High Performance Perfluoropolymer Films and Membranes

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ABSTRACT: Membrane processes are receiving increasing attention in the scientific community and in industry because in many cases they offer a favorable alternative to processes that are not easy to achieve by conventional routes. In this context, membranes made with perfluorinated polymers are of particular interest because of the unique features demonstrated by these materials. Both highly hydrophobic and hydrophilic membranes have been developed from appropriate perfluoropolymers that were, in turn, obtained by copolymerizing TFE with special monomers available on an industrial scale. Highly hydrophobic membranes obtained from the glassy copolymers of TFE and 2,2,4-trifluoro-5 trifluoromethoxy-1,3 dioxole (Hyflon® AD) exhibit properties that make them particularly well suited for use in optical applications, in the field of gas separation, and in gas–liquid contactors. Conditions for preparing membranes that are adequate for use in various applications are exemplified. Hydrophylic highly conductive proton exchange membranes obtained from the copolymer of TFE and a short-side-chain (SSC) perfluorosulfonylfluoridevinylether (Hyflon Ion) find interesting application in the field of fuel cells, especially in view of the current tendency to move to high temperature operation. The advantages offered by these hydrophobic and hydrophylic perfluorinated materials for use in membrane technology are discussed. Comparison of membrane properties and performance is made with other membranes available on the market.

KEYWORDS: perfluorinated membranes; Hyflon AD; gas separation; Hyflon Ion; membrane contactors; hydrophobic membranes; ion exchange membranes; fuel cells

INTRODUCTION

Fluoropolymer materials are capturing greater and greater interest in industrial applications because of the remarkable combination of properties that they exhibit when compared to other polymeric materials. The most well-known property for which fluoropolymers are employed in high-demanding applications is their outstanding thermal and chemical resistance. However, the peculiar nature of the carbon–fluorine bond confers on these materials other unique physical properties (e.g., electrical, optical, and superficial) that can be valuably exploited in the most variegated fields.

Perfluoropolymers represent the ultimate in resistance to hostile chemical environments and high service temperature because of the high bond energy of C–F and

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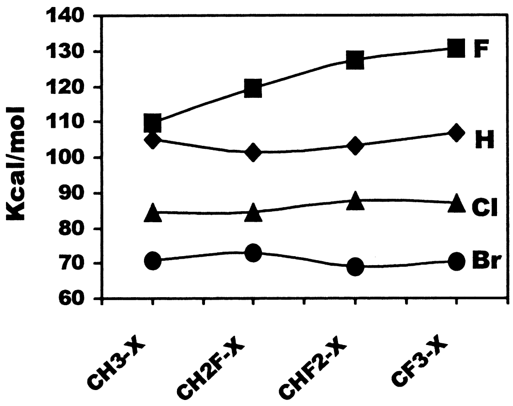


FIGURE 1. C–*X* bond energy in the model molecules CH_3–*X*, CH_2F–*X*, CHF_2–*X*, and CF_3–*X*, with X = H, F, Cl, and Br.

C–C bonds of fluorocarbons, equal to 485kJ/mol and 360kJ/mol, respectively. C–*X* bond energy data reported for the substituted methane model molecules CH_3–*X*, CH_2F–*X*, CHF_2–*X*, and CF_3–*X*, where X = H, F, Cl, or Br, show that the maximum C–*X* bond energy is attained for the CF_3X molecule when $X = F^1$ (see FIGURE 1). In many applications fluoropolymers offer the highest protection afforded by any polymer available today, to a huge variety of chemicals, such as acids and alkalis, fuels and oils, low molecular weight esters, ethers and ketones, aliphatic and aromatic amines, and strong oxidizing substances.

Monomers used for the synthesis of fluorinated polymers can be briefly classified into two categories, base monomers and special monomers, the former represented by those monomers that constitute the basic structure of modern fluoropolymers and the latter by those other monomers that add specially desired characteristics to match specialty application requirements.

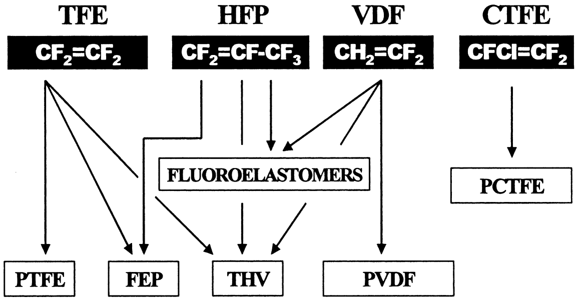


FIGURE 2. Constitution of base fluorinated homo- and copolymers.

Within this scheme, base fluoromonomers are tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidenefluoride (VDF), and chlorotrifluoroethylene (CTFE). Proper combination of these monomers yields homo- or copolymers with the most diverse characteristics: PTFE, FEP, fluoroelastomers, PVDF, PCTFE, and THV (see Figure 2). Hydrogenated monomers (e.g., ethylene) can be included in the structure (e.g., ECTFE, VDF/HFP/ethylene rubbers). In the field of films and membranes the base polymers mentioned above find wide application: just to mention some examples, films for anticorrosion (PTFE and FEP), films for protective packagings (PCTFE), microfiltration and ultrafiltration membranes (PVDF and PTFE), vapor permeable clothes and shoes (PTFE), and separators for lithium ion batteries (PVDF).

Special monomers produced on an industrial scale by Solexis are reported in Figure 3. These are perfluorovinylethers, such as perfluoromethylvinylether (MVE), perfluoropropylvinylether (PVE) and perfluorosulfonylfluoridevinylether (SFVE); perfluorinated cyclic monomers, such as 2,2,4-trifluoro-5 trifluoromethoxy-1,3 dioxole (TTD); or fluorinated diolefines, such as dodecafluoro-1,9 decadiene. MVE and PVE are used as perfluorinated modifiers both in semi-crystalline melt processable perfluoropolymers (e.g., MFA and PFA) and ultra-high resistance rubbery polymers (perfluoroelastomers). The main use of diolefine is in peroxide-curable fluoroelastomers and perfluoroelastomers to control the microstructure of the polymer chain and realize special polymer architectures by the so called “branching and pseudoliving” technology.[2] The two special monomers, TTD and SFVE reported in Figure 3 are those that find the most advanced application in the field of films and membranes. TFE–TTD copolymers are used to produce amorphous pellicles for photomask protection in far-UV microlithography and highly hydrophobic membranes, whereas TFE–SFVE copolymers have been employed for the preparation of perfluorinated high ionic conductance hydrophylic membranes. These two membrane typologies,

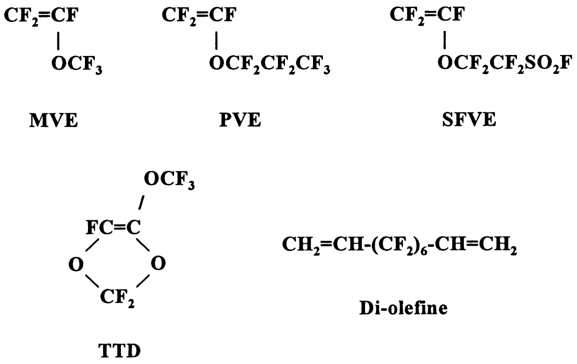


FIGURE 3. Structure of special fluoromonomers produced industrially by Solexis: perfluoromethylvinylether (MVE), perfluoropropylvinylether (PVE), perfluorosulfonylfluoridevinylether (SFVE), 2,2,4-trifluoro-5 trifluoromethoxy-1,3 dioxole (TTD), and dodecafluoro-1,9 decadiene (diolefine).

that is, hydrophobic and hydrophylic, based on TFE–TTD and TFE–SFVE copolymers, respectively, are discussed in two separate sections.

HYDROPHOBIC AMORPHOUS PERFLUOROPOLYMER MEMBRANES

TFE–TTD copolymers, known commercially as Hyflon® AD, are amorphous perfluoropolymers with glass transition temperatures (T_g) greater than room temperature.[3] They show a thermal decomposition temperature exceeding 400°C and are highly transparent to light from far UV to near infrared.

TFE–TTD copolymers are synthesized by free radical polymerization. The structure of the resulting Hyflon AD polymer is depicted in FIGURE 4. Amorphous polymers are obtained when m/n is less than about 4; that is, when the TTD molar content is higher than about 20%. Due to the cyclic structure and the effective steric hindrance of the side group, chain motion is severely hindered and high T_g glassy polymers result. When $m = 0$, that is for the case of TTD homopolymer, $T_g = 170°C$. At increasing m/n values (decreasing TTD content), T_g decreases. In TABLE 1 we show T_g values for various TTD contents. In this table, T_g values for two other amorphous glassy polymers, commercially available from Du Pont (Teflon® AF) and Asahi Glass (Cytop®), are included for comparison.[4,5] The structure of these two polymers is also shown in FIGURE 4. Teflon AF is obtained by the copolymerization of perfluoro-2,2 dimethyldioxole (PDD) with TFE. Cytop is obtained by the cyclopolymerization of perfluoro-butenylvinylether (BVE), which offers a controlled alternate structure but fixes the content of the cyclic portion of the chain to 50%, thus limiting the T_g of the polymer to 108°C.

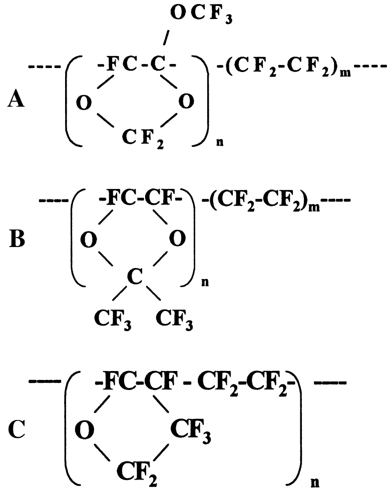


FIGURE 4. Structure of three commercial perfluorinated amorphous glassy polymers: (**A**) Hyflon AD, (**B**) Teflon AF, and (**C**) Cytop.

