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From Vinylidene Fluoride (VDF) to the Applications of VDF-Containing Polymers and Copolymers: Recent Developments and Future Trends[†]

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[†] Dedicated to Professor Bernard Boutevin in honor of his 60th birthday.

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1. Introduction

Fluorinated polymers$^{1-5}$ are attractive niche macromolecules because of their versatility (they range from thermoplastics, elastomers, and plastomers to thermoplastic elastomers, and they can be semicrystalline or totally amorphous). In addition, they display a unique combination of relevant properties (mainly linked to the low polarizability and the strong electronegativity of the fluorine atom, to its small van der Waals radius (1.32 Å), and to the strong C−F bond (485 $\mathrm{kJ \cdot mol^{-1}}$). Hence, fluoroplastics with high fluorine contents exhibit high thermal, chemical, aging, and weather resistance, excellent inertness to solvents, to hydrocarbons, to acids, and to alkalies, low surface energy (oil and water repellency), low dielectric constants, low flammability, low refractive index, and moisture absorption. Furthermore, the presence of the strong C−F bond has a crucial impact on the high resistance to oxidation and to hydrolytic stability.

Hence, these specialty polymers$^{1-5}$ have found many applications: building industries (paints and coatings resistant to UV and graffiti), petrochemical and automotive industries, aerospace and aeronautics (use of elastomers as seals, gaskets, and O-rings for use in extreme temperatures for tanks of liquid hydrogen or hydrazine in boosters of space shuttles), chemical engineering (high performance membranes), optics (core and cladding of optical fibers), textile treatment, stone (especially coatings for old monuments), and microelectronics. Despite their high price (mainly linked to the cost of purifying the gaseous monomers, to unusual processes of polymerization, and to the small scale of production), these polymers have found major developments in modern technologies.

However, fluoroplastics have various drawbacks: the homopolymers are often crystalline, hence inducing a poor solubility in common organic solvents, and are not easily cured or cross-linked. This is why the generation of fluorinated copolymers$^{4-8}$ (composed of a mixture of comonomers that inserts (bulky) side groups that produce disorder in the macromolecule, thus reducing or getting rid of the high crystallinity of the homopolymer) has extensively grown without possessing the disadvantages of homopolymers mentioned above.

2. Synthesis and Homopolymerization of Vinylidene Fluoride

2.1. Introduction

Because of its excellent combination of properties and processability, PVDF [24937-79-9] has reached the largest volume of fluoropolymers after PTFE. Homopolymers derived from VDF (or VF_2) [75-38-7] are semicrystalline long chain macromolecules that contain 59.4 wt % fluorine and 3 wt % hydrogen. The high level of intrinsic crystallinity (ca. 60%) confers stiffness and toughness and creep resistant properties rending them suitable thermoplastics.

However, copolymers of VDF containing various comonomers can fall into three categories: (i) when the amount of comonomers in the copolymer is small compared with that of VDF, the resulting materials are also thermoplastic with a lower crystallinity than that of PVDF;^{9} (ii) for a higher content of comonomer, thermoplastic elastomers can be obtained;$^{6-8}$ (iii) for even higher percentage(s) of comonomer(s), the produced copolymers are elastomeric and amorphous with low intermolecular forces.

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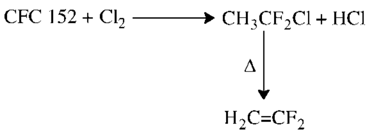
Although PVDF has found interesting high tech applications (chemical process equipