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Fluoropolymers for Membranes

1.1 Membrane Technology

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 NaSO₄ from natural salt mines, to purify NaCl, and to concentrate Na₂CO₃ [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

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- <i>co</i> -TFE)	MF/UF, MD
	P(VDF- <i>co</i> -HFP)	MF/UF, MD, PV, fuel cell, lithium-ion battery
	P(VDF- <i>co</i> -CTFE)	MF/UF, NF, MD, PV, fuel cell
	PVDF- <i>g</i> -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- <i>co</i> -perfluoropropyl vinyl ether) (PFA)	Fuel cell
	Poly(tetrafluoroethylene- <i>co</i> -hexafluoropropylene) (FEP)	MD, fuel cell
	Poly(ethylene- <i>alt</i> -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

Source: Reproduced from Cui et al. [28]/with permission of Elsevier.

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(vinylidene fluoride-*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.


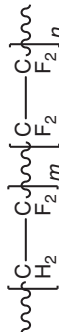
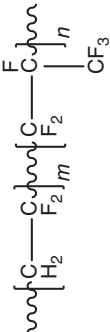
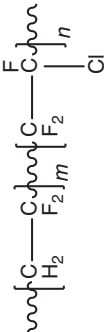
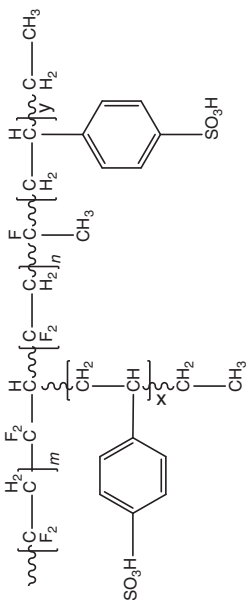
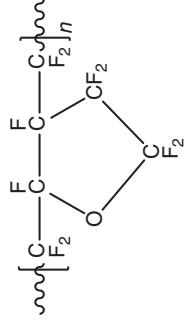
Polymer	Chemical structure
PVDF homopolymer	
P(VDF-co-TFE)	
P(VDF-co-HFP)	
P(VDF-co-CTFE)	
PVDF-g-PSSA	

Table 1.3 (Continued)

Polymer	Chemical structure
Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP)	
Poly(ethylene- <i>alt</i> -tetrafluoroethylene) (ETFE)	
ECTFE	
Other fluoropolymers	
PVF	

Cytop



Hyflon AD

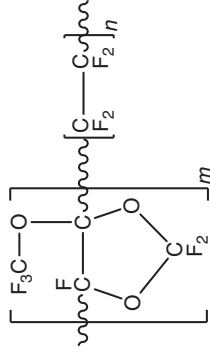


Table 1.4 Critical surface tension membranes of major polymeric membrane materials.

Polymer	Critical surface tension (dynes/cm)
Polyvinylidene fluoride (PVDF)	25–28.5
Polyfluoroethylene (PFE)	22
Polytetrafluoroethylene (PTFE)	18.5
Fluorinated ethylene propylene (FEP)	16
Ethyltetrafluoroethylene (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 $-\text{CH}_2-\text{CF}_2-$. 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 TTTGTTG' 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).

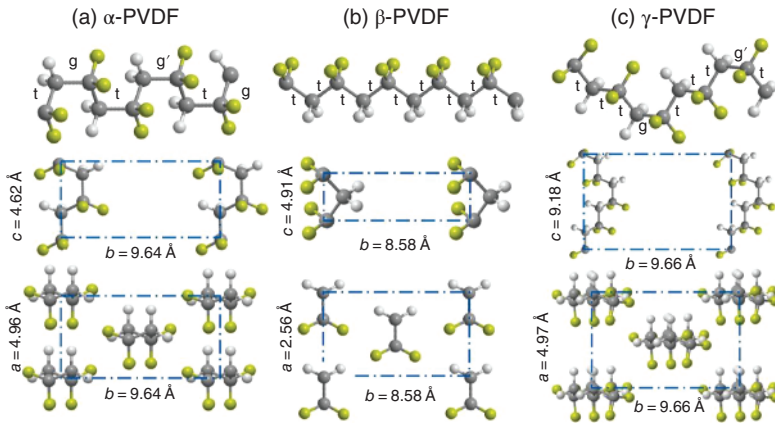


Figure 1.1 Schematic representation of the chain conformation for the α , β , and γ phases of PVDF. The gray, white, and yellow spheres represent carbon, hydrogen, and fluorine atoms, respectively. Source: Reproduced from Wang et al. [64]/with permission of Elsevier.

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	$a = 4.96 \text{ \AA}$ $b = 9.64 \text{ \AA}$ $c = 4.62 \text{ \AA}$	$a = 8.58 \text{ \AA}$ $b = 4.91 \text{ \AA}$ $c = 2.56 \text{ \AA}$	$a = 4.97 \text{ \AA}$ $b = 9.66 \text{ \AA}$ $c = 9.18 \text{ \AA}$	$a = 4.96 \text{ \AA}$ $b = 9.64 \text{ \AA}$ $c = 4.62 \text{ \AA}$	$a = 4.97 \text{ \AA}$ $b = 9.66 \text{ \AA}$ $c = 9.18 \text{ \AA}$
Number of chains per lattice	2	2	2	—	—
Molecular conformation	TGTG'	TTT	TTTGTTG'	TGTG'	TTTGTTG'
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 2 θ 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).

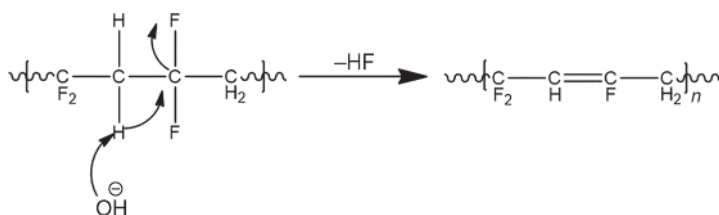
PVDF has been recognized as one of the most excellent chemical-resistant materials [71]. Although PVDF has strong corrosion resistance to chemicals such as halogens, oxidants, and inorganic acids, as well as aliphatic, aromatic, and chlorinated solvents, it is still incompatible with strong bases and 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	$\sim 10^{-4}$	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 ·H ₂ O	0.01 M (pH = 12)	Not resistant

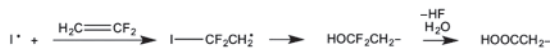
Source: Adapted from Saxena and Shukla [70].

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

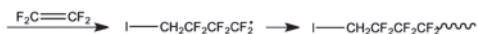
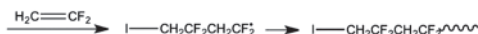
Poly(vinylidene fluoride-*co*-tetrafluoroethylene) (P(VDF-*co*-TFE)) is produced by free radical copolymerization of two monomers, VDF and TFE. Scheme 1.2 shows the reaction path of the copolymerization process. The reaction path of the copolymerization process is depicted in Scheme 1.2. VDF or TFE monomers can be attacked by the initiator. In the case of VDF monomer, there are two alternative beginning points: the CH₂ end or the CF₂ end. The attack on the CF₂ carbon results in the formation of an HO CF₂CH₂- end, which is unstable and can undergo HF elimination and hydrolysis to yield HOOCCH₂- chain ends. Attack on the CH₂ carbon is favored during propagation, such that the free radical is concentrated on the CF₂ 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

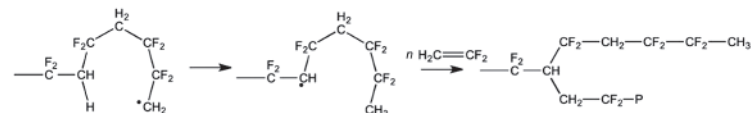
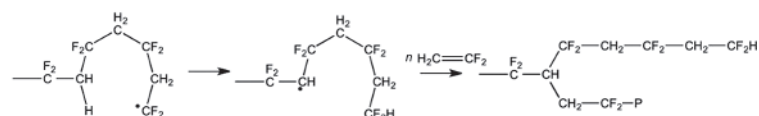
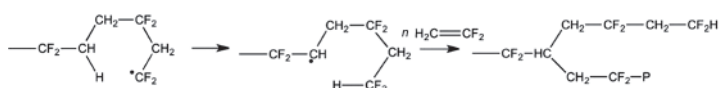
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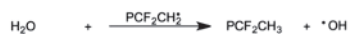
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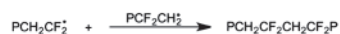
Intramolecular chain transfer:



Intermolecular chain transfer:



Termination by coupling:

I₂ = initiator

P = polymer

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.

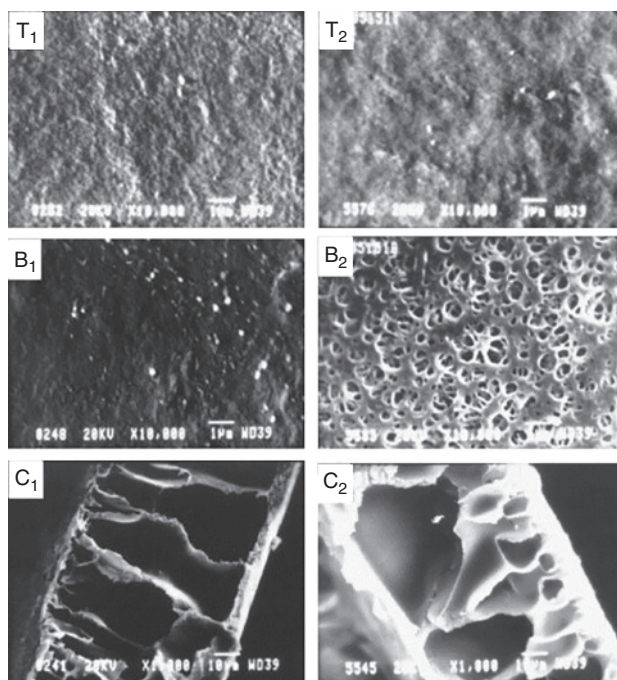


Figure 1.2 Microphotographs taken with the SEM method of a P(VDF-*co*-TFE) membrane prepared from 12 wt% polymer solutions with an additive of 4.6 wt%. (1) LiCl, (2) $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$; T: top surface, B: bottom surface, C: cross-section. Source: Feng et al. [84]/with permission of Elsevier.

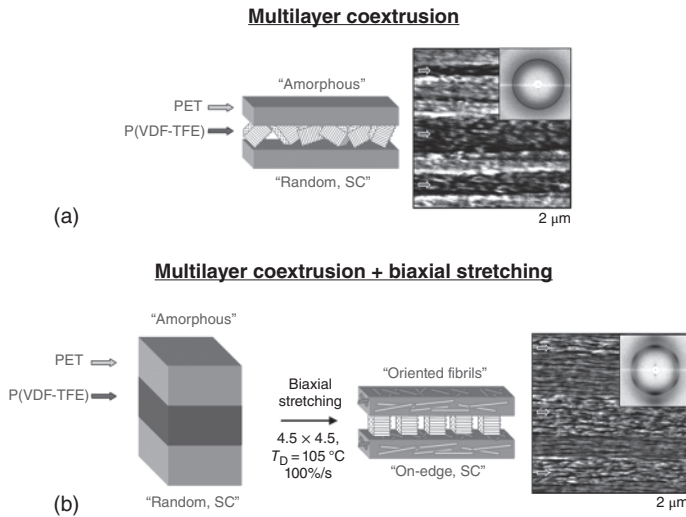
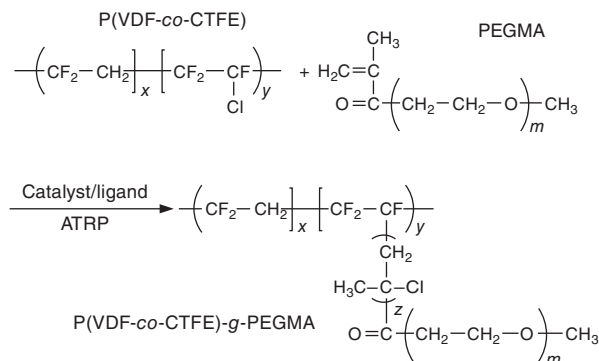


Figure 1.3 Structures obtained in the PET/P(VDF-TFE) multilayer system through (i) multilayer coextrusion and (ii) biaxial stretching of thick PET/P(VDF-TFE) multilayer films at high draw ratios. The wide-angle X-ray scattering images were taken through the extrusion direction of the multi-layer films. 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].

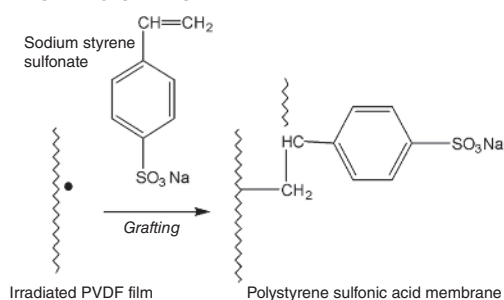


Scheme 1.5 Schematic illustration of the processes for the modification of P(VDF-co-CTFE) by PEGMA via ATRP. Source: Liu et al. [89]/with permission of Elsevier.

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

Single-step grafting method



Conventional two-step grafting method

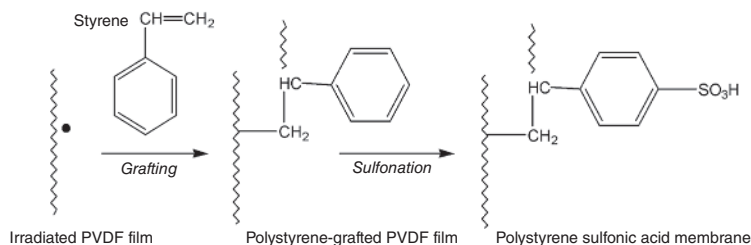


Figure 1.4 A schematic representation of the current method of single-step reaction to prepare sulfonic acid membrane (PVDF-g-PSSA) and two-step method. Source: Reproduced from Nasef et al. [90]/with permission of Elsevier.