TABLE 1. Glass transition temperature (T_g) for amorphous perfluoropolymers at various compositions

Polymer	TFE	TTD	PDD	BVE	T_g
	(% mol)				(°C)
TTD homopolymer	—	100	—	—	170
Hyflon AD 80	15	85	—	—	135
Hyflon AD 60	40	60	—	—	110
PDD homopolymer	—	—	100	—	335
Teflon AF 2400	13	—	87	—	240
Teflon AF 1600	35	—	65	—	160
Cytop	—	—	—	100	108

TFE–TTD copolymers exhibit very high thermal stabilities, as shown by the weight loss at increasing temperatures obtained by TGA. One-percent weight losses are measured at temperatures as high as 400°C, demonstrating thermal stabilities typical of perfluoropolymers (see FIGURE 5).

Two characteristics of TFE–TTD copolymers that make them very attractive for membrane preparation are their high solubilities in perfluorinated solvents and their low solution viscosities.[6] Both features allow great flexibility in the selection of proper conditions for the preparation of membranes with various structures. Moreover, low solution viscosities imply greater ease of purification. This aspect is very important, since it is often crucial in the polymer and polymeric solutions to avoid the presence of both suspended and dissolved contaminants, such as dust or dissolved organic molecules. In fact contaminants can substantially affect properties, such as light transmittance and signal attenuation of optical devices. This is of

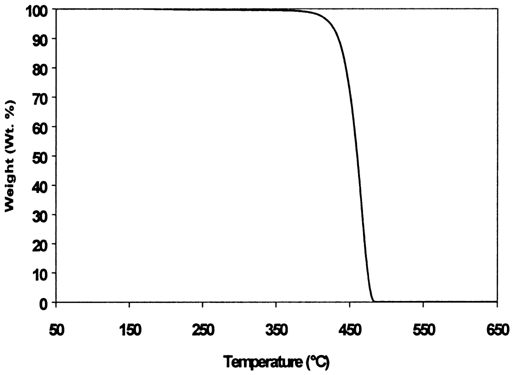


FIGURE 5. Dynamic TGA (in air at 10°C/min) of a Hyflon AD 80 membrane.

capital importance in the preparation of composite membranes, where the permselective layer is extremely thin and no defects are allowed.

Various procedures have been tuned to prepare membrane typologies to match application requirements. Examples of preparation methods and conditions for obtaining various membrane structures are reported in TABLE 2. In these preparation examples, Galden® HT 110 and Galden HT 55 are perfluopolyether oils with the following structure:

$$-(CF_2-CF_2O)_n-(CF_2O)_m-.$$

Normal boiling points are equal to 110°C and 55°C, respectively.

Flat sheet porous and non porous symmetric membranes can be obtained by following the evaporation method.[7] Laboratory membranes can be prepared by using a Braive Instruments knife to cast a 10% wt/wt polymeric solution on glass plates with various initial thicknesses and evaporation temperatures. Flat sheet laboratory asymmetric membranes can be prepared by following the dry–wet phase inversion method, with 10% wt/wt polymeric solutions.[7,8] The solvent can be Galden HT, the nonsolvent *n*-pentane, also using in this case a Braive Instruments knife to cast the polymeric film on glass plates at various initial thicknesses and coagulation bath temperatures. Flat sheet laboratory porous and non porous composite membranes of 1 μm thick films on PVDF inert supports were prepared by the spin coating process.[7,8]

Protective Pellicles for Microlithography

Symmetric dense films of Hyflon AD find application as UV resistant protective films for the semiconductor industry because of their high transparency at the far-UV wavelength, where conventional nitrocellulose pellicles are degraded due to high energy absorption. In this application, transparent pellicles are used in microlithography to cover the photomask and avoid dust depositing on it and disturbing the preparation of the photoresist. The protective film puts the dust particles out of focus (see FIGURE 6). The increase of information density requires the use of microlithography

TABLE 2. Examples of preparation procedures for various flat sheet membrane types obtained from Hyflon AD 60

Membrane type	symmetric	asymmetric	composite
Method	solution casting	dry–wet phase inversion	spin coating
Solvent	Galden HT 110	Galden HT 55	C_7F_{16}
Solution concentration	10%w/w	10%w/w	1%w/w
Temperature for solvent elimination	50°C	25°C	25°C
Non-solvent	—	n-C_5H_{12}	—
Temperature of coagulation bath	—	12°C	—
Support	glass	glass	PVDF

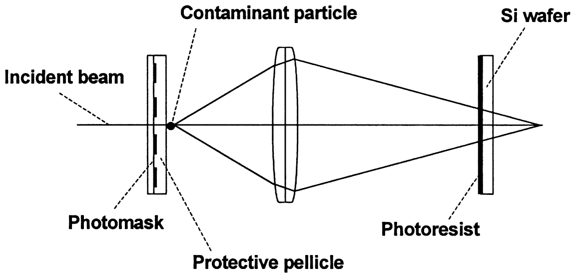


FIGURE 6. Use of the protective transparent pellicle in the microlithography process.

at ever lower wavelengths. Therefore, pellicles with high transparency at wavelengths as low as 193 nm, with a future target of 157 nm, are needed. FIGURE 7 shows the transmittance of Hyflon AD in the UV region.

Gas Separation Membranes

Hyflon AD membranes show values of permeability and selectivity to gases that make them interesting for gas separation applications. Asymmetric Hyflon AD 60 membranes give, under steady-state conditions, selectivity values for O_2/N_2 and CO_2/N_2 that are about 3 and 8, respectively, in the pressure range 5–7.5 bar. TABLE 3 gives mean permeance values to N_2, CO_2, and O_2 for these asymmetric membranes.

Permeability and selectivity values found on composite Hyflon AD membranes are in good agreement with values found on asymmetric membranes. Permeance values to N_2, CO_2, O_2, H_2, and CH_4 of composite membranes are reported in TABLE 4. Since the permselective Hyflon AD layer in this case is 1 μm thick, the permeances expressed in GPU coincide numerically with permeabilities expressed in Barrer. In TABLE 4, permeability values for Teflon AF are reported for comparison,[4] together

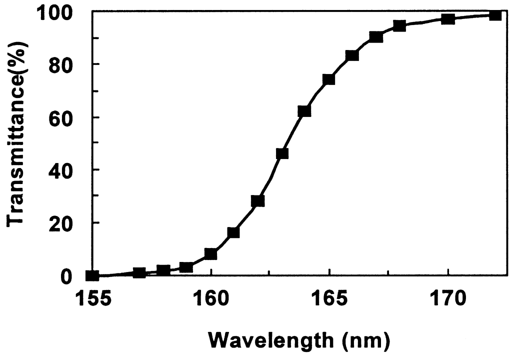


FIGURE 7. Light transmittance in the UV wavelength region for Hyflon AD.

TABLE 3. Gas permeances of Hyflon AD 60 asymmetric membranes as a function of differential pressure

Δp (bar)	Permeance (GPU)		
	N_2	CO_2	O_2
1	—	15.3	6
5	1.7	14	5.3
7.5	1.7	14.7	5.3
10	1.8	15.3	—

1 GPU = 10^{-6} cm^3 (STP)/cm^2 sec cmHg.

with the T_g values of the various polymers. Examination of these data shows that, independently of the fluoropolymer type and gas, a linear correlation exists between permeability and T_g (see FIGURE 8, where data for N_2, O_2, and H_2 are plotted). In this respect, gas permeation is often attributed to the presence of voids at the molecular scale and to their size distribution. Amorphous perfluoropolymers show an experimental density that is lower than that expected theoretically. Considering the chemical structure of amorphous perfluoropolymers, the low values of the experimental density can be ascribed, at least qualitatively, to differences in chain packing resulting from the low chain mobility and steric hindrance offered by the large dioxole groups. In other words, the high chain stiffness leads to difficulties in the close packing of chain segments and thus to "nanovoids". Since, in amorphous perfluoropolymers, T_g is mainly related to the macromolecular chain stiffness, which controls the dimension of nanosize holes, it follows that the higher the T_g value, the higher is gas permeation.

Hydrophobic Porous Membranes

Symmetric porous membranes with pore size between 30 and 80 nm have shown no permeation to water at pressures as high as 10 bar. On the other hand, high permeation to gases, such as O_2, N_2, and CO_2 were observed. Composite membranes prepared by casting the polymeric solution (1% weight) on PVDF supports have shown a unique combination of features:

TABLE 4. Gas permeability data (expressed in Barrer) of amorphous perfluoropolymers with various glass transition temperatures

Polymer	T_g (°C)	$P(N_2)$	$P(CO_2)$	$P(O_2)$	$P(H_2)$	$P(CH_4)$
Hyflon AD 80	135	77	473	194	563	49
Hyflon AD 60	110	17	124	51	202	8
Hyflon AD 40	91	8	64	26	—	—
Teflon AF 2400	240	490	2,800	990	2,200	340
Teflon AF 1600	160	—	—	340	—	—

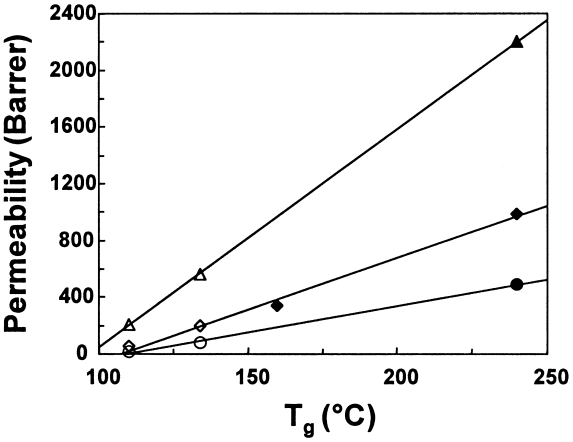


FIGURE 8. Correlation between ◇ oxygen, ○ nitrogen, and △ hydrogen gas permeability and T_g for amorphous perfluoropolymers.

