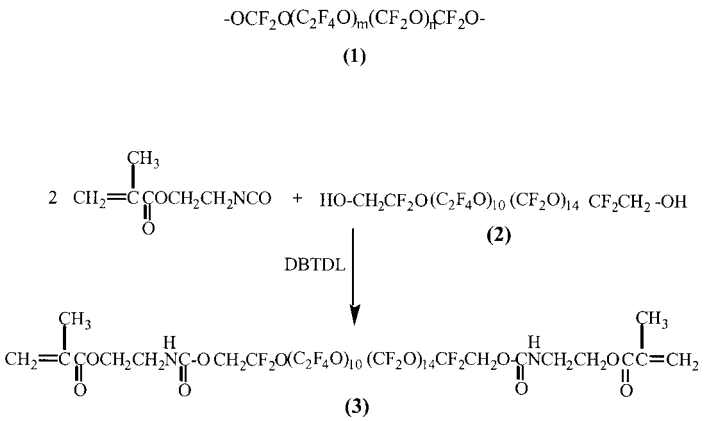

Figure 1 Synthesis of the PFPE dimethacrylate **(3)** using IEM and the PFPE diol **(2)**.

the porous voids which over time helps anchor the implant in place.

Perfluoropolyethers (PFPEs) **(1)** (Fig. 1) are a family of fluoropolymer oils made from low-temperature photooxidation of fluorinated olefins such as hexafluoropropylene and tetrafluoroethylene.[9] PFPEs are characterized by their high chemical and thermal stability and low coefficient of friction and surface tension.[10] This has made them particularly useful as premium-grade lubricants,[11] vacuum fluids,[12] and surface coatings for magnetic recording media.[13] In the biomedical area, PFPEs have been investigated in the development of extended-wear contact lenses due to their very high oxygen permeability.[14] More recently, PFPEs have been found to support the growth and attachment of a wide variety of cell line types, including corneal epithelial and endothelial cells, which will probably broaden the range of potential applications of these materials.[15]

This article describes the development of a new class of fluorinated porous membranes based on a dimethacrylate derivative **(3)** of a PFPE diol **(2)** (Fig. 1). The effect of solvent concentration on the degree of porosity and its effect on the protein permeability of the PFPE membrane was investigated along with the changes in the mechanical properties and membrane surface structure.

EXPERIMENTAL

Materials

Perfluoropolyether (PFPE) diol **(2)** (Fomblin Z-Dol^{TM}) was purchased from Ausimont S.p.A (Milan, Italy). Isocyanatoethyl methacrylate (IEM) was supplied by Showa Denko (Tokyo, Japan). Dibutyltin dilaurate and isopropyl acetate (IPAc) were purchased from Aldrich Chemicals (Castle Hill, Australia). HFE-7100^{TM} was purchased from 3M Corp. (Sydney, Australia). Isopropanol and ethanol were purchased from BDH Chemicals (Bayswater, Australia). All solvents were of analytical grade and were used without further purification. The photoinitiator Darocur 1173 was supplied by Ciba Speciality Chemicals (Sydney, Australia). The e-PTPE membrane (0.22-micron pore size) was purchased from Millipore (Bedford, MA). The polypropylene molds used for casting and UV polymerization of the PFPE dimethacrylate **(3)** were supplied by Ciba Vision Corp. (Atlanta, GA). The flat polypropylene molds had a diameter of 20 mm and a thickness of 160 or 250 microns. The Philips BLE-1800B longwave UV-A lamps with an output of 1 mW/cm^2 (at a distance of 25 cm) were purchased from the Medos Co. (Melbourne, Australia).

A D-[1-^{14}C]-glucose solution (specific activity 11.0 MBq/mg, MW = 180, radiochemical purity >99%) and [^{3}H]-inulin in a crystalline solid (specific activity 3.56 MBq/mg, MW = 5200, radiochemical purity >98%) were purchased from Amersham Australia Pty. Ltd. (North Ride, Australia). A human serum albumin solution (concentration 200 g/L, albumin purity >95%) from CSL Ltd. (Melbourne, Australia) was provided by the Australia Blood Bank and a sodium iodide (^{125}-I) solution (specific activity 100 MBq/25 mL) was purchased from Australian Radioisotopes (Lucas Heights, Australia).

Preparation of Perfluoropolyether Dimethacrylate (3)

The perfluoropolyether dimethacrylate was prepared by an adaptation of the method reported by Rice and Ihlenfeld.[14] The PFPE diol **(2)** (50 g, M_n

= 2040) and IEM (7.73 g) were placed into a round-bottom flask fitted with a Teflon-coated magnetic stirrer bar. The flask was sealed and stirred vigorously to produce a milky white emulsion. The dibutyltin dilaurate catalyst (DBTDL; 25 mg) was added to the PFPE mixture after 1 min. Soon after the addition of the catalyst, an exotherm developed and the white mixture became transparent. The mixture was stirred overnight to ensure a complete reaction. A sample was analyzed by infrared (IR) spectroscopy for the disappearance of the isocyanate band at 2270 cm^{-1}. Upon completion of the reaction, the PFPE dimethacrylate **(3)** was filtered through a 0.22-micron e-PTPE membrane to remove any urea by-product formed by the reaction of the isocyanate with trace quantities of water which may be present in the PFPE diol **(2)**.

Table I Solubility Characteristics of the PFPE Dimethacrylate (3) in Various R—OH Solvents

Solvent	Solubility Ratio
Methanol	> 6.0
Ethanol	1.8
Propan-2-ol	1.7
Propan-1-ol	0.9
3-Methyl-butan-2-ol	2.3
Pentan-3-ol	1.6
3-Methyl-butan-1-ol	0.2
Cylopentanol	0.2
2-Methyl-butan-1-ol	0.1
Hexan-3-ol	1.6
Hexan-1-ol	0.5

Solubility of PFPE Dimethacrylate (3)

The PFPE dimethacrylate **(3)** (1 g) was placed into a glass sample vial fitted with a magnetic stirrer bar. The sample vial was placed on a magnetic stirrer plate and the desired solvent was slowly added dropwise until the solution became cloudy and the mixture separated into two distinct phases. The sample vial was then weighed to determine the amount of solvent added. The solubility ratio (w/w) is expressed as solvent:PFPE dimethacrylate.

Polymerization of PFPE Dimethacrylate (3)

The PFPE dimethacrylate **(3)** was placed into a glass sample vial furnished with a Teflon-coated magnetic stirrer bar and diluted with isopropanol according to the ratios outlined in Table I. The clear colorless solution was thoroughly mixed for 5 min; then the photoinitiator Darocur 1173 was added (0.3% w/w of the PFPE mixture). The mixture was stirred for a further 5 min prior to casting.

The PFPE–isopropanol mixture was dispensed into polypropylene molds using a glass pipette. The molds were placed in a clamping assembly to keep the two halves of the mold together. The clamping assembly was then placed over two broad spectrum UV lamps with an output of 1 mW/cm^2 and polymerized for 2 h. Upon completion, the flat membranes (approximately 10) were demolded and placed in HFE-7100 (50 mL) for extraction. After 4 h, the HFE-7100 was decanted and replaced with IPAc (50 mL). The membranes were left to extract overnight, at which point the IPAc was decanted and replaced with ethanol (50 mL).

After spending 6 h in ethanol, the membranes were subjected to a graded solvent exchange from ethanol to water by successively transferring the membranes into 75, 50, and 25% (v/v) ethanol–water. The membranes spent approximately 10 min in each solution. The water was decanted and replaced with fresh water after 30 min.

Water-content Measurements

The hydrated membrane was placed on lint-free tissue paper to dry the excess surface water and then weighed on a four-figure balance. The membrane was then dried under a vacuum at 40°C to a constant weight. The water content was then calculated as follows:

$$\% \text{ Water content} = \frac{\text{hydrated weight} - \text{dry weight}}{\text{hydrated weight}} \times 100$$

Permeability of PFPE Membranes

The diffusive permeability of membranes to glucose, inulin, and albumin were measured using a two-chamber device with the membrane clamped between the chambers according to the procedure described by Sweeney et al.[16] Briefly, one chamber was filled with a solution containing radio tracers, that is, ^{14}C-glucose and ^{3}H-inulin or ^{125}I-albumin; the other chamber was filled with a control solution devoid of a radio tracer. The concen-

tration of the tracer that passed through the membrane was measured after 5 min and at various intervals over the next 1 (glucose–inulin) and 2 (albumin) h. The permeability of the membrane was calculated from the slope of the concentration versus time plot. The exposed membrane area was 0.385 cm^2. Experiments were conducted at room temperature (22 ± 1°C).

Modulus Measurements of PFPE Membranes

The tensile elastic modulus testing was performed on a Vitrodyne V-200 materials tester (Liveco Inc., Burlington, VT). The displacement resolution of this machine was 2.5 mm and the force resolution, using a 0.05-N load cell, was 0.1 mN.

Samples were cut through the center of the porous PFPE membranes, using parallel mounted razor blades. Uniformity of the strip width was verified using a Nikon Profile Projector at 50× magnification. The mean width of the parallel strips was 3.11 ± 0.01 mm. After cutting, the strip samples were stored in isotonic saline for at least 24 h prior to testing.

The initial specimen gauge length was approximately 6 mm. The parallel strip samples were clamped in the materials tester so that the initial gauge length corresponded with the central 6-mm diameter of the membrane. Sample thickness was obtained by taking thickness measurements at eight points over the central 6-mm diameter of the intact membrane with an electronic micrometer and then averaging the measurements. Testing was performed at room temperature (23 ± 2°C), at a strain rate of 20% min^{-1}, with the samples immersed in isotonic saline.

Scanning Electron Microscopy of PFPE

Morphology studies on the PFPE membranes were performed on a Philips XL-30 scanning electron microscope (SEM) in the field-emission mode. All the samples were analyzed at 2 kV to prevent beam damage to the polymers. All samples were sputter-coated with platinum prior to analysis.

RESULTS AND DISCUSSION

The PFPE dimethacrylate **(3)** was prepared using an adaptation of the method reported by Rice and Ihlenfeld,[14] who utilized the high oxygen permeability characteristics of PFPEs to investigate the development of extended-wear contact lenses. Two molar equivalents of the highly reactive isocyanate (IEM) were reacted with the PFPE diol **(2)** in the presence of the DBTDL catalyst to generate the bis-urethane **(3)** with the residual methacrylate groups (Fig. 1). The initially inhomogeneous, milky white mixture quickly becomes clear and homogeneous as the reaction proceeds and an exotherm develops. As the exotherm dissipates, the solution becomes increasingly viscous but an adequate stirring rate is maintained. A more recent method reported by Priola et al.[17,18] includes the fluorinated solvent 1,2-dichlorotetrafluoroethane, which improves the mixing efficiency of the reaction but adds an extra step of having to strip the solvent upon completion. For simplicity, we did not use a solvent in small-scale reactions (less than 250 g), but we found the non-CFC solvents such as HFE-7100 (3M Corp.) and Vertrel-XF (DuPont) work equally well if required. Prior to use, the PFPE dimethacrylate **(3)** was filtered through a 0.22-micron e-PTFE membrane to ensure that it was free of any urea byproducts which can be generated by the reaction of the isocyanate with water.

The PFPE dimethacrylate **(3)** is extremely hydrophobic and has limited solubility in many organic solvents. We sought to utilize this characteristic by attempting to generate a stable solvent mixture with **(3)** in a proportion that allowed the PFPE and solvent to remain in distinct phases, preferably in a bicontinuous phase structure. This phase separation is required to enable the PFPE to polymerize around the solvent phase. Upon complete polymerization, the solvent is removed to leave in its place a series of porous channels.

To establish a suitable mixture, we tested the solubility of the dimethacrylate **(3)** in a range of linear and branched alcohols ranging in chain length from C1 to C6 (Table I). Somewhat surprisingly, the PFPE dimethacrylate **(3)** increased in solubility as the polarity of the solvent increased**,** with the outcome of the solubility being methanol > ethanol > propan-1-ol > hexan-1-ol for the linear alcohol series (Table I). All the dissolved PFPE dimethacrylate solutions formed clear, stable homogeneous mixtures up to their maximum solubility ratios, at which point a phase transition occurred and the solutions become hazy, then separated into two phases.

PFPEs and fluorocarbons, in general, are known to have poor compatibility with hydrocar-

Table II Ratio (by Weight) of PFPE Dimethacrylate (3) to Isopropanol Used in the Preparation of Porous PFPE Membranes

Sample	Monomer (**1**)	Isopropanol
1	1.0	1.3
2	1.0	1.0
3	1.0	0.9
4	1.0	0.8
5	1.0	0.7
6	1.0	0.6
7	1.0	0.5
8	1.0	0.4
9	1.0	0.3
10	1.0	0.2

Each formulation was polymerized with 0.3% (w/w) of the photoinitiator Darocur 1173.

bons. It was hypothesized that reducing the alkyl chain length by using branched alcohols in place of their linear analogs would improve the solubility characteristics with the PFPE dimethacrylate **(3)**. Indeed, with the C3, C5, and C6 alcohols, the more highly branched forms led to dramatic increases in solubility over their linear analogs (Table I). Therefore, it would appear that reducing the alkyl chain length in the solvent, for example, from one C6 chain in hexan-1-ol to two C3 chains in hexan-3-ol, significantly improves the ability of the solvent to stabilize the dispersed PFPE dimethacrylate.

In this study, we polymerized a series of 10 isopropanol–PFPE dimethacrylate **(3)** formulations (Table II) designed to systematically investigate the effect of solvent levels on the ability to generate porous PFPE membranes. In each case, the UV polymerization of samples 1–10 (Table II) produced a white polymer disk. To ensure that the polymer disks were free of unreacted macromonomers, oligomers, or initiator, they were extracted with the fluorinated non-CFC solvent HFE-7100 and isopropyl acetate. Since the fluorinated polymer disks contain no hydrophilic monomers, they cannot adsorb appreciable quantities of water. Therefore, to gain insight into the extent of the void volume or porosity within the polymer, water was introduced via a graded solvent exchange from ethanol (which can wet the fluorinated membrane) to water. Measuring the water content of the now hydrated polymer disks allows us to gauge the change in porosity (Table III) since the water can only occupy the void volume in the polymer because the hydrophobic PFPE backbone cannot absorb water. As a control, a nonporous PFPE polymer film (made with the absence of any solvent) was put through the same graded solvent exchange from ethanol to water to ensure that residual ethanol or absorbed water made no significant contribution to the water content. The control nonporous PFPE film had a water content of less than 0.1%. While the dry PFPE membrane was white in color, during the graded solvent exchange into water, the membranes became progressively more transparent due to the increased refractive index matching with water.

The results in Table III show that on a weight per weight basis the water content of the PFPE membranes ranged from a high of 56% to 7%, indicating that a significant degree of porosity was achieved. The degree of porosity induced in the PFPE membranes appears to be directly proportional to the solvent level used in the polymerization of each sample. It would appear that the PFPE is polymerizing in a discrete phase around the solvent since the degree of porosity or water content is determined by the level of solvent used across samples 1–8 (Table III). It may be possible that the isopropanol is acting as a small surfactant molecule to stabilize the PFPE–solvent interface. This relationship appears to break down at high PFPE concentrations (sample 9, Table III) where the degree of porosity or water content begins to fall below the level of the solvent used. This may indicate a transition from an open porous structure, where the pores are intercon-

Table III Variation in Tensile Elastic Modulus of the Porous PFPE Membranes as a Function of Water Content

Sample	Modulus (MPa)	Percent Solvent in Formulation	Percent Water Content of Membrane
1	0.17 ± 0.03	56	56
2	0.55 ± 0.04	50	52
3	0.83 ± 0.03	48	50
4	1.55 ± 0.03	44	46
5	2.01 ± 0.10	42	43
6	3.01 ± 0.12	37	37
7	4.37 ± 0.15	33	33
8	8.74 ± 0.52	29	25
9	14.3 ± 0.52	23	15
10	N/A	16	7

All the PFPE membranes were 163 ± 8 microns in thickness. N/A = modulus outside range of instrument.

Table IV Permeability of Porous PFPE Membranes to Glucose, Inulin, and Albumin

Sample	Permeability (E-06 cm/sec)			Thickness (Microns)
	Glucose	Inulin	Albumin	
2	72.3 ± 4	22.7 ± 2	6.3 ± 2	254 ± 2
4	70.1 ± 1	23.0 ± 3	6.7 ± 2	254 ± 2
6	51.0 ± 1	17.0 ± 4	4.6 ± 1	255 ± 2
8	27.8 ± 1	9.8 ± 1	1.3 ± 0.3	254 ± 2
10	0.6	—	—	255 ± 2

nected from the anterior to posterior surface, to a closed pore structure, where the pores are predominantly isolated from one another. This is supported by the sharp reduction in glucose permeability from samples 8 and 10 (Table IV).

At high water content (samples 1–3, Table III), the porous PFPEs were characterized by a low mechanical strength of less than 1 MPa measured as the tensile elastic modulus. Despite this, the membranes could be handled quite easily without tearing. The modulus increases gradually as the porosity decreases (samples 3–6), but, then, the modulus rises sharply from 4.37 (sample 7) to 8.74 MPa (sample 8) (Fig. 2).

SEM analysis of the surface topography of the PFPE membranes revealed an open porous mesh or coral-like structures. Sample 1 (Fig. 3) was composed of fused globular latex particles ranging in sizes from 200 to 700 nm with a large irregular pore structure. The presence of a fused globular structure also goes some way to explaining the relatively low mechanical strength of the membrane. This was also the case in sample 4. However, in sample 6, which was polymerized with only 0.6 parts by weight of isopropanol (Table II), both the size and size distribution of the globular PFPE particles were greatly reduced over samples 2 and 4. A coral-like structure becomes increasingly evident in the SEM images of samples 7 and 9 as the water content of the membranes is reduced. Indeed, this shift in structure away from fused globular particles corresponds well with the sharp transition observed in the tensile elastic modulus of samples 6 and 7 (Table III and Fig. 2). A similar range of surface topographies was observed when the PFPE dimethacrylate **(3)** was polymerized in the presence of ethanol, hexan-3-ol, and other alcohols listed in Table I. Palani et al.[19] and Chieng et al.[20] also produced porous membranes from the microemulsion polymerization of methyl methacrylate with acrylic acid or hydroxyethyl methacrylate and produced a similar array of polymer morphologies. The ability of the PFPE dimethacrylate **(3)** to polymerize in discrete phases in which the void volume is directly proportional to the amount of solvent used in the formulation (Table III) along with the fused globular morphologies (Fig. 3) may indicate that a nonaqueous microemulsion is involved; however, further studies are required to elucidate the mechanism of membrane formation.

The permeability of the porous PFPE membranes was evaluated against a range of small, medium, and large molecular weight biological molecules including glucose (M_w = 180), inulin (M_w = 1500), and human serum albumin (M_w = 67,000). The high water content samples 2 and 4 displayed the same permeability characteristics to all the three substrates tested (Table IV). This perhaps is not surprising given the large open porosity of both samples that have a very similar structure (Fig. 3). As the water content of the membranes decreases further (samples 6 and 8), the permeability to glucose, inulin, and albumin decreases accordingly.

The permeability results at first appear a little lower than would be expected from the open porosity of the membranes in Figure 3. Two factors contribute to the permeability: First, the permeability is measured in terms of the passive diffusion of glucose, inulin, and albumin across the membrane; they are not being forced across the membrane barrier. In addition, the PFPE membranes are extremely hydrophobic, so they provide extra resistance to the diffusion of aqueous solutions. Second, the membranes were quite thick at 254 microns (e.g., as compared to a com-

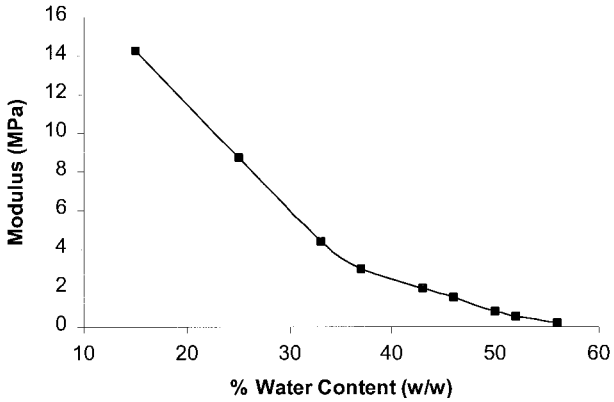

Figure 2 Relationship between modulus and percent water content of PFPE membranes.

