

# PERFLUORO POLYMER MEMBRANES

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## ABSTRACT

Membranes made with perfluorinated polymers are of particular interest due to the unique features demonstrated by these materials. Both highly hydrophobic and hydrophilic membranes have been developed from appropriate perfluoropolymers, which were in turn obtained by copolymerization of TFE with special monomers available at the industrial scale. Highly hydrophobic membranes obtained from the glassy copolymers of TFE and 2,2,4 trifluoro-5 trifluoromethoxy-1,3 dioxole (Hyflon<sup>®</sup> AD) show properties which make them particularly suited for use in the field of gas-liquid contactors and membrane distillation. Hydrophilic highly conductive proton exchange membranes obtained from the copolymer of TFE and a short-side-chain (SSC) perfluorosulfonylfluoridevinylether (Hyflon<sup>®</sup> Ion) find interesting application in the field of fuel cells, especially in view of the current tendency to move to high temperature operation.

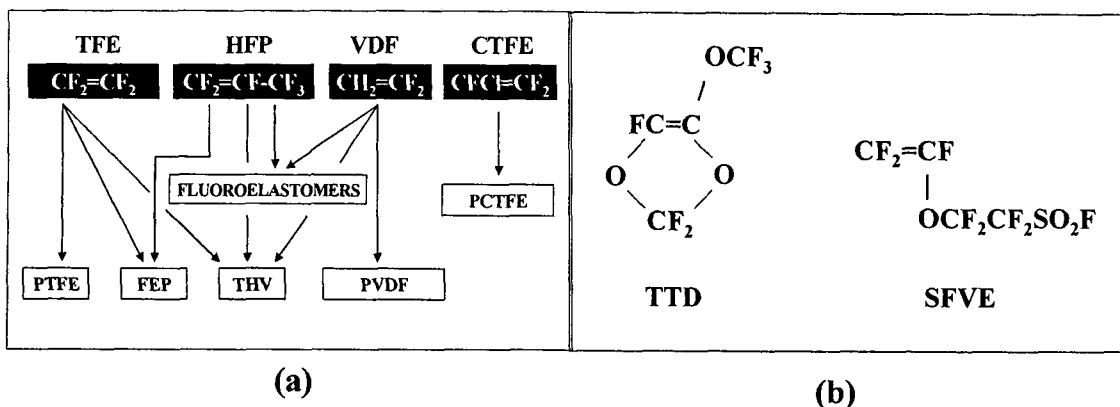
## INTRODUCTION

Besides outstanding thermal and chemical resistance, the peculiar nature of the carbon-fluorine bond confers to perfluoropolymer materials other unique physical properties (e.g., electrical, optical, superficial, etc.) which can be valuably exploited in the most different fields of utilization.

Monomers used for the synthesis of fluorinated polymers can be briefly subdivided into two categories, i.e., base monomers and special monomers, the former being represented by those monomers which constitute the basic structure of modern fluoropolymers and the latter by those other monomers which add special desired characteristics for matching specialty application requirements.

Within this scheme, base fluoromonomers are tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VDF) and chlorotrifluoroethylene (CTFE). Proper combination of these monomers yields homo- or copolymers with the most diverse characteristics: PTFE, FEP, fluoroelastomers, PVDF, PCTFE, THV (Fig. 1a). In the field of films and membranes the base polymers mentioned here above find wide application: just to mention some examples, films for anticorrosion (PTFE, FEP), films for protective packagings (PCTFE), microfiltration and ultrafiltration membranes (PVDF, PTFE), vapor permeable clothes and shoes (PTFE), separators for lithium ion batteries (PVDF).