- excellent organophobicity and hydrophobicity;
- gas fluxes many times those of commercial gas separation membranes; and
- chemical resistance and wear resistance.

Measures of contact angle to distilled water, compared with experimental results obtained on self-supported membranes and other commercial membranes, are reported in TABLE 5. Contact angles of 120° and above for the amorphous perfluoropolymer membranes demonstrate the extremely hydrophobic character of these membranes.

To test the organophobic character of the membranes, contact angle to hexadecane was measured. In this case the contact angle is about 65°, which is a high value

TABLE 5. Contact angle to water for various membranes

Membrane Polymer	Contact Angle to H_2O
PMMA	76
PEEK-WC-NO2	80
PES	82
PVDF	90
PE	96
PTFE	118
Hyflon AD 60	120
Hyflon AD 60 on PVDF	122

TABLE 6. Contact angle to hexadecane for various membranes

Membrane Polymer	Contact Angle to $C_{16}H_{34}$
PS	1
PTFE	39
CMS-7 on PP[a]	57
Hyflon AD 60	60
CMS-7 on PS[a]	63
Hyflon AD 60 on PVDF	65

[a] Compact Membrane Systems, Inc.

compared to other values reported in the literature (see TABLE 6). This result confirms the strong organophobicity of the membranes, which corresponds to excellent fouling resistance and inertness.

Oxygen permeation data through Hyflon AD composite membranes, in comparison to commercial gas separation membranes, are reported in TABLE 7.

In consideration of the above properties a particularly promising application can be found in the field of membrane contactors, that is, equipment in which membranes are used to improve mass transfer coefficients compared to traditional extraction and absorption processes.

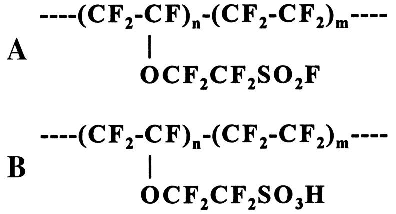
HYDROPHYLIC PERFLUOROPOLYMER MEMBRANES

TFE and perfluorosufonylfluoridevinylether (SFVE) are copolymerized by free radical polymerization to obtain the polymer depicted in FIGURE 9A (Hyflon Ion). Amorphous polymers are obtained when *m*/*n* is less than about 4; that is, when the SFVE molar content is higher than about 20%. The glass transition temperature of the polymer is a function of polymer composition, but increases typically from about

TABLE 7. Oxygen permeances through various membrane types

Membrane Polymer	Permeance to O_2 (GPU)
Generon polycarbonate[a]	7
Permea polysulfone[a]	15
Dow 4-methylpentene-1[a]	90
Ethyl cellulose[a]	100
Gore-TEX	350 (5 bar, 16°C)
Silicone Rubber[a]	500
Hyflon AD 60 on PVDF	700 (5 bar, 27°C)

[a] Compact Membrane Systems, Inc.



$$\text{----}(CF_2\text{-}\underset{\displaystyle OCF_2CF_2SO_2F}{\underset{|}{CF}})_n\text{-}(CF_2\text{-}CF_2)_m\text{----}$$

$$\text{----}(CF_2\text{-}\underset{\displaystyle OCF_2CF_2SO_3H}{\underset{|}{CF}})_n\text{-}(CF_2\text{-}CF_2)_m\text{----}$$

FIGURE 9. Structure of **(A)** Hyflon Ion and **(B)** Hyflon Ion H.

5°C to 50°C for SFVE content decreasing from 30% to 10% (molar). SFVE contents yielding amorphous polymers correspond to T_g values below ambient temperature, therefore amorphous Hyflon Ion polymers are rubbers at room temperature. These can be dissolved in a variety of perfluorinated or partially fluorinated solvents. On the other hand, when a crystalline phase appears, TFE-SFVE copolymers become scarcely soluble in any solvent. In this case, films can be prepared taking advantage of the melt-processability of the polymer.

Thermal stability of the Hyflon Ion polymers is very high, because of their perfluorinated nature. TGA shows 1% weight losses at temperatures as high as 420°C (see FIGURE 10).

After synthesis of the polymer in the sulfonyl fluoride form shown in FIGURE 9A, the polymer is transformed into an ionomer (i.e., an ion-containing polymer) by conversion of the $-SO_2F$ group to $-SO_3X$, where X is a metal or hydrogen atom. This conversion is typically carried out in alkaline aqueous solutions at medium temperature (e.g., 80°C). The polymer is finally treated with a strong acid solution if the $-SO_3H$ form of the functional group is required in the application. Therefore, the