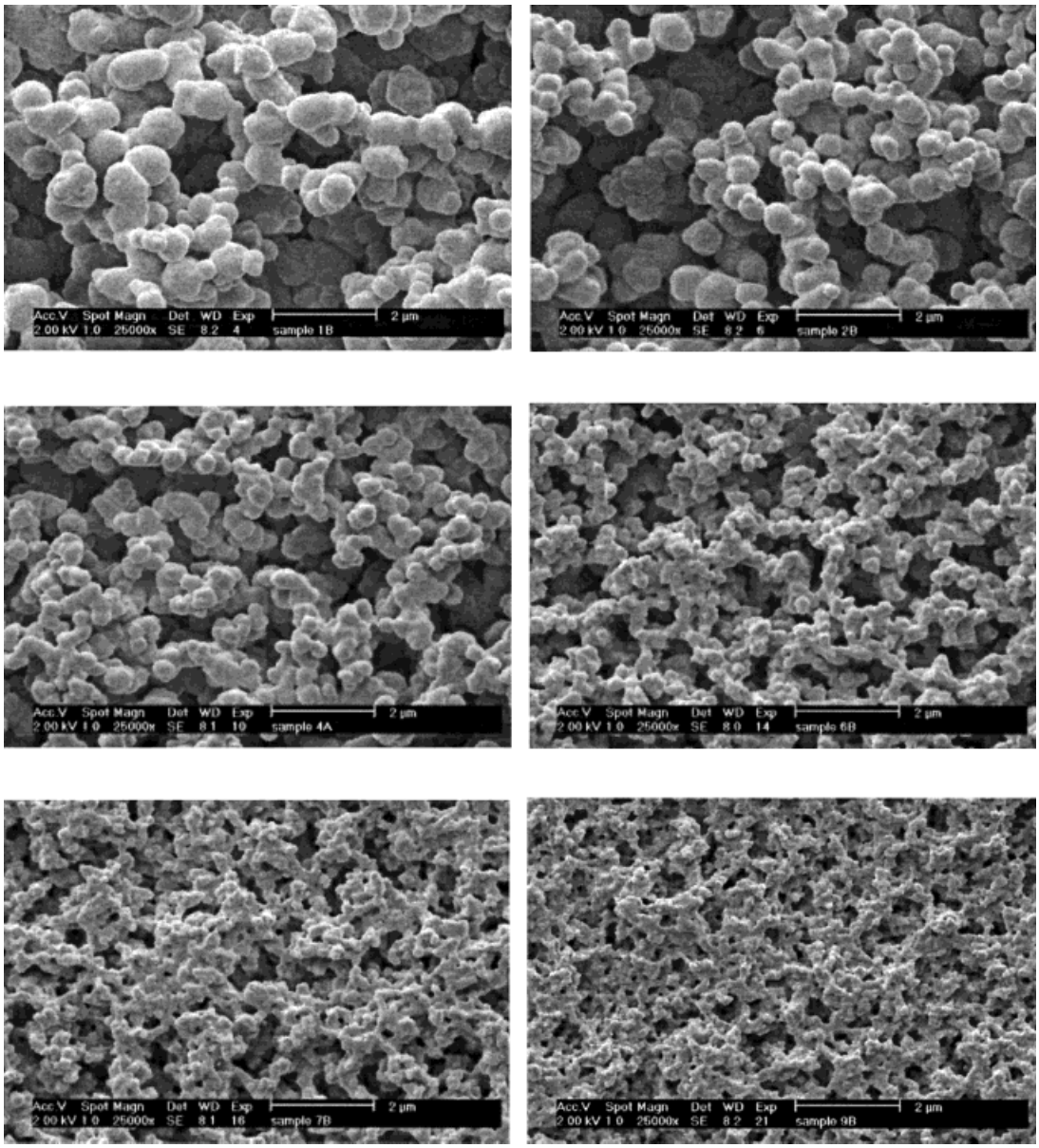

Figure 3 SEM images of porous PFPE membranes. (Top left) Sample 1; (top right) sample 2; (middle left) sample 4; (middle right) sample 6; (bottom left) sample 7; (bottom right) sample 9. Scale bar = 2 microns.

mercial track-etched polycarbonate such as Poretics™ which is approximately 6 microns thick), so the resistance encountered for diffusion through a 254-micron PFPE membrane is comparatively quite high**.** However, as a point of reference, when sample 2 was cast as an 80-micron-thick film, the glucose, inulin, and albumin permeability was measured to be 518, 196, and 37E-06 cm/s, respectively, which is substantially higher than are the permeability data recorded for the 254-micron-thick PFPE sample in Table IV.

CONCLUSIONS

Porous PFPE membranes were generated from the UV polymerization of a nonaqueous dispersion of a PFPE–dimethacrylate **(3)** in isopropanol. The porosity generated in the PFPE membranes was controlled by altering the level of the solvent used in the polymerization. Despite some of the high levels of porosity achieved, the PFPE membranes remained easy to handle. The membranes also displayed a high permeability to a range of small,

medium, and high molecular weight biological molecules. The combination of porosity with the established properties of PFPEs such as biocompatibility, high oxygen permeability, and thermal and oxidative stability provides enormous potential for these polymers in the field of bioreactors, liquid separation, and biomaterials.

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