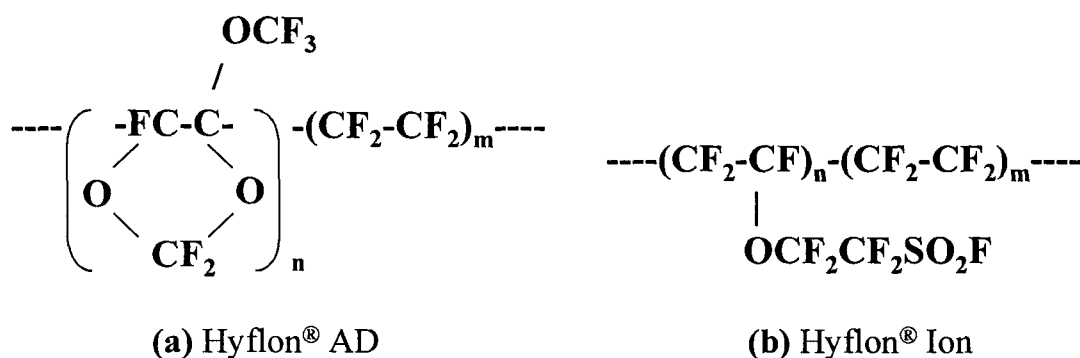
Two special monomers produced at the industrial scale by Solvay Solexis are reported in Fig. 1b. These find advanced application in the field of membranes. TFE-TTD copolymers are used to produce amorphous highly hydrophobic membranes, while TFE-SFVE copolymers have been employed for the preparation of perfluorinated high ionic conductance hydrophilic membranes.



**Fig. 1. (a)** Base fluorinated polymers **(b)** Structure of the special monomers 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) and SSC perfluorosulfonylfluoridevinylether (SFVE).

### HYDROPHOBIC AMORPHOUS PERFLUOROPOLYMER MEMBRANES

The structure of TFE-TTD copolymers, known commercially as Hyflon<sup>®</sup> AD, is reported in Fig. 2a. These are synthesized by free radical polymerization. Amorphous polymers are obtained when  $m/n < 4$  about, i.e., 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, with  $T_g$  values as high as 170°C. Thermal stability exceeds 400 °C.



**Fig. 2. (a)** Structure of Hyflon<sup>®</sup> AD and **(b)** Structure of Hyflon<sup>®</sup> Ion.

Two characteristics of TFE-TTD copolymers which make them very attractive for membrane preparation are their high solubilities in perfluorinated solvents and their low solution viscosities.<sup>1</sup> Both features allow great flexibility in the selection of proper conditions for the preparation of membranes with different structures. Moreover, low solution viscosities imply greater ease of purification, which is of capital importance especially in the preparation of thin film composite membranes where the permselective layer allows no defects.

Porous composite membranes prepared by casting a thin film of polymer in the form of solution (1% weight in perfluoropolyether solvent Galden<sup>®</sup> HT 55) on microporous PVDF supports have shown a unique combination of features:

- excellent hydrophobicity and organophobicity;
- gas fluxes higher than those of commercial microporous films;

- high chemical resistance.

The pores in the thin hydrophobic layer have been observed by AFM to be in the submicron range (typically 100 nm) and to be dimensionally almost monodisperse. No permeation to liquid water at pressures as high as 10 bar has been observed.

Measures of contact angle to distilled water compared with experimental results obtained on self-supported membranes and other commercial membranes, are reported in Table 1. Contact angles up to 120° and above for the amorphous perfluoropolymer membranes demonstrate the extremely hydrophobic character of these membranes.

Membrane Polymer	Contact Angle to H <sub>2</sub> O
PMMA	76
PEEK-WC-NO <sub>2</sub>	80
PES	82
PVDF	90
PE	96
PTFE	118
HYFLON <sup>®</sup> AD 60	120
HYFLON <sup>®</sup> AD 60 on PVDF	122

**Table 1:** Contact angle to water for different membranes.

To test the organophobic character of the membranes, contact angles to hexadecane were measured, obtaining values around 65°, which confirm the strong organophobicity of the membranes. This implies good fouling resistance and inertness.