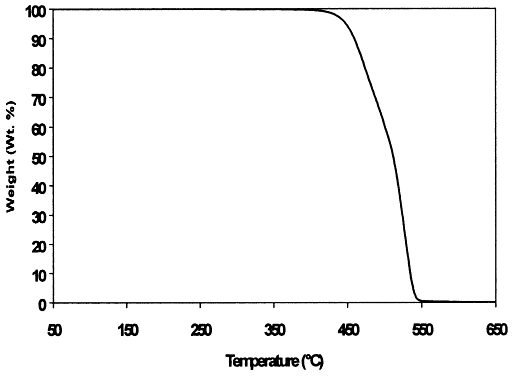


FIGURE 10. Dynamic TGA (in air at 10°C/min) of Hyflon Ion ($-SO_2F$ precursor) with EW = 1,000 g/mol.

sulfonyl fluoride form of the polymer can be considered the precursor form of the ionomer in the salt or acid form (FIG. 9B, Hyflon Ion H). Transformation of the precursor into an ionomer dramatically changes its properties.[9] This is due to strong coulombic associations that lead to the formation of ionic regions, commonly referred to as clusters. TFE rich ionomers can, therefore, be thought of as consisting of three different phases: an amorphous phase, a crystalline phase, and an ionic phase.

Perfluorinated sulfonate ionomers find effective or potential application in the form of membranes in a wide variety of fields, ranging from electrochemical electrolyzers (chloralkali[10] and HCl electrolysis[11]), to fuel cells (proton exchange membrane fuel cells[10] and direct methanol fuel cells[12]), energy storage and delivery devices (lithium ion batteries[12] and Br_2/S batteries[13]), microfiltration,[14] reverse osmosis and ultrafiltration,[12] pervaporation,[12] electrodialysis,[15] diffusion dialysis,[15] and membrane catalytic reactors.[16]

Short-Side-Chain (SSC) Ionomers and Related Membranes

Conventional ion-exchange perfluoropolymer membranes such as Nafion® (Du Pont), Aciplex® (Asahi Chemical), Flemion® (Asahi Glass), and Gore-Select™ (Gore and Associates) are based on the so-called long-side-chain (LSC) polymers.[9,17,18] Compared to Hyflon Ion (SSC) these polymers have a longer pendant group carrying the ionic functionality. The most extensively used and studied LSC ionomer is Du Pont's Nafion, which was developed in the late 1960s as polymer electrolyte for a GE fuel cell designed for NASA spacecraft missions. Since then, Nafion and polymers of the same family have found wide application in the chloralkali industry, due to their very high chemical inertness. The very high chemical stability of Nafion has been demonstrated in fuel cell applications by operating lifetimes in excess of 57,000 hours.

In the mid 1980s, Ballard Power Systems showed significant improvements in fuel cell performance using SSC ionomer membranes obtained from Dow Chemical.[19] The chemical structure of the Dow membrane was the same as Hyflon Ion (FIG. 9); that is, the Dow polymer was obtained by copolymerizing TFE with SFVE, shown in FIGURE 3. Six-cell stacks giving four times the power obtained with a standard Nafion membrane were demonstrated.

As well as improved power output, another important aspect of SSC ionomers compared to LSC ionomers is their different behavior with temperature. SSC ionomers in the protonic form ($-SO_3H$) present a primary transition, defined as the α-transition, at about 160°C, whereas LSC ionomers show this transition at about 110°C.[20] This difference is very important when the use of the membrane in a fuel-cell system is considered. First, the fact that SSC ionomers present the α-transition at 160°C implies that one necessary condition for the membrane to operate up to such a high temperature is ensured. An increase of the fuel-cell temperature is highly desirable since this means a reduction of the complexity of the system, both in terms of cooling and fuel pre-processing (CO content reduction), and consequent lower cost. In direct methanol fuel cells, higher temperatures are also required to increase the fuel oxydation kinetics. Second, if the fuel cell system for any reason goes out of control and the temperature of the stack rises locally or on the whole, the SSC ionomer membrane has a good capability for recovery. In fact, if the temperature exceeds the α-transition temperature, a catastrophic change in the membrane structure can result.[21] The higher the transition temperature, the lower is the probability for this to happen. Last, but not least, SSC ionomers, as a consequence of their lower molecular weight pendant group, show a crystallinity content that is higher than corresponding LSC ionomers of the same equivalent weight (EW).[9,22] Therefore, lower EW (i.e., higher ionic content) membranes can be prepared with same crystallinity (i.e., similar mechanical properties) or same EW membranes with higher crystallinity (i.e., higher mechanical properties). This last possibility is quite important because higher mechanical properties make it possible to achieve membranes with lower thickness, which in turn means higher membrane conductance and peak power. These are highly desirable especially in automotive applications.

A New Technology for SSC Ionomers and Membranes

A number of patents and papers on the Dow polymer and membrane appeared during the 1980s and the immediately following years.[9,19,20,22–29] Since then, interest in SSC membranes seemed to reduce. No industrial development and commercialization of these very promising experimental membranes followed.

The process developed by Dow[30] for the synthesis of the SSC monomer is illustrated in FIGURE 11. As it can be seen, the scheme involves a large number of steps. This complexity was probably one of the main obstacles to the industrial development of these ionomers and membranes, although very interesting fuel cell membrane properties were envisaged.

Recently, Solexis has applied its proprietary fluorovinylether process to the production of the SSC monomer on an industrial scale. This process, which is extremely simple compared to the old Dow process, is outlined in FIGURE 12. Within this process, the fluorination and fluoro-olefine addition steps are, in practice, a single reaction step.

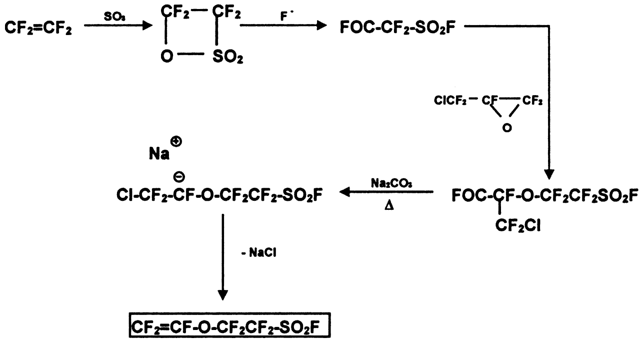


FIGURE 11. Dow route for the synthesis of the SSC sulfonylfluoridevinylether monomer.

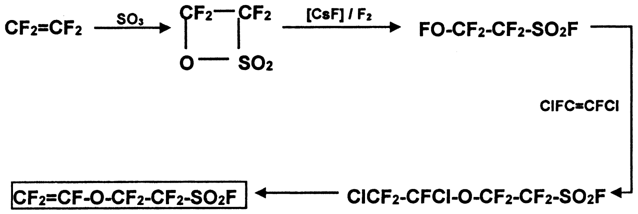


FIGURE 12. Solexis route for the synthesis of the SSC sulfonylfluoridevinylether monomer.

Hyflon Ion-FM 900 Membranes

Based on its capability for producing this monomer on an industrial scale, Solexis has started a research and development project to create new ionomer membranes for fuel cells and other applications. Starting from the monomers, ionomers are synthesized by taking advantage of a proprietary microemulsion polymerization process.[31] This technology, broadly applied to the polymerization of other fluoropolymers, is able to give very high polymerization kinetics and high molecular weight polymers with accurate control of the molecular structure.

Many Hyflon Ion ionomers were polymerized on a pilot scale in a broad range of molecular weights and EWs, from amorphous soluble ionomers to highly crystalline ionomers. Many different membranes have been prepared with these ionomers.

Self-supported crosslinked membranes have been prepared with EW from 500 to 700 g/mol and thickness from 100 to 300 μm.[32] These membranes have shown very

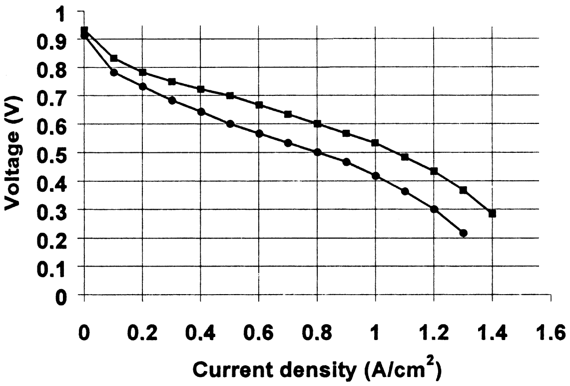


FIGURE 13. Comparison between polarization curves obtained with (■) a self-supported (melt extruded) and (●) supported (on expanded PTFE) membrane. Both membranes have the same thickness (20 μm) and were prepared with the same ionomer (Hyflon Ion, EW = 900).

high average conductivities, up to 10^{-1} S/cm under fuel cell operation, which implies high conductances (exceeding 3 S/cm^2) despite their thickness. However, the mechanical properties are insufficient, probably due to their excessive hydration. In addition, the compression molding process, used at the laboratory scale for crosslinked membrane formation, appears to be not easily industrially viable.

Composite membranes have also been prepared with EW from 750 to 1,100 g/mol and thickness from 20 to 80 µm. The ionomer in the acid form, dissolved at ambient[33] or high[34] temperature in water–ethanol mixtures, has been used to impregnate perfluorinated porous supports.[35] Dissolution at low temperature is assisted by addition of a small amount of fluoropolyether in the solvent mixture.[33] These membranes have also shown high conductance (up to 4 S/cm^2) as expected considering the low thickness. They possess also good mechanical properties. However the casting method, used on a laboratory scale to prepare small membrane samples, appears to be quite complex and is especially susceptible to inconsistency, so also not easily industrially viable. Moreover, for the more crystalline higher EW polymers, the limited gain in mechanical stability due to the support is countered by a loss in conductivity due to the presence of a fraction of volume that is occupied by the non-conducting material (see FIGURE 13).

Finally, self-supported semicrystalline membranes have been prepared with EW higher than 750 g/mol and thickness as low as 15 µm. These membranes show very good conductance and also very good mechanical properties; they are easy to handle, even at extremely low thickness. Furthermore, the ionomer, tuned with the appropriate molecular weight distribution, gave high quality and consistent membranes by film extrusion. This last process appeared to be the most viable and low cost industrial process. An activity was therefore carried out to select the ionomer that gave the best combination of processability, conductance, mechanical properties, and dimensional stability, while also being able to guarantee extremely low membrane thickness and high duration.

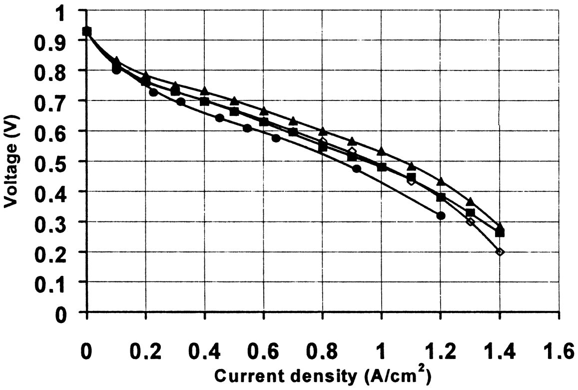


FIGURE 14. Comparison between polarization curves obtained with Hyflon Ion–FM EW = 900 membranes of various thicknesses (● 65 µm, ■ 40 µm, and ▲ 20 µm) and (○) a Gore-Select membrane.

TABLE 8. Stress and strain at break for Hyflon Ion–FM membranes and other commercial membranes, measured at RH = 50% and 23°C

Membrane	Stress (MPa)		Strain (%)	
	MD	TD	MD	TD
Hyflon Ion–FM EW = 800	23	20	130	120
Hyflon Ion–FM EW = 900	30	23	90	140
Nafion 115	30	26	119	188
Gore-Select[36]	34	24	—	—

Membranes conditioned under the measurement conditions: MD, machine direction; TD, transverse direction.

The resulting fuel cell membranes were perfluorosulphonic acid (PFSA) Hyflon Ion–FM membranes with EW = 900 g/mol. Membrane properties, in comparison with commercial Nafion 115, Nafion 117, and Gore-Select membranes, are reported in FIGURE 14 and in TABLES 8–10.

CONCLUSIONS

Fluoropolymer membranes offer, in many cases, the key to processes not easily achievable by conventional routes. Hydrophilic membranes have been used for many years in the chlorine and caustic electrolytic process as the sole ecologic alternative to mercury and asbestos diaphragm processes; they have also been used in fuel cells developed in the 1960s for the NASA space program. More recently, the use of hydrophobic membranes is being developed for applications, such as gas purification and gas–liquid contactors.

The chemistry that leads to such membranes is accessible to few companies in the world. A process developed by Solexis is particularly suitable for producing special fluoromonomers of crucial importance to the development of advanced

TABLE 9. Stress and strain at break for Hyflon Ion–FM membranes and other commercial membranes, measured at RH = 50% and 23°C

Membrane	Stress (MPa)		Strain (%)	
	MD	TD	MD	TD
Hyflon Ion–FM EW = 800	14	15	100	125
Hyflon Ion–FM EW = 900	22	17	70	110
Nafion 115	23	18	85	110
Gore-Select	32	17	—	—

Membranes pretreated by soaking in water at 100°C for 30 min. MD, machine direction; TD, transverse direction.

Table 10. Dimensional increase (%) in the plane directions from the dehydrated to the hydrated state (water soaking at 25°C and 100°C) for Hyflon Ion–FM membranes and other commercial membranes

Membrane	25°C		100°C	
	MD	TD	MD	TD
Hyflon Ion–FM EW = 800	7	8	18	20
Hyflon Ion–FM EW = 900	2	5	6	16
Nafion 117	8	10	10	12
Nafion 115	2	10	4	20
Gore-Select	—	—	3	3

fluoropolymer membranes. In particular, two special monomers produced on an industrial scale are the basis for the two classes of hydrophobic and hydrophilic membranes.

A cyclic monomer (2,2,4-trifluoro-5 trifluoromethoxy-1,3 dioxole) is the basis for the production of amorphous perfluoropolymers known commercially as Hyflon AD, showing T_g higher than room temperature, thermal decomposition temperature exceeding 400°C, and high transparency to light from far UV to near infrared. These polymers have been used to prepare protective pellicles for microlithography that are transparent in the far UV, gas separation membranes that show an optimum compromise between permeability and selectivity, and hydrophobic porous membranes that show excellent hydrophobicity and organophobicity and allow gas fluxes many times those of commercial gas separation membranes. A special sulfonyl fluoride monomer and a proprietary microemulsion polymerization process available from the Solexis technology are the basis for the production of short-side-chain ionic perfluoropolymers called Hyflon Ion. Based on these new ionomers, self-supported and composite sulfonic acid membranes for fuel cells are currently under development. Compared to presently commercial membranes, self-supported Hyflon Ion membranes show high conductivity, superior mechanical properties, and a higher ionic T_g, which is a necessary condition for running the cell at a higher temperature without damaging the membrane. The chemical stability has not yet been proved in long life tests, but the perfluorinated chemical structure guarantees the success of the tests currently being performed.

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