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Fluoropolymers for Membranes

1.1 Membrane Technology

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The birth of membrane science is one of the symbols of the development of modern science. With the development of membrane science, it has spread to various fields of social production and has been applied to many fields worldwide. It will cause qualitative changes in the separation and purification processes in some industrial sectors.

In terms of environmental protection, membrane technology has been used for seawater desalination [1, 2], brackish water desalination [3–5], ultrapure water preparation, and industrial wastewater treatment [6, 7]. For example, in China, Jiangsu Province Membrane Science and Technology Research Institute uses membrane technology for the treatment of nickel and chromium electroplating wastewater, papermaking wastewater concentration, phenol removal from gas and petroleum wastewater, and municipal and factory wastewater treatment.

In chemical industry, membrane technology has been successfully employed for the separation, purification, and concentration of organic and inorganic salts, as well as for the concentration and recovery of high molecular organic materials and the purification of precious metals [8–10]. Some research institutes have used ultrafiltration membranes to concentrate and purify lignin from pulp waste in the world [11]. The membrane technology is also used to extract NaCl and $NaSO_4$ from natural salt mines, to purify NaCl, and to concentrate Na_2CO_3 [12].

In medical and pharmaceutical industries, membrane technology can be used not only for the separation of bacteria and viruses but also for the concentration and separation of milk, juice, and herbal preparations [13–15]. For example, membrane separation technology is considered a promising cleaner approach, along with chemical extraction, to produce ephedrine from *Ephedra sinica* Stapf [16]. Chlortetracycline (96%) and nitrate (99%) are removed by membrane biofilm reactors (MBfRs) [17]. At present, membrane technology has been used abroad to make artificial kidneys and artificial lungs [18].

In the field of biotechnology, membrane technology has been used in developed countries to improve enzyme and cell recovery, the development of new cell culture

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devices and the development of enzyme-engineered membrane reactors, as well as the concentration or isolation of proteases, saccharification enzymes, etc. [19, 20].

Membrane technology is widely used in the food industry. It has been applied to the extraction of edible protein in soybeans, beans, and rapeseed, the removal of soy sauce, vinegar, and amino acids, and the purification of edible oils. It is also widely used in purification, concentration, and decontamination of fruit juice, fruit wine, beer, and mead [21, 22]. For example, reverse osmosis technology and ultrafiltration technology can be used to concentrate and purify jam, juice, milk, and vegetable juice and maintain their original flavor [13, 23].

Water is considered to be the world's most valuable renewable resource and an important aspect of life. The world's population tripled in the twenty-first century and will increase by another 40–50% in the next 50 years. Due to population growth, coupled with industrialization and urbanization, the demand for freshwater is increasing rapidly. In addition, some existing freshwater resources have gradually become polluted due to human or industrial activities. In the coming decades, the problem of water scarcity worldwide will become increasingly serious. As a result, many researchers have been looking for suitable ways to obtain freshwater by purifying and reusing it to support future generations. Water purification is an important process of removing chemicals, organic and biological pollutants, and suspended solids from water to obtain satisfactory water [24, 25].

Membrane technology has dominated water purification technologies due to its low cost and high efficiency [26]. Unlike other types of membranes, fluoropolymer membranes are leading the membrane separation industry and market due to their economic and practical benefits. However, there are some limitations in its application, including chemical, mechanical, and heat resistance. Improving flux and selectivity and reducing membrane contamination are the most important problems in membrane applications [27]. In order to remove barriers and reduce problems in membrane technology, a great deal of research has been carried out to develop new materials and methods to manufacture and modify fluoropolymer membranes.

Fluoropolymer membranes are widely used in water treatment applications such as desalination, water softening, purification of industrial and municipal wastewater, production of ultra-pure water, and in the food, chemical, and pharmaceutical industries. The membrane process has the significant advantages of simple operation, flexibility, high effectiveness, high reliability, low energy consumption, good stability, good environmental compatibility, easy control, handling, and scale-up, and is suitable for a variety of operating conditions including temperature, pressure, and pH. However, in more serious applications, there are still unresolved problems with the application of fluoropolymer membranes. Membrane fouling, inadequate separation and retention, treatment of concentrates, membrane life, and resistance to certain chemicals are among the most important and well-known problems associated with fluoropolymer membranes. Table 1.1 lists the representative membrane processes and requirements for membrane materials.

Table 1.1 Representative membrane processes and requirements for membrane materials.

Membrane process	General mechanism	Main properties	Ref.
MF/UF	Pressure-driven liquid passes through the membrane pores	Hydrophilic used in aqueous systems, while hydrophobic used in oil systems	[28, 29]
MD	Thermally driven, water vapor passes through the membrane pores	Hydrophobic, high porosity	[30]
Membrane crystallization (MCr)	Thermally driven, vapor passes through the membrane pores	Hydrophobic used for hydrophilic (aqueous) crystallizing solutions, while hydrophilic used for oleophilic solutions	[31, 32]
Membrane emulsification (ME)	Pressure-driven, contentious phase passed through the membrane pores	Hydrophobic used for producing O/W emulsions, while hydrophilic used for producing W/O emulsions	[33, 34]
Osmotic distillation	Vapor pressure-driven, vapor diffuses through the membranes	Hydrophobic typically	[35]
PV	Concentration-driven, vapor passes through the membranes	Hydrophilic for dehydration of organic solvents or organic mixtures; hydrophobic for removal of organic solvents or volatile organic compounds (VOCs) from water; organophilic for organic/organic separation	[36, 37]
Proton-exchange membrane (PEM)	Proton transports in membranes	High proton conductivity, mechanical, chemical and thermal stability, good barrier properties for gas and methanol	[38, 39]
Membrane separator for Li-ion battery	Transport ionic charge carriers and prevent electric contact between anode and cathode electrodes	High ionic conductivity and good barrier for electron	[40]
Gas separation membrane	Pressure-driven	High diffusivity and/or high solubility to permeate gases	[41]
Membrane gas absorption (MGA)	Concentration gradient-driven, gas passes through the membrane pores	Hydrophobic	[42, 43]

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1.2 Fluoropolymers for Membranes

In the past few decades, there has been an increase in interest in the quest for innovative materials that exhibit the required characteristics for a certain application. A material with low polarizable and electronegative fluorine atoms (van der Waals radius of 1.32 Å) will have a short C—F bond with a high bond energy dissociation of about 4.85 kJ mol^{-1} [44]. Because of their exceptional qualities, including thermal stability, chemical inertia (against solvents, oils, water, acids, and bases), low refractive index, dielectric constant, dissipation factor, and water absorption, as well as superior weather resistance, durability, and oxidation resistance, fluoropolymers are therefore good niche candidates. They thus have a wide range of high-tech uses.

Fluoropolymers represent a significant advancement in modern high-tech industries due to their exceptional properties, which confer high added value across various applications. Their unique combination of chemical resistance, thermal stability, and low surface energy positions them as critical materials in advanced technologies, offering substantial improvements in performance and durability in demanding environments. These polymers are applied widely in the following advanced technologies: automotive industries [45] (c. 300 g of fluoropolymers per car, and in components of fuel cells and lithium-ion batteries (LIBs)), aerospace and aeronautics [46] (use of elastomers as seals, gaskets, O-rings for application at extreme temperatures for tanks of liquid hydrogen, or hydrazine in boosters of space shuttles), petrochemical [47] (pipes and coatings as liners), microelectronics, chemical engineering [28] (high-performance membranes), textile treatment, building (paints and coatings resistant to UV and graffiti, and stone protection, especially coatings of old monuments for the cultural heritage), and optics [48] (core and cladding of optical fibers). A special class of fluoropolymers can be obtained by photopolymerization, which is particularly attractive because it can be done at room temperature, has fast kinetics, and can be finished without any solvents [49]. Most fluoropolymers for membrane processes are shown in Table 1.2, and their respective chemical structures are presented in Table 1.3.

1.3 PVDF and Its Copolymer

Polyvinylidene fluoride (PVDF) is widely used in the membrane industry because of its excellent properties such as high mechanical resistance, thermal resistance, chemical resistance, and relatively high hydrophobicity. PVDF membranes are used for ultrafiltration and microfiltration, membrane contactors such as membrane distillation (MD), membrane crystallization (MCr), and membrane condensation [50–57].

Table 1.4 lists typical polymer materials and their critical surface tensions. PVDF remains the best choice for membrane contactors because PP and PTFE membranes cannot easily be fabricated by traditional phase conversion process [52].

Table 1.2 Fluoropolymers for membrane process.

Polymer		Membrane process
PVDF homopolymer		MF, UF, MD, MCr, ME, PV
PVDF copolymer	P(VDF-*co*-TFE)	MF/UF, MD
	P(VDF-*co*-HFP)	MF/UF, MD, PV, fuel cell, lithium-ion battery
	P(VDF-*co*-CTFE)	MF/UF, NF, MD, PV, fuel cell
	PVDF-*g*-PSSA	Fuel cell
	P(VDF-TrFE)	Lithium-ion battery, tissue regeneration
PTFE homopolymer		MD, MC, PV, MGA
PTFE copolymer	Perfluorosulfonic acid (PFSA)	Fuel cell, lithium-ion battery, chlor-alkali industry
	Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA)	Fuel cell
	Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)	MD, fuel cell
	Poly(ethylene-*alt*-tetrafluoroethylene) (ETFE)	Fuel cell
Other fluoropolymers	Poly(ethylene chlorotrifluoroethylene) (ECTFE)	PV, MD, MC, and MF/UF
	PCTFE	—
	PVF	Fuel cell
	PFE	Fuel cell
	Hyflon® AD, Teflon® AF, Cytop®	Gas separation, have potential in MD, MC

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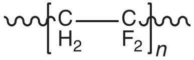
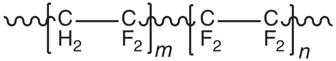
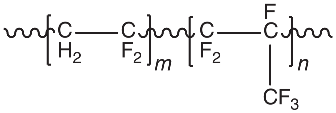
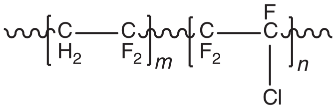
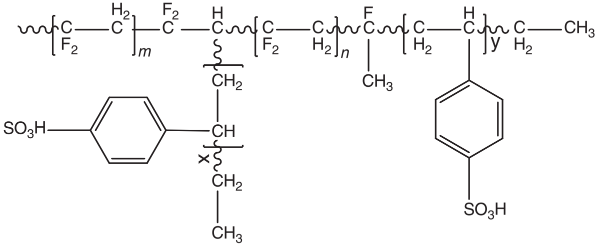
PVDF is superior to other membrane materials due to its high mechanical strength and excellent chemical resistance, making it suitable for water treatment. Due to its low extractability, PVDF is also suitable for biomedical and bioseparation processes. PVDF also exhibits thermodynamic compatibility with other polymers such as polymethyl methacrylate (PMMA), polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG) in a wide range of blended compositions, which can be used to manufacture membranes with desired properties [58–60]. PVDF can be further chemically modified to obtain some specific properties [59, 60], and can be cross-linked by electron beam radiation or gamma radiation [61, 62].

Beside homopolymeric PVDF, PVDF copolymers also can be used as membrane materials, such as poly(vinylidenefluoride-*co*-hexafluoropropylene) (P(VDF-HFP)), poly(vinylidene difluoride-*co*-chlorotrifluoroethylene) (P(VDF-CTFE)), poly(vinylidene fluoride-*co*-tetrafluoroethylene) (P(VDF-*co*-TFE)), poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), and poly(vinylidene fluoride)-graft-poly-(styrene

Table 1.3 Chemical structures of main fluoropolymers for membranes.

Polymer		Chemical structure
PVDF homopolymer	PVDF	
PVDF copolymer	P(VDF-*co*-TFE)	
	P(VDF-*co*-HFP)	
	P(VDF-*co*-CTFE)	
	PVDF-*g*-PSSA	

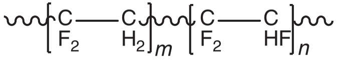
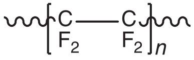
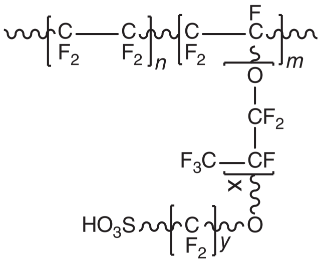
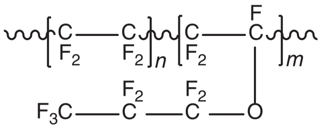
	P(VDF-TrFE)	
Poly(tetrafluoroethylene) homopolymer	PTFE	
PTFE copolymer	Perfluorosulfonic acid (PFSA)	
	Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA)	

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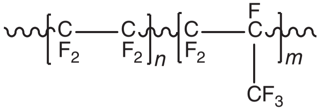
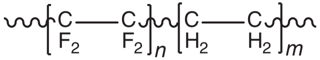
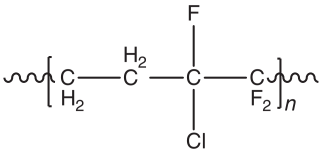
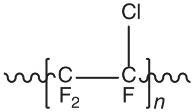
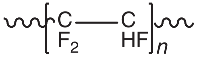
Table 1.3 (Continued)

Polymer		Chemical structure
	Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)	
	Poly(ethylene-*alt*-tetrafluoroethylene) (ETFE)	
ECTFE	Poly(ethylene chlorotrifluoroethylene) (ECTFE)	
Other fluoropolymers	PCTFE	
	PVF	

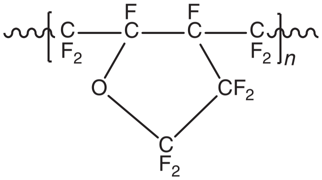
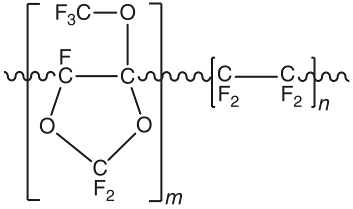
Cytop	
Hyflon AD	

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Table 1.4 Critical surface tension membranes of major polymeric membrane materials.

Polymer	Critical surface tension (dynes/cm)
Polyvinylidene fluoride (PVDF)	25–28.5
Polyfluoroethylene (PFE)	22
Polytetrafluoroethylene (PTFE)	18.5
Fluorinated ethylene propylene (FEP)	16
Ethylentetrafluoroethylene (ETFE)	17
Polyacrylonitrile (PAN)	44
Polysulfone (PS)	41
Polyphenylene oxide (PPO)	41
Polyethylene (PE)	31
Polypropylene (PP)	29

sulfonic acid) (PVDF-g-PSSA). The properties of PVDF and PVDF copolymers will be introduced in the following.

1.3.1 Homopolymeric PVDF

PVDF is a kind of semicrystalline macromolecule, which contains 59.4 wt% fluorine and 3 wt% hydrogen [62, 63] (chemical structure is shown in Table 1.3). Commercial PVDF is generally produced by polymerization in emulsion or suspension using free radical initiators, forming a repeating unit of $–CH_2–CF_2–$. PVDF presents a crystallinity of 35–70%, depending on their process condition and heat history. A higher crystallinity endows PVDF with higher mechanical properties, such as higher stiffness, toughness, and creep resistance. Like most of polymers, molecular weight, molecular weight distribution, extent of irregularities along the long polymer chain, crystallinity, and crystalline form are the major factors for PVDF properties.

PVDF exists at least five crystalline phases as reported. The crystal polymorphs are named α, β, γ, δ, and ε. α-, β-, and γ-phases are the most frequent PVDF phases [24] (Figure 1.1). The α- and δ-phases display the same TGTG′ conformation. The β-phase displays a TTT structure. Additionally, the ζ- and γ-phases exhibit the same TTTGTTTG′ conformation. The most thermodynamically stable form is the β-form, although the α-form is kinetically advantageous.

Table 1.5 provides an overview of the PVDF's characteristics throughout its several polymorphs. The slightly greater van der Waals radius of the fluorine atom (1.35 Å) compared to the hydrogen atom (1.20 Å) is directly related to the polymorphism of PVDF. In fact, for synthetic homopolymers, PVDF hardly ever has these five types of crystalline phases [67].

The α-phase PVDF is non-polar. On both sides of the C main chain, hydrogen and fluorine atoms alternate regularly to form a helix-like shape (Figure 1.1a).

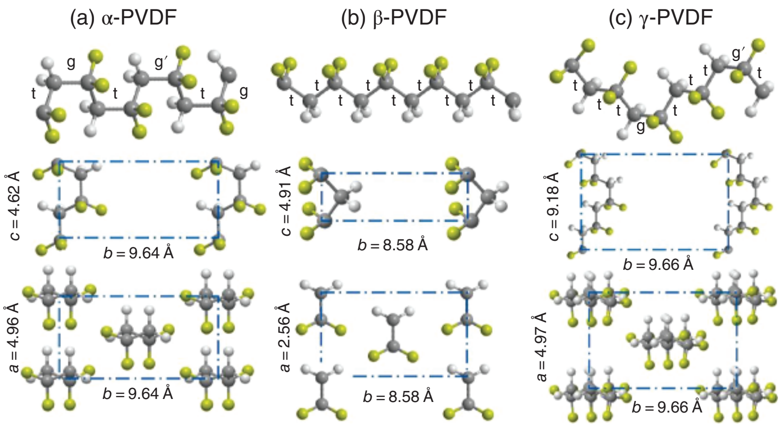


Figure 1.1 Schematic representation of the chain conformation for the α, β, and γ phases of PVDF. The gray, white, and yellow spheres represent carbon, hydrogen, and fluorine atoms, respectively. Source: Reproduced from Wang et al. [64]/with permission of Elsevier.

Table 1.5 Properties of PVDF with different polymorphs [65, 66].

	α-phase	**β-phase**	**γ-phase**	**δ-phase**	**ε-phase**
Crystal system	Monoclinic	Orthorhombic	Monoclinic	—	—
Polarity	Nonpolar	Polar	Polar	Polar	—
Lattice constants	$a = 4.96$ Å $b = 9.64$ Å $c = 4.62$ Å	$a = 8.58$ Å $b = 4.91$ Å $c = 2.56$ Å	$a = 4.97$ Å $b = 9.66$ Å $c = 9.18$ Å	$a = 4.96$ Å $b = 9.64$ Å $c = 4.62$ Å	$a = 4.97$ Å $b = 9.66$ Å $c = 9.18$ Å
Number of chains per lattice	2	2	2	—	—
Molecular conformation	TGTG′	TTT	TTTGTTTG′	TGTG′	TTTGTTTG′
Density, Observed at 30 °C (g ml^{-1})	1.77	1.81	1.80	—	—
FTIR peak (cm^{-1})	408, 532, 612, 766, 795, 855, 976, 1182, 1400	445, 470, 511, 600, 840, 1270	431, 512, 776, 795, 812, 833, 840, 1233, 18.5, 19.2, 20.4	—	—
Peak of 2θ of X-ray diffraction (°)	17.66, 18.30, 19.90, 26.56	20.26	18.50, 19.20, 20.04	—	—

The conformation is zigzag in the β-phase. The piezo-, pyrro-, and ferroelectric characteristics of PVDF are derived from the regular organization of the C–F strong dipole along the polymer chain [67]. The intermediate, polar conformation of the γ-phase is TTTGTTTG′ [68]. These different crystalline phase structures have already been characterized [67, 69].

PVDF is resistant to a wide range of oils, solvents, and acids. The amorphous and crystalline PVDF areas have glass transition (T_g) and melting temperatures (T_m) between −40–−30 °C and 155–192 °C, respectively. The density of amorphous PVDF is 1.68 g cm^{-3}. The densities of the α, γ, and β polymorphs are 1.92, 1.93, and 1.97 g cm^{-3}, in that order. PVDF typically has a density of 1.75–1.78 g cm^{-3} and a crystallinity degree of about 40%. At 230 °C and 1.0 bar, the melt density of a PVDF homopolymer is approximately 1.45–1.48 g cm^{-3} [70]. A list of some physical and mechanical properties is shown in Table 1.6.

PVDF's solubility is governed by "like-dissolve-like" principle. PVDF can dissolve in very few polar aprotic solvents, such as dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP).

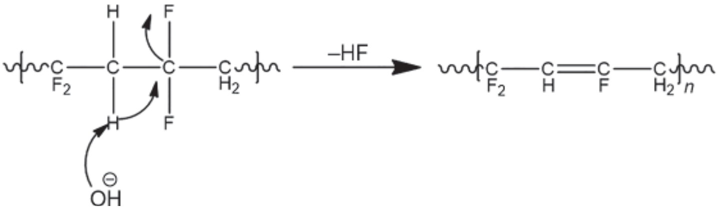
PVDF has been recognized as one of the most excellent chemical-resistant materials [71]. Although PVDF has strong corrosion resistance to chemicals such as halogens, oxidants, and inorganic acids, as well as aliphatic, aromatic, and chlorinated solvents, it is still incompatible with strong bases and many ketones [60]. Many investigations have fundamentally confirmed that PVDF membrane

Table 1.6 Physical and mechanical properties of PVDF.

Property (standard)	PVDF	Criterion
Color	White	—
Density (g cm^{-3})	1.78	—
Melting point (°C)	155–192	ASTM D-3418
Glass transition temperature (°C)	−40 to −30	—
Heat deflection temperature (0.5 MPa)	148	—
Relative density (g cm^{-3})	1.76–1.80	ASTM D-792 (Solid)
Tensile stress at 23 °C (MPa)	35–55	ASTM D-638
Elongation at 23 °C (%)	25–500	ASTM D-638
Young's modulus at 23 °C (MPa)	1340–2000	ASTM D-638
Izod impact strength at 23 °C (J m^{-1})	160–530	ASTM D-256
Thermal expansion coefficient	~10^{-4}	ASTM D-696
Processing temp. range (°C)	200–300	–
Relative permittivity (1 kHz)	7.5–13.2	ASTM D-150
Dielectric strength (kV mm^{-1})	260–950	ASTM D-149
Dissipation factor (1 kHz)	0.0163–0.019	ASTM D-150
LOI (%)	44	ASTM D-2863

Source: Adapted from Saxena and Shukla [70].

materials were susceptible to alkaline conditions [72–76]. PVDF membrane will change from white to brown, and then to black after exposure in the NaOH solution [72, 73], thus becoming brittle [72, 73, 77, 78]. This is interpreted as a dehydro-fluorination reaction, which removes hydrogen fluoride (HF) units from PVDF chain, thus forming C = C bond [71, 74, 78, 80]. Scheme 1.1 shows the alkaline degradation process of PVDF.



Scheme 1.1 Diagram of the alkaline degradation mechanism of PVDF. Source: Reproduced from Zhang et al. [71]/with permission of Elsevier.

According to Hashim et al., the mechanical strength and crystallinity of PVDF decreased as a result of the interaction between PVDF and NaOH, which was activated even at low NaOH concentrations. The reaction also became more intense as the treatment duration was prolonged. The reaction was expedited and enhanced as the sodium hydroxide concentration and treatment temperature were increased. PVDF membranes are more vulnerable to the effects of NaOH solutions than KOH solutions, according to Rabuni et al. [79–82]. A list of stability of PVDF membrane materials in harsh caustic environments is shown in Tables 1.7 and 1.8.

Table 1.7 Performance of PVDF resistance to organic solvents.

Chemical solvent	20 °C	50 °C
Dimethyl formamide (DMF)	Not resistant	Not resistant
Dimethyl sulfoxide (DMSO)	Not resistant	Not resistant
Dimethylacetamide (DMAc)	Not resistant	Not resistant
N-Methylpyrrolidone (NMP)	Not resistant	Not resistant
Acetone	Not resistant	Not resistant
Tetrahydrofuran (THF)	Limited resistant	Limited resistant
Benzene	Resistant	Limited resistant
Chlorobenzene	Resistant	Resistant
Chloroform	Resistant	Resistant
Ethyl acetate	Resistant	Limited resistant
Cyclohexane	Resistant	Resistant

Source: Adapted from Saxena and Shukla [70].

Table 1.8 Performance of PVDF resistance acids and alkali.

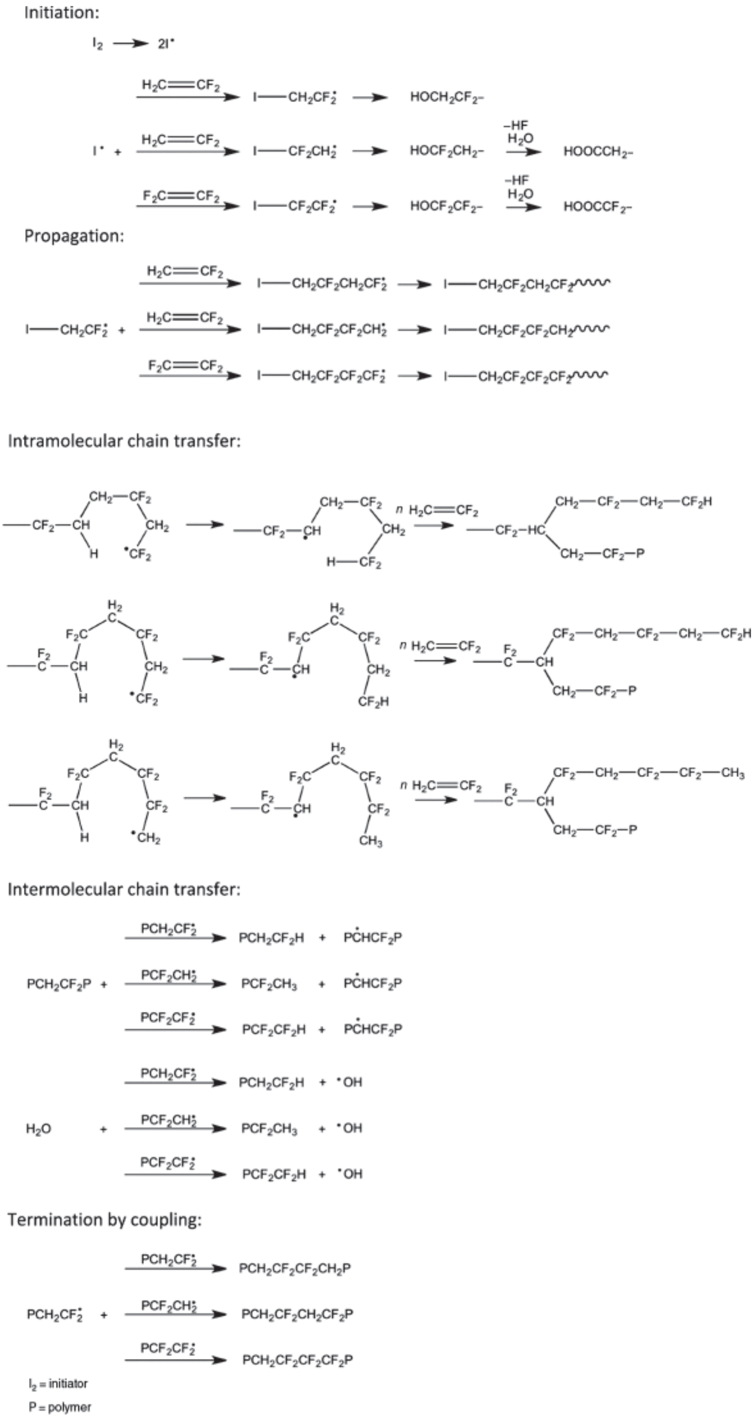
Chemical solvent	Mass/molar concentration	20 °C, 30 days
Acetic acid	10%	Resistant
Acetic acid	100%	Resistant
Formic acid	(10%)	Resistant
Hydrochloric acid		Resistant
Hydrogen peroxide	(90%)	Resistant
Nitric acid	(10%)	Resistant
Sulfuric acid	(10%)	Resistant
Sulfuric acid	(90%)	Resistant
Sulfuric acid	fuming/monohydrate	Not resistant
NaOH	0.01 M (pH = 12)	Not resistant
KOH	0.01 M (pH = 12)	Not resistant
CaOH	0.01 M (pH = 12)	Not resistant
MgOH	0.01 M (pH = 12)	Not resistant
LiOH	0.01 M (pH = 12)	Not resistant
$NH_3 \cdot H_2O$	0.01 M (pH = 12)	Not resistant

Source: Adapted from Saxena and Shukla [70].

1.3.2 Poly(Vinylidene Fluoride-*co*-Tetrafluoroethylene) (P(VDF-*co*-TFE))

Poly(vinylidene fluoride-*co*-tetrafluoroethylene) (P(VDF-*co*-TFE)) is produced by free radical copolymerization of two monomers, VDF and TFE. Scheme 1.2 shows the reaction path of the copolymerization process. The reaction path of the copolymerization process is depicted in Scheme 1.2. VDF or TFE monomers can be attacked by the initiator. In the case of VDF monomer, there are two alternative beginning points: the CH_2 end or the CF_2 end. The attack on the CF_2 carbon results in the formation of an $HOCF_2CH_2$– end, which is unstable and can undergo HF elimination and hydrolysis to yield $HOOCCH_2$– chain ends. Attack on the CH_2 carbon is favored during propagation, such that the free radical is concentrated on the CF_2 carbon. This method of chain propagation, known as normal addition, is preferred for steric and electronic reasons. In comparison, inverse addition, which forms head-to-head structures but is not common, occurs in around 1–6% of monomer additions and is affected by reaction parameters such as temperature. The precise structure of the chain and branch end will be determined by these types of monomer addition.

As indicated in Scheme 1.2, chain branches can be formed via intramolecular or intermolecular chain transfer reactions. Intramolecular chain transfer reactions, also known as backbiting reactions, can occur and result in the formation of short-chain branches. Because of the lower bond strength of the C—H bond, the



Scheme 1.2 Reaction pathways for copolymerization of VDF and TFE via free radical polymerization. Source: Reproduced from Li et al. [83]/with permission of American Chemical Society.

assault on CH_2 carbons is preferred over the attack on CF_2 carbons, as illustrated in Scheme 1.2.

P(VDF-*co*-TFE) has an excellent mechanical character and can be dissolved in common solvents, indicating the possibility of fabricating microporous membranes using the phase inversion method. The hydrophobicity results in membrane capacity, which can be exploited in the MD process. The phase inversion procedure was used to create flat-sheet microporous for MD [84]. Figure 1.2 depicts the P(VDF-*co*-TFE) membrane morphologies. A cross-section of the P(VDF-*co*-TFE) membrane from LiCl revealed a finger-like structure with a length of several microns reaching up to the membrane surface. P(VDF-*co*-TFE) membranes outperform PVDF membranes in terms of mechanical performance and hydrophobicity. In the MD process, the membrane was successfully used to the MD process and retained higher hydrophobicity than PVDF membrane.

P(VDF-*co*-TFE) has recently been used to create a range of new polymer inclusion membranes (PIMs) for Cr(VI) transport. The membranes demonstrated a high permeability coefficient and improved selectivity for Cr(VI) transport when bifunctional ionic liquid extractants were used as carriers in conjunction with an ionic liquid plasticizer [85]. They could be utilized to eliminate metal ions and contribute to environmental conservation.

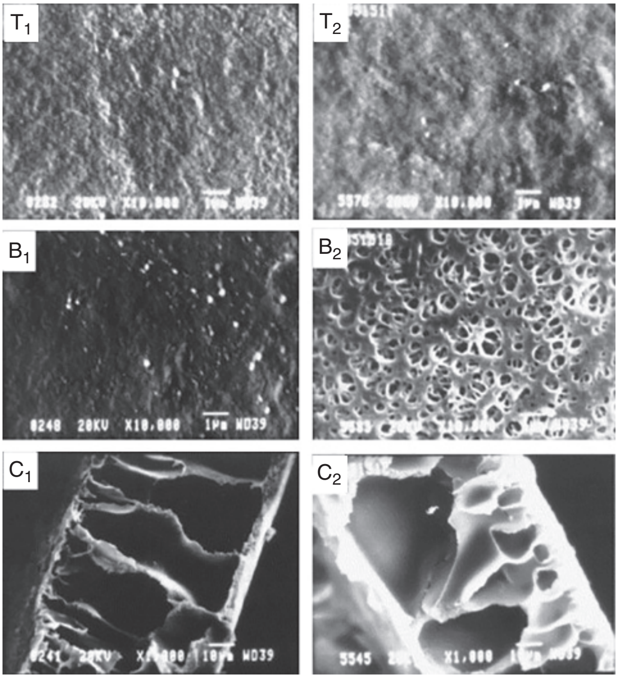
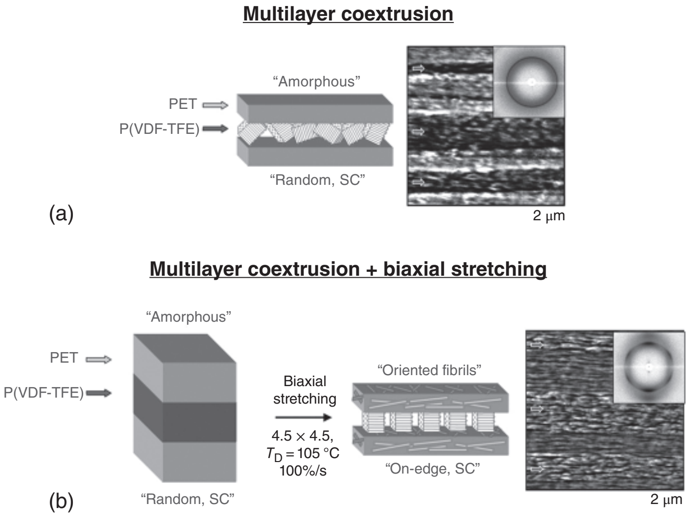


Figure 1.2 Microphotographs taken with the SEM method of a P(VDF-*co*-TFE) membrane prepared from 12 wt% polymer solutions with an additive of 4.6 wt%. (1) LiCl, (2) $LiClO_4 \cdot 3H_2O$; T: top surface, B: bottom surface, C: cross-section. Source: Feng et al. [84]/with permission of Elsevier.



Multilayer coextrusion

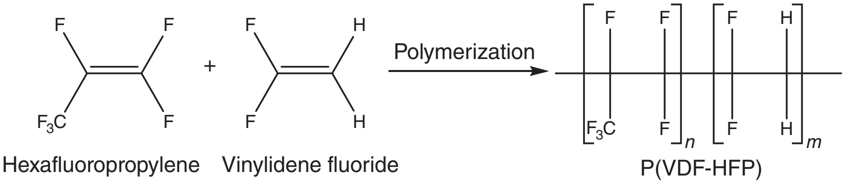
Multilayer coextrusion + biaxial stretching

Figure 1.3 Structures obtained in the PET/P(VDF-TFE) multilayer system through (i) multilayer coextrusion and (ii) biaxial stretching of thick PET/P(VDF-TFE) multilayer films at high draw ratios. The wide-angle X-ray scattering images were taken through the extrusion direction of the multi-layer films. The arrows in the atomic force microscopy images indicate the P(VDF-TFE) layers. Source: Carr et al. [86]./with permission of John Wiley & Sons.

In a different context, the utilization of P(VDF-TFE) and polyethylene terephthalate (PET) copolymers involves the combined effects of co-extrusion and biaxially oriented forced assembly of nanolayers. This process is employed to fabricate polymer multilayer films, which exhibit high energy density and can function as polymer film capacitors with significant potential, as depicted in Figure 1.3. The aforementioned films have a maximum breakdown field of 1000 kV mm^{-1} when subjected to a divergent field employing a needle/planar electrode configuration. The energy density of materials subjected to homogeneous electric fields, as measured using planar/planar electrodes, can reach up to 16 J cm^{-3}. The observed breakdown characteristics and the extent of damage are shown to be associated with the limited morphology of PET and P(VDF-TFE). The dielectric constant of the effective P(VDF-TFE) layer is increased by the solid biaxial stretching of the edge P(VDF-TFE) crystals, resulting in an enhanced dielectric contrast between the PET and P(VDF-TFE) layers. The aforementioned phenomenon results in the accrual of supplementary charges at the interface of the layers, consequently resulting in the expansion of tree routes and branches, finally augmenting breakdown and energy storage properties. Furthermore, an assessment was conducted on the hysteresis features of these materials, in addition to their energy storage and breakdown characteristics. The observed hysteresis behavior can be altered by modifying the morphology of the P(VDF-TFE) layer, which in turn allows for control over the low-field dielectric loss (or ion migration behavior) [86].

1.3.3 Poly(Vinylidene Fluoride-*co*-Hexafluoropropene) (P(VDF-*co*-HFP))

P(VDF-HFP) (chemical structure is shown in Table 1.3) is an inert fluoropolymer that has lower crystallinity and good mechanical strength than PVDF, can withstand high temperatures, and has strong hydrophobicity. P(VDF-HFP) can be produced from vinylidene fluoride (VDF) and hexafluoropropylene (HFP) by emulsion polymerization as shown in Scheme 1.3.



Scheme 1.3 Synthetic schemes of P(VDF-HFP) copolymer.

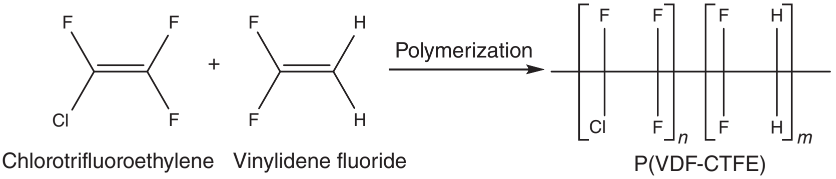
The molecular chain structure of P(VDF-HFP) is similar to that of PVDF. Relatively speaking, the crystallinity of P(VDF-HFP) is lower than that of PVDF, so its piezoelectric performance is worse than that of PVDF, but its flexibility is much better than that of PVDF. Due to the introduction of hexafluoroethylene, which increases the F content, it is also more hydrophobic than PVDF. In addition, the gelability of PVDF-HFP is better than that of PVDF, and it is easier to cast into a membrane. In addition, we can regulate the crystallization behavior and crystallinity of polymers by adjusting the ratio of VDF and HFP monomers during copolymerization. When the molar percentage of HFP is 5–15%, a flexible fluoropolymer material with low crystallinity can be obtained. If the molar percentage of HFP is further increased to more than 19%, HFP fragments with larger steric hindrance will completely obstruct the regular arrangement of VDF fragments and obtain completely amorphous fluoroelastomers [87]. In general, increasing the proportion of HFP fragments decreases the crystallinity of the polymer.

In terms of piezoelectric materials, P(VDF-HFP) is an excellent dielectric material with a high dielectric constant, good physical properties, stable chemical properties, strong solvent resistance, excellent aging resistance, and UV resistance as well as good processability. Meanwhile, P(VDF-HFP) is a semi-crystalline thermoplastic polymer, which contains various crystal phases, such as α, β, and γ crystal phases. The β crystal phase is considered to be the main contributor to the piezoelectric properties of P(VDF-HFP). The film process promotes the transition from the α crystal phase to the β crystal phase, thereby improving the dielectric properties of the material. Therefore, P(VDF-HFP) is a feasible choice for piezoelectric materials. The addition of nanoparticles and other methods can also significantly improve the content of β crystal phase inside, thereby improving piezoelectric performance.

For the lithium battery, the existing polypropylene, polyethylene (PE), and other lithium battery isolation film have the shortcomings of low porosity, low liquid absorption rate, poor thermal stability, and cannot meet the requirements of high rate charge and discharge. However, P(VDF-HFP) has become a hot material for isolation films because of its high dielectric constant, good heat resistance, chemical resistance, and electrochemical properties. In terms of adhesive application, the fluorinated adhesive prepared by chemically modified PVDF-HFP grafted with maleic anhydride can effectively bond PTFE to metal.

1.3.4 Poly(Vinylidene Fluoride-*co*-Chlorotrifluoroethylene) P(VDF-*co*-CTFE)

P(VDF-CTFE) (chemical structure is shown in Table 1.3) is another common PVDF-based copolymer, similar to P(VDF-HFP), which has high mechanical strength and good chemical and thermal stability. Its polymerization scheme is shown in Scheme 1.4.



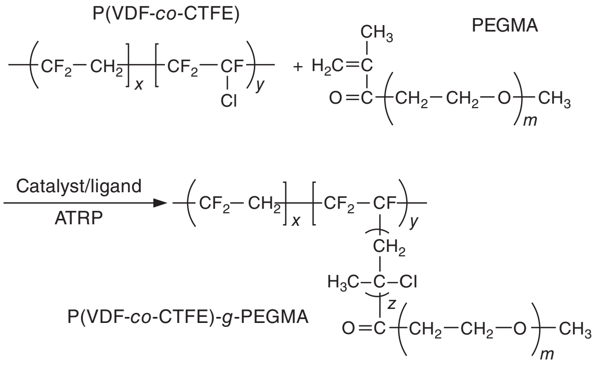
Scheme 1.4 Synthetic schemes of P(VDF-CTFE) copolymer.

The polymerization of CTFE and VDF is random copolymerization. The crystallinity of P(VDF-*co*-CTFE) copolymer is significantly lower than that of CTFE homopolymer. Its glass transition temperature is $-40\,°\mathrm{C}$ (T_g of PVDF) to $45\,°\mathrm{C}$ (T_g of PCTFE). And according to the proportion of VDF added in the polymerization process, the properties of the final copolymer are different. When the P(VDF-*co*-CTFE) copolymer containing a small amount of VDF is a semi-crystalline copolymer with a hexagonal structure, when the molar fraction of VDF is 25–70%, the prepared copolymer is an amorphous polymer with elastomer properties as the main component [65]. A VDF percentage above 70% results in a thermoplastic with a monoclinic crystal structure. These copolymers are called flexible PVDF. The type of P(VDF-*co*-CTFE) copolymer resin can be divided according to the molar ratio of CTFE to VDF in the polymer structure.

Additionally, PVDF-CTFE's CTFE segment makes it simple to graft using atom transfer radical polymerization (ATRP) without sacrificing its chemical, mechanical or thermal stability. A PVDF-CTFE-g-PSSA composite NF membrane, for instance, was created [88]. It is possible to directly modify P(VDF-*co*-CTFE) membranes by using ATRP polymerization [89] (Scheme 1.5).

1.3.5 Poly(Vinylidene Fluoride)-*g*-Poly(Styrene Sulfonic Acid) PVDF-*g*-PSSA

PVDF-g-PSSA is a graft copolymer of PVDF with high conductivity and good structural properties. It is widely used in the preparation of proton exchange membranes,



Scheme 1.5 Schematic illustration of the processes for the modification of P(VDF-*co*-CTFE) by PEGMA via ATRP. Source: Liu et al. [89]/with permission of Elsevier.

and proton exchange membranes can be used in microbial fuel cells (MFCs) and direct methanol fuel cells (DMFCs). Proton exchange membranes are an important part of MFC and DMFC. In other words, the proton exchange membrane is an indispensable heart for MFC and DMFC.

Figure 1.4 is the schematic representation of the current method of single-step reaction to prepare sulfonic acid membrane (PVDF-g-PSSA) and two-step method [90]. There are various synthesis methods for PVDF-g-PSSA. The reported synthetic

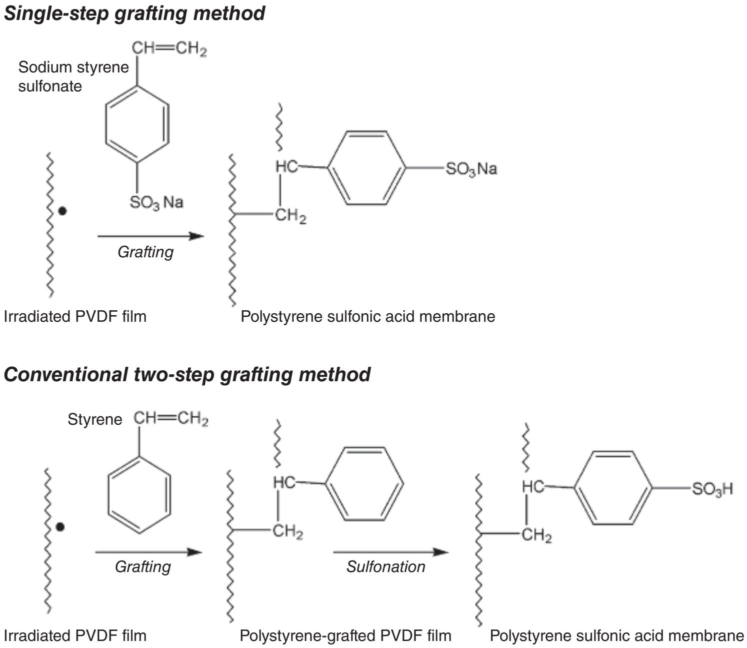


Figure 1.4 A schematic representation of the current method of single-step reaction to prepare sulfonic acid membrane (PVDF-*g*-PSSA) and two-step method. Source: Reproduced from Nasef et al. [90]/with permission of Elsevier.

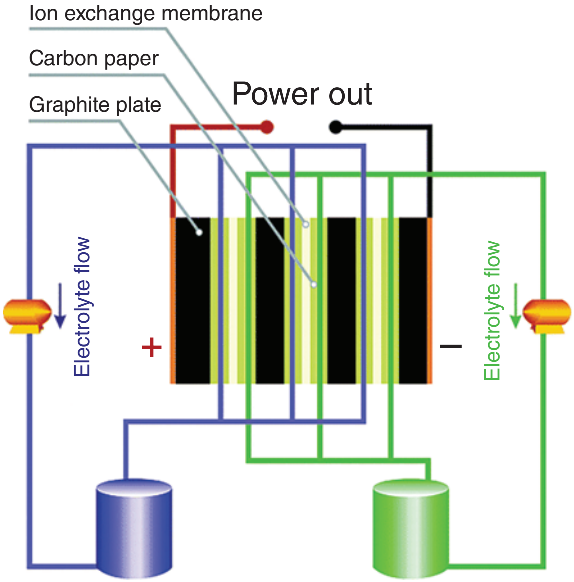


Figure 1.5 Schematic illustration of a vanadium redox flow battery. Source: Reproduced from Xuanli Luo et al. [91]./with permission of American Chemical Society.

methods include radiation grafting, which can be divided into co-irradiation and pre-irradiation, BPO-initiated grafting and ATRP grafting. The most common synthesis method is radiation grafting.

PVDF-g-PSSA is widely used in vanadium redox flow batteries (VRBs) (Schematic illustration of a VRB is shown in Figure 1.5) [91]. The PVDF-g-PSSA membrane prepared by solution grafting has a high conductivity of $3.22 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at 30 °C. ICP studies show that compared with Nafion 117, the vanadium ion permeability of PVDF-g-PSSA membrane is greatly reduced. Of all these membranes, pentavalent vanadium ions have the lowest permeability and trivalent vanadium ions the highest. With a low-cost PVDF-g-PSSA membrane, VRB outperforms Nafion 117 under the same operating conditions, and its energy efficiency reaches 75.8% at $30\,\mathrm{mA\,cm^{-2}}$. After more than 200 cycles, the VRB with PVDF-g-PSSA membrane can continue to function at a current density of $60\,\mathrm{mA\,cm^{-2}}$.