Oxygen permeance values up to 700 GPU at  $\Delta P=5$  bar and 27°C have been measured, indicating the high gas transport rates through the porous thin layer. As a comparison, 350 GPU at  $\Delta P=5$  bar and 16°C were measured on Gore-Tex films.

In consideration of the above properties, particularly promising applications can be found in the field of membrane contactors, membrane distillation and isothermal membrane distillation (osmotic distillation).

## HYDROPHYLIC PERFLUOROPOLYMER MEMBRANES

TFE and perfluorosulfonylfluoridevinylether (SFVE) are copolymerized by free radical polymerization to obtain the polymer depicted in Fig. 2b (Hyflon<sup>®</sup> Ion). Amorphous polymers are obtained when  $m/n < 4$  about, i.e., when the SFVE molar content is higher than about 20%. These are rubbers at room temperature, which can be dissolved in a variety of fluorinated solvents. On the other hand, when a crystalline phase appears (SFVE < 20%), TFE-SFVE copolymers become scarcely soluble in any solvent. In this case, films can be prepared e.g. by melt-processing techniques.

After synthesis of the polymer in the sulfonyl fluoride form (Fig. 2b), the polymer is transformed into an acid polymer (ionomer) by conversion of the -SO<sub>2</sub>F group to -SO<sub>3</sub>H. This conversion is typically carried out in alkaline aqueous solutions at medium temperature (e.g. 80°C) followed by acidification with a strong acid. Transformation of the -SO<sub>2</sub>F precursor polymer into an ionomer dramatically changes its properties.<sup>2</sup> This is due to strong coulombic associations which lead to the formation of ionic regions commonly referred to as ion clusters.

The wide-spread reference perfluorinated ionomer for ion-exchange membranes is Nafion<sup>®</sup> (Du Pont), which is based on the so-called “long-side-chain” (LSC) polymer.<sup>2</sup> Compared to Hyflon<sup>®</sup> Ion this polymer has a longer pendant group

carrying the ionic functionality. Therefore, the Hyflon<sup>®</sup> Ion structure is referred to as “short-side-chain” (SSC) structure.

An important aspect of SSC ionomers compared to LSC ones is their different behavior with temperature. SSC ionomers in the protonic form (-SO<sub>3</sub>H) present a primary transition, defined “ $\alpha$ ” transition, around 160°C, while LSC ionomers show this transition at about 110°C.<sup>2</sup> This difference is very important when the use of the membrane in the fuel cell system is considered. The fact that SSC ionomers present the  $\alpha$  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). Moreover, SSC ionomers, as a consequence of their lower molecular weight pendant group, show a crystallinity content higher than correspondent LSC ionomers of the same equivalent weight (EW).<sup>2</sup> Therefore, lower EW (i.e., higher ionic content) membranes can be prepared with similar mechanical properties. This last possibility is quite important because higher mechanical properties allow to achieve membranes with lower thickness, i.e., higher membrane conductance.

Starting from the monomers, ionomers were synthesized taking advantage of a microemulsion polymerization process.<sup>3</sup> Many Hyflon<sup>®</sup> Ion ionomers were polymerized at the pilot scale in a broad range of molecular weights and EWs, i.e., from amorphous soluble ionomers to highly crystalline ones. Different membranes were prepared with these ionomers.

Self-supported cross-linked membranes were prepared with EW from 500 to 700 g/eq and thickness from 100 to 300  $\mu\text{m}$ .<sup>4</sup> These membranes have shown very high average conductivities, up to 10<sup>-1</sup> S/cm under fuel cell operation, which imply high conductances (above 3 S/cm<sup>2</sup>) despite their thickness. However, the compression molding process, used at the laboratory scale for crosslinked membrane formation, appears to be not easily industrially viable.

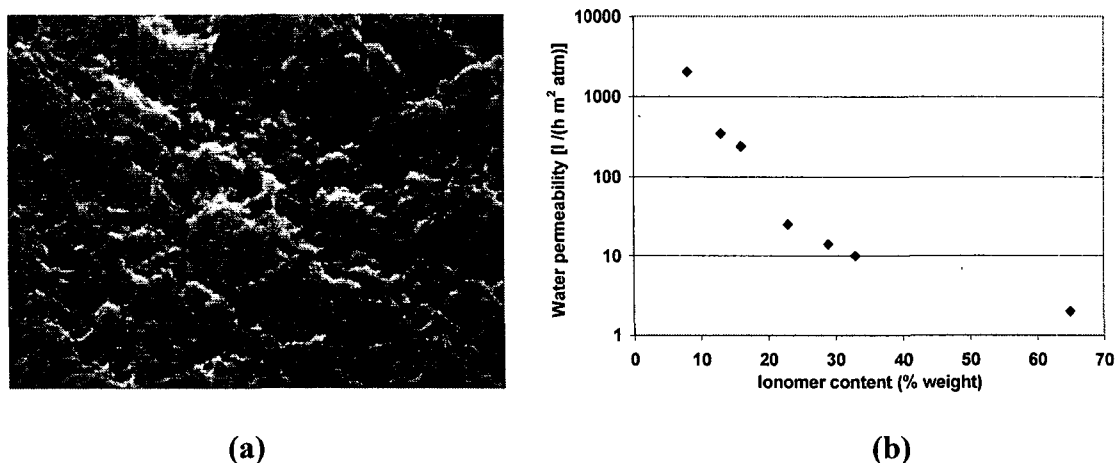
Membrane	Stress (Mpa)		Strain (%)	
	MD	TD	MD	TD
Hyflon <sup>®</sup> Ion EW=770	14	15	100	125
Hyflon <sup>®</sup> Ion EW=870	22	17	70	110
Nafion <sup>®</sup> 115 (EW=1100)	23	18	85	110
Gore-Select <sup>®</sup>	32	17	-	-

**Table 2:** Stress and strain at break for Hyflon<sup>®</sup> Ion extruded membranes and other commercial membranes. MD: machine direction, TD: transverse direction.

Self-supported semi-crystalline membranes with EW>750 g/eq and thickness down to 15  $\mu\text{m}$  were prepared by film extrusion. These membranes have shown very high conductance and also very good mechanical properties and easy handling, even at extremely low thickness. Membrane mechanical properties, compared to commercial Nafion<sup>®</sup> 115 and Gore-Select<sup>®</sup> membranes, are reported in Table 2. Membranes were pretreated by soaking in water at 100°C, and measurements were carried out immediately at RH=50% and 23°C. It can be seen that similar mechanical

properties compared to Nafion 115 are obtained on Hyflon<sup>®</sup> Ion at far lower EWs, which implies higher ion conductivities.

Finally, composite membranes on 40  $\mu\text{m}$  thick Gore-Tex substrates were also prepared with crosslinked and non-crosslinked amorphous ionomers in the EW range 450 to 600 g/eq.<sup>5,6</sup> Membranes with different ionomer contents were prepared, ranging from 8% to 75% by weight. Above about 30% ionomer content, the membranes were substantially impermeable to gases (Gurley test), while below this value the membranes were porous (see Fig. 3a) allowing high gas fluxes. Besides obtaining high conductivities in fuel cell tests, due to low EWs, these membranes showed very high water permeabilities. Water permeability was a strong function of ionomer content. This dependence is shown in Fig. 3b. For high ionomer content (>30%) non-porous membranes, high water permeability is beneficial for fuel cell application, to prevent the problem of anode dehydration. Ultra-high water permeable hydrophilic porous membranes with low (<30%) ionomer contents can instead find interesting use in filtration applications, due to their extreme ease of wetting and chemical resistance.



**Fig. 3.** (a) Microporous hydrophilic composite Hyflon<sup>®</sup> Ion membrane (b) Water permeability (liter /h m<sup>2</sup> atm) of hydrophilic Hyflon<sup>®</sup> Ion membranes as a function of ionomer content.

## REFERENCES

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