1.3.6 Poly(Vinylidene Fluoride-Trifluoroethylene) (P(VDF-TrFE))

VDF can be copolymerized with trifluoroethylene (TrFE) [92, 93] in various proportions to form random semi-crystalline thermoplastic copolymers. In contrast to PVDF, which requires mechanical stretching or poling to create net dipoles (β-phase) in the material, P(VDF-TrFE) can form a crystal structure with dipoles that permanently polarize the polymer without the need for these treatments [94]. It could be a useful starting material for tissue engineering applications, modifying cell behavior, and cell proliferation in a three-dimensional matrix [94].

P(VDF-TrFE) microporous membrane separators for LIBs can be prepared using the solvent-cast approach (chemical structure described in Table 1.3) [95], and Figure 1.6 shows porous P(VDF-TrFE) structures obtained by solvent evaporation

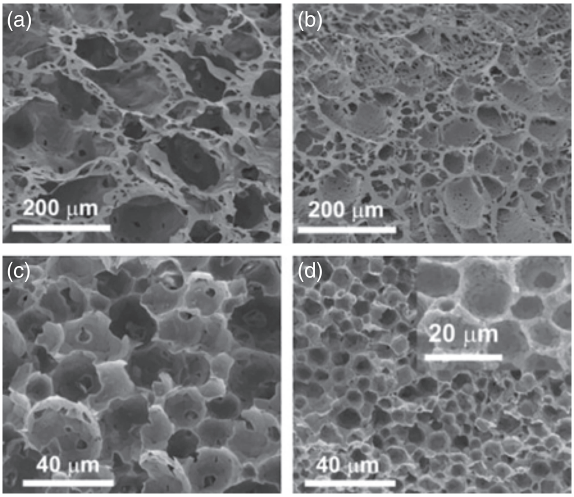


Figure 1.6 SEM microphotographs of the surface and cross-section (a, b) of 5/95 P(VDF-TrFE)/DMF and (c, d) 20/80 P(VDF-TrFE)/DMF samples obtained by solvent evaporation at room temperature.
Source: California et al. [96]/with permission of Elsevier.

at room temperature [96]. Additionally, electrospinning can produce P(VDF-TrFE) copolymer membranes with low dielectric constant and good flexibility [97].

In a tissue engineering application known as directed tissue regeneration, a membrane is crucial to isolating periodontal abnormalities of the gingival connective and epithelial tissues and achieving the regeneration of bone, periodontal ligament, and cementum from their own cells. An excellent material should have acceptable electromechanical capabilities as well as biocompatibility to promote periodontal tissue regeneration. *In vitro* biocompatibility of a composite membrane of poly(vinylidene-trifluoroethylene)/barium titanate (P(VDF-TrFE)/BT was superior to that of ordinary expanded PTFE (ePTFE) [98].

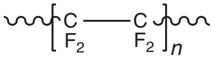
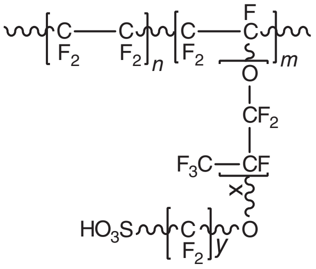
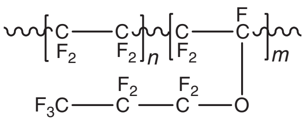
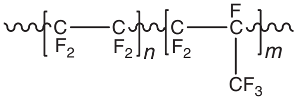
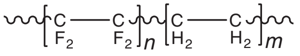
1.4 PTFE and Its Copolymer

Porous polytetrafluoroethylene (PTFE) membranes exhibit chemical inertness and have found extensive applications in many membrane separation processes, such as MD, oil–water separation, and gas–solid separation. The prevalent types of Teflon membranes are plates and hollow fibers. PTFE membranes are primarily manufactured using drawing, spinning, and pore-forming techniques. To enhance the performance of PTFE membranes and achieve enhanced results in the target application, several modification techniques were employed. These techniques included wet chemistry, plasma treatment, radiation exposure, atomic layer deposition, and high-temperature melting. Table 1.9 presents the chemical structures of homopolymeric and copolymer PTFE.

1.4.1 Homopolymeric PTFE

PTFE (chemical structure is shown in Table 1.9) is a perfluoropolymer material in which all hydrogen atoms in PE are replaced with fluorine atoms. The structural

Table 1.9 Chemical structures of homopolymeric and copolymer PTFE.

Polymer		Chemical structure
Poly(tetrafluoroethylene) homopolymer	PTFE	
PTFE copolymer	Perfluorosulfonic acid (PFSA)	
	Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA)	
	Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)	
	Poly(ethylene-*alt*-tetrafluoroethylene) (ETFE)	

formula is: $-[CF_2-CF_2]_n-$. PTFE is a white, hydrophobic solid whose properties depend strongly on its molecular weight. PTFE surface free energy is very low and almost does not adhere to any substance, due to its strong C—C and C—F bonds and carbon skeleton, has excellent high-temperature resistance, chemical resistance, environmental resistance, electrical insulation, oxidation resistance, strong hydrophobicity, and high fracture toughness, which is protected by a uniform spiral sheath formed by the electron cloud of fluorine atoms [28]. Table 1.10 lists the salient properties of PTFE.

These characteristics make it suitable for a variety of applications, such as exhaust-gas treatment [100], MD [101, 102], osmotic distillation (OD) [103, 104], and oil–water separation [105].

Specific membrane qualities are required depending on the application. Different membrane applications can benefit from a custom-made PTFE membrane. The most essential properties of porous membranes in gas–solid separation are solid phase rejection and gas permeability. A high pore size of about 5 μm, a narrow pore size distribution, and a thickness of less than 50 μm are necessary for effective membrane separation performance. Furthermore, for gas–solid separation, PTFE

Table 1.10 Physical and chemical properties of PTFE.

Property (standard)	PTFE	Criterion
as-polymerized PTFE	335	
Melting point (°C)		D3418
Glass transition (°C)	−103	—
Decomposition point (°C)	590	—
Phase transition (°C)	19	—
Processed PTFE		
Theoretical density/g cm^{-3} (at 23 °C)	2.16	ASTM D4895
Tensile strength/MPa (at 23 °C)	31	ASTM D4894
Compressive strength/MPa (at 23 °C)	4.4	ASTM D695
Hardness/shore D	55	ASTM D2240

Source: Reproduced from Puts et al. [99]/with permission of American Chemical Society.

membranes with high porosity and specific surface area are required [106]. PTFE nanofibers are usually prepared by biaxial stretching and electrospinning to achieve a higher specific surface area, allowing for a larger contact area between particles and fibers while maintaining adequate particle retention and breathability. This is done to meet the requirements of the gas–solid separation process. MD is a thermally driven technique for separating molecules across hydrophobic membranes by taking advantage of the temperature differential. The mass transfer coefficient and heat transfer coefficient are the two main factors that determine how effective the MD process is [107]. The structure and chemical characteristics of the membrane influence mass and heat transfer optimization in MD. Because of its low thermal conductivity and hydrophobicity, PTFE membrane is employed in the MD process to minimize heat loss. Furthermore, PTFE has a pore structure suitable for MD and a low inlet pressure. The pore diameters of PTFE membranes employed in MD are usually around 0.5 μm. Additionally, the membrane in the oil–water separation process needs to be either oleophobic (also oleophilic and hydrophobic) or hydrophobic (also oleophilic and hydrophobic) [108–110], depending on the water–oil supply (oil-in-water emulsion or water-in-oil emulsion).

The biaxial stretching method used to prepare PTFE membranes was originally developed by Stein [111] and has been used for several years in the preparation of porous PTFE membranes. In the following decades, the biaxial stretching method was adopted and modified by many researchers. Bukchon, etc. [112] prepared porous PTFE membrane by mechanical operation, and the formation mechanism of the porous structure in PTFE was proposed. The fibril is formed in the crack by tensile action and oriented in the direction of tensile action. The spatial unit size of the periodic structure depends on the amount of PTFE, the average molecular weight, and the stretching conditions. The schematic of the various stages of

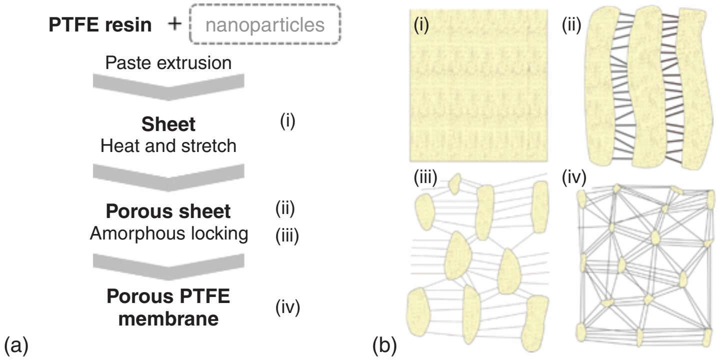


Figure 1.7 (a) Preparation process of porous PTFE membrane [113] and (b) schematic of PTFE stretching process in different stages: (i) raw PTFE sheet, (ii) early-stage stretching or strip crack process, (iii) node-forming stage or uniaxial tension process, and (iv) uniform node connection or biaxial tension process. Source: Wikol et al. / W. L. Gore & Associates, Inc.

the PTFE stretching process and the preparation procedure for the porous PTFE membrane [113] are shown in Figure 1.7.

Due to its perfect fiber shape and great productivity, electrospinning has garnered a lot of attention as a process for creating nano-/submicron fibers. After the polymer fluid is exposed to a high-voltage electric field via a micro-nozzle, it hardens into a fiber membrane. Since PTFE has a high viscoelasticity, spinning molten PTFE into fibrils is challenging [114]. Consequently, in order to facilitate the electrospinning process of creating PTFE membranes, additives are added to the PTFE emulsion. Xiong et al. blended various quantities of poly(vinylalcohol) (PVA) into a PTFE emulsion in order to electrospun a porous PTFE membrane [115]. The PVA mass ratio and emulsion concentration both have significant impacts on the membrane shape. Electrospun composite fibers with varying PVA to PTFE mass ratios are shown in Figure 1.8 as scanning electron microscopy (SEM) images: (i) 10 : 90, (ii) 20 : 80, (iii) 30 : 70, (iv) 40 : 60, and (v) 50 : 50. The surfactant tends to be more stable at high emulsion concentrations, which causes the fiber's diameter to increase. The fibers are comparatively uniform when the PVA mass ratio exceeds 3 : 7.

1.4.2 Perfluorosulfonic Acid-PFSA

The structure of perfluorosulfonic acid (PFSA) polymers is divided into two parts (seen in Table 1.9): one is a hydrophobic PTFE backbone and the other is a branched chain with a hydrophilic ion exchange group (sulfonic acid group) at the end. In the PFSA structure, the sulfonic acid group ($–SO_3^-$) is fixed on the polymer molecular chain through a covalent bond, and the sulfonic acid group formed by combining with H^+ can dissociate in a protic solvent (H_2O) and can move freely.

Generally, the proton conductivity of such proton exchange membranes under high humidity conditions can reach $0.1\,S\,cm^{-1}$ or more. The sulfonic acid group in

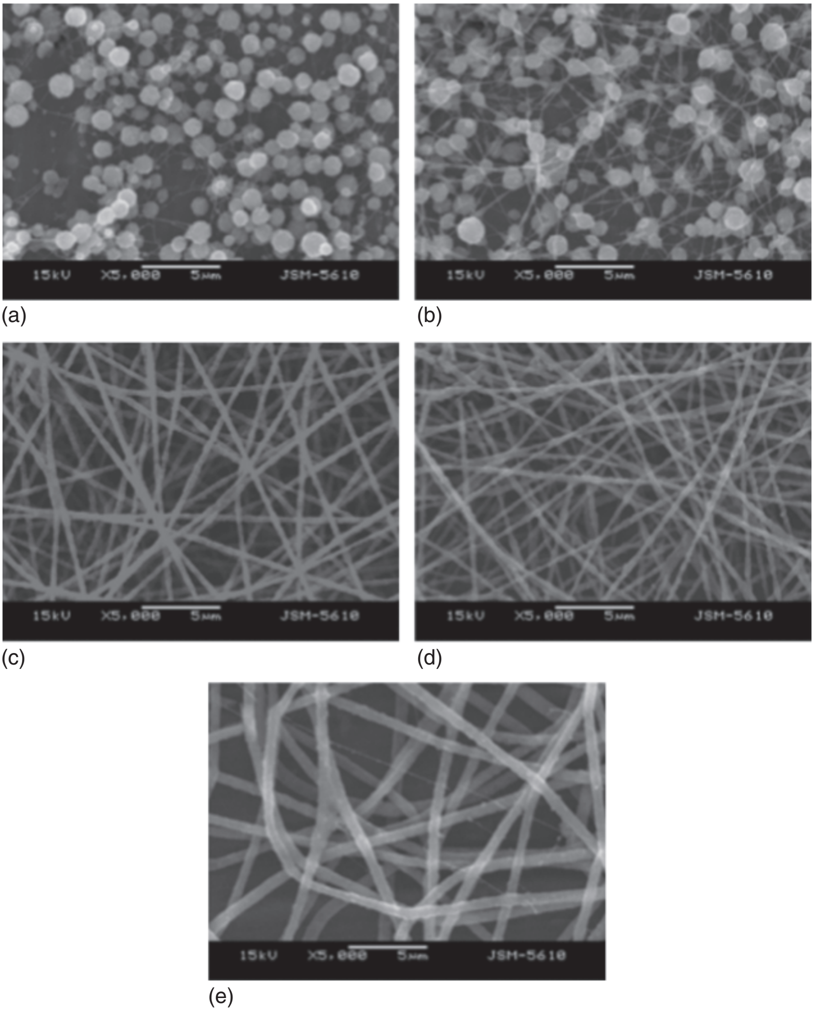


Figure 1.8 Scanning-electron-microscopy (SEM) images of electrospun composite fibers with different mass ratios of PVA to PTFE: (a) 10 : 90, (b) 20 : 80, (c) 30 : 70, (d) 40 : 60, and (e) 50 : 50. Source: Xiong et al. [115]/with permission of Cambridge University Press.

the PFSA resin is connected with the perfluoroalkyl group, and the fluorine atom has a strong electron-attracting property, which significantly improves the acidity of the sulfonic acid group. Trifluoromethanesulfonic acid (CF_3SO_3H) is 1000 times stronger than sulfuric acid, so it is called super acid. This property makes the PFSA resin have better proton conductivity. On the other hand, the molecular chain backbone of PFSA resin uses fluorocarbon chains while the C—F bond has a high bond energy ($4.85 \times 10^5\ \mathrm{J\,mol^{-1}}$) and a large fluorine atom radius (0.64×10^{-10} m). A protective barrier can be formed near the C—C bond. So, the tetrafluoroethylene segment of the PFSA resin has good hydrophobicity, and the polymer membrane has high chemical stability and strong mechanical strength [116].

PFSAs have found widespread application as solid electrolytes in electrochemical technologies, notably as proton-exchange membranes (PEMs) in polymer-electrolyte fuel cells (PEFCs) and as sodium-ion conductors in the chlor-alkali industry. These particular applications have been pivotal in driving research efforts focused on PFSAs since the 1970s when DuPont successfully developed the first commercially available PFSA ionomer known as Nafion [117]. The Nafion membrane, which is a PFSA-based membrane, is widely utilized in fuel cell applications and is readily accessible in the commercial market. Despite extensive research spanning several decades, Nafion continues to be the predominant solid electrolyte utilized in a wide range of energy storage and conversion devices. This is primarily attributed to its inherent electrochemical properties, which enable efficient ion and solvent transportation within chemically inert and mechanically resilient substrates. Consequently, Nafion effectively restricts the movement of electrons as well as reactants and products. The lifespan of PFSA membranes varies significantly, spanning from several thousand to tens of thousands of hours. This variability is influenced by various factors, including the specific end groups of the resin, the membrane's inherent features, and the operating circumstances during fuel cell testing.

Nafion is a random copolymer composed of an electrically neutral semicrystalline polymer backbone (PTFE) and a randomly tethered side-chain (polysulfonyl fluoride vinyl ether) with a pendant ionic group, SO_3^-, that is associated with a specific counterion (e.g., $-SO_3^- + H^+ \rightarrow -SO_3H$). The inherent disparity between the covalently bound pendant group and backbone leads to spontaneous phase separation, which is further intensified by solvation (when water or solvent molecules are introduced). The distinctive capability of transporting ions and solvents is attributed to the phase separation form of PFSA. PFSA, in essence, can be described as a flexible polymer that is influenced by its structure through electrostatic contact transmission and mechanical functions. Nonetheless, the morphology of the system is contingent upon a multitude of interactions and equilibriums between the mechanical energy linked to the hydrophobic backbone's deformation and the chemical/entropic energy connected to the hydration of hydrophilic ionic groups and their respective side chains. The equilibrium of this balance is regulated and influenced by a diverse array of environmental and material characteristics that dictate the relationship between the structure and properties of PFSAs, as outlined in Figure 1.9.

1.4.3 Poly(Tetrafluoroethylene-*co*-Perfluoropropyl Vinylether) (PFA)

Similar to other fluorocarbons like PTFE and fluorinated ethylene propylene, PFA has a similar coefficient of friction, dielectric properties, and chemical resistance. Its wear resistance, shore hardness, and mechanical strength are better than PTFE and equivalent to PTFE at temperatures over 150 °C. Similar to PTFE, PFA exhibits good heat resistance between −200 and 260 °C, but it also has a higher creep resistance.

PFA, whose chemical structure is displayed in Table 1.9, has a strong mix of physicochemical, structural, and thermal properties, making it a viable material for

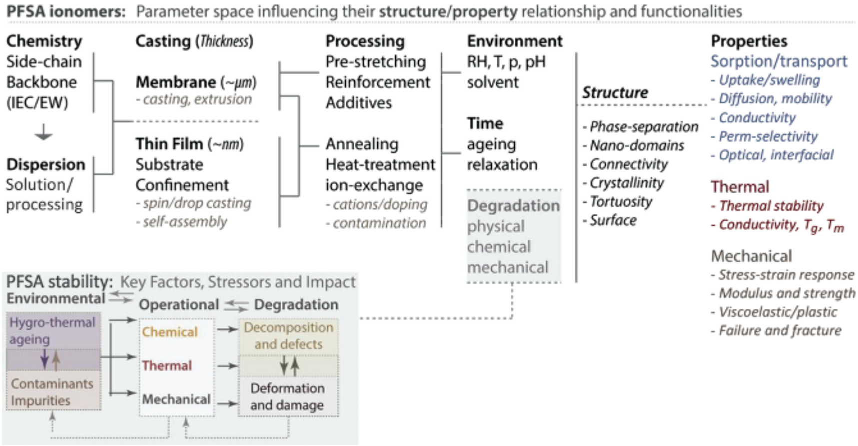
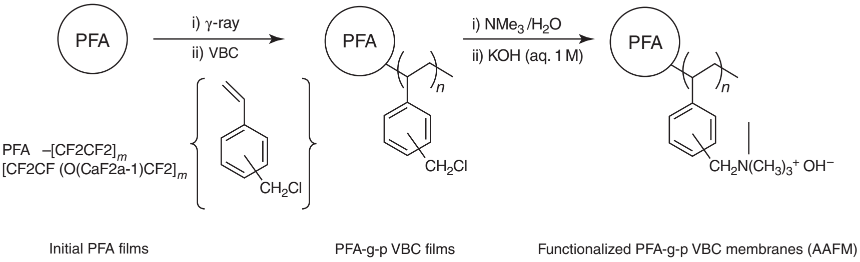


Figure 1.9 Material, processing, and environmental parameter space controlling the structure/property relationship of PFSA ionomers and their stability and degradation. Source: Reproduced from Kusoglu and Weber [116]/with permission of American Chemical Society/CC by 4.0.

fuel cell membranes [118]. After reacting with various monomers, PFA membrane has high radiation resistance, stable free radicals, and a high grafting rate. Therefore, high irradiation doses can be applied to membrane preparation without affecting its inherent mechanical properties [119].

To construct an alkaline anion-exchange membrane (AAEM) (Scheme 1.6), vinylbenzyl chloride (VBC), a versatile monomer, can be copolymerized onto pre-irradiated PFA membrane, followed by quaternary-ammonium-functionalization and hydroxylation [120]. With a maximum power density of 16 mW cm^{-2} and a maximum conductivity of 0.05 S cm^{-1} at 60 °C, this type of AAEM shows great promise for usage in direct alcohol AAEM fuel cells (DA$_3$EMFC).



Scheme 1.6 Preparation process of irradiation grafted membranes. Source: Reproduced from Liu et al. [120]/with permission of Elsevier.

1.4.4 Tetrafluoroethylene Hexafluoropropylene Copolymer-FEP

FEP (chemical structure is shown in Table 1.9) is a random copolymer formed by the polymerization of tetrafluoroethylene and hexafluoropropylene. Its molecular structure is equivalent to the structure formed by the substitution of an

F atom on a PTFE molecular chain with a $-CF_3$ group. Like PTFE, FEP also has a perfluorinated molecular structure with excellent chemical resistance, thermal stability, mechanical properties, electrical insulation properties and strong hydrophobicity. In addition, compared with the defect of poor processing performance of PTFE, the presence of the side group $-CF_3$ makes the FEP molecular chain more flexible, the glass transition temperature and melting point of FEP are reduced, and the melt viscosity is reduced, and the processability is significantly improved [121]. These characteristics make it an excellent membrane-forming polymer material and have attracted widespread attention from researchers worldwide.

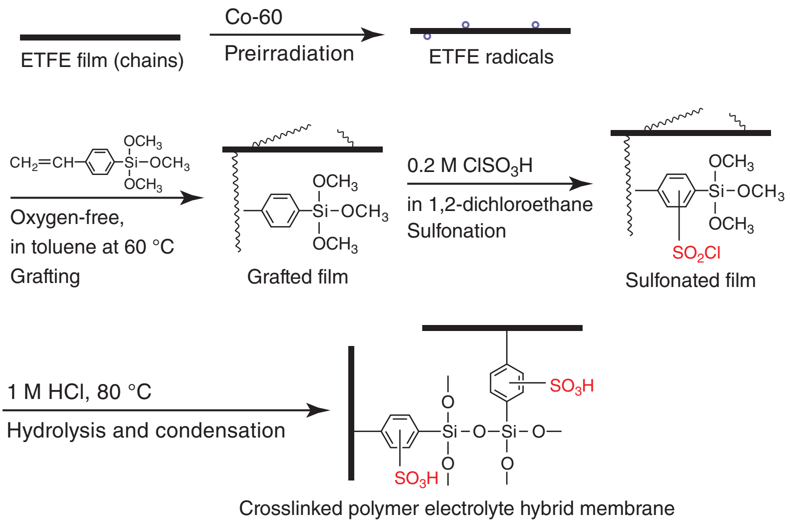
The extremely low surface free energy restricts the development of FEP separation membranes. At present, researchers mostly study the modification of FEP to increase its surface free energy and surface activity to expand the application field of FEP separation membranes. In recent years, researchers have contributed a lot to the preparation of FEP separation membranes. Huang etc. used dioctyl phthalate (DOP) as a plasticizer and composite inorganic particles as a pore-forming agent, and adopted melt spinning FEP hollow fiber microporous membrane was prepared by the stretching method. FEP/activated carbon/inorganic particle hybrid microporous membrane was prepared by hot pressing using composite inorganic particles as a pore-forming agent and activated carbon as an additive, etc. Using FEP dispersion emulsion as the membrane-forming polymer and PVA as the spinning carrier, FEP ultrafine fiber membranes were prepared by electrostatic spinning and suitable sintering process.

1.4.5 Ethylene Tetrafluoroethylene Copolymer-ETFE

A “head-to-tail, tail-to-tail” isomeric form of PVDF can be produced by combining partially fluorinated ethylene tetrafluoroethylene copolymer (ETFE) membrane with hydrocarbon and fluorocarbon structures (chemical structure is shown in Table 1.9). These membranes offer excellent mechanical qualities and strong radiation resistance. High radiation resistance enables it to be pre-irradiated with high gamma rays in subsequent grafts, and good mechanical properties enable it to exist in fuel cell stacks for a long time. Scheme 1.7 illustrates the use of ETFE to prepare a novel cross-linked polymer electrolyte hybrid membrane [119]. Grafted membranes based on ETFE have the benefit of low cost, but they can also produce high thermal stability and proton conductivity through cross-linking [122, 123].

1.5 ECTFE and Other Fluoropolymers

ECTFE is a fluorine-containing polymer formed by alternating polymerization of ethylene monomer and trichloroethylene monomer at 1 : 1. Melting point is 464 °F (242 °C), density is $1.68\,\mathrm{g\,cm^{-3}}$. Its molecular structure formula is shown in Table 1.11. In 1946, DuPont first synthesized ECTFE. ECTFE was commercialized for the first time by DuPont in 1974, which was known as Halar®. In 1986, Applied Chemical Organization transferred ECTFE products and technologies to Ausimont USA Inc. In 2001, Ausimont was purchased by the Solvay Group of Belgium.

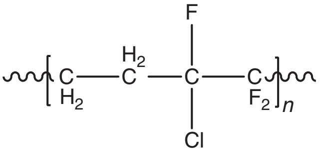
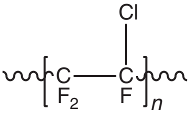
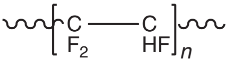
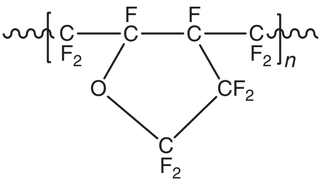
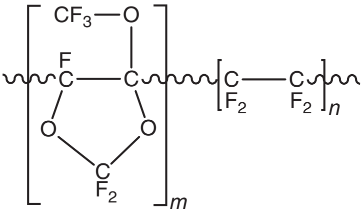


Scheme 1.7 Scheme for the preparation of a new cross-linked polymer electrolyte hybrid membrane using ETFE. Source: Reproduced from Chen et al. [119]/with permission of Elsevier.

As an alternating copolymer of ethylene and chlorotrifluoroethylene, it has a unique chemical structure, where the content of fluorine is 39.5%, and it has three carbon—fluorine bonds and one carbon—chlorine bond [124]. Because of the low polarizability and strong electronegativity of fluorine atom, C—F bond has a large bond energy (485 kJ mol^{-1}). Therefore, ECTFE with a higher fluorine content exhibits high heat resistance, chemical corrosion resistance, durability, and weather resistance, especially for many solvents, hydrocarbons, inactivity of various acids and bases, low capacitance, low flammability, low refractive index, low surface energy (neither oil-wet nor water-wet), and hygroabsorbency [28, 125, 126]. ECTFE is also more resistant to water vapor, hydrogen chloride, and chlorine gas than regular fluoropolymers – of which chlorine permeability is the best – because it contains chlorine atoms. For these reasons, it is frequently employed in severe conditions that are exposed to chlorine. Long-term exposure to UV radiation does not significantly alter the characteristics of ECTFE, making it suitable for usage in the construction sector in products like UV-resistant paint. ECTFE is also very resistant to solvents; at temperatures below 120 °C, no solvent can harm it [127]. ECTFE is therefore better than other fluorinated materials in terms of its ability to withstand high temperatures, strong acids and alkalis, and chemical resistance. As a result, it is the perfect material for creating high-performance microporous membranes.

At present, due to its good toughness and high strength, ECTFE has better weather resistance and chemical corrosion resistance than PTFE and PVDF [128]. It is frequently applied as a coating to prevent corrosion and safeguard pipelines [129, 130]. For instance, it is applied on stainless steel exhaust pipes as a coating to handle different corrosive airflows in a range of industrial settings,

Table 1.11 Chemical structures of ECTFE and other fluoropolymers.

Polymer		Chemical structure
ECTFE		
Other fluoropolymers	PCTFE	
	PVF	
	Cytop	
	Hyflon AD	

including clean rooms. When carrying hydrofluoric acid that contains unique corrosive chemicals, the adhesion and hardness of the ECTFE-coated induced draft fan impeller are twice that of the PTFE coating. Furthermore, ECTFE can be applied on the surface of solar photovoltaic modules as an anti-corrosion film resin. ECTFE resins have proven to offer outstanding chemical, weather, and corrosion resistance in various applications. However, the application of ECTFE as a porous membrane in the field of water treatment is less studied. Table 1.11 lists chemical structures of ECTFE and other fluoropolymers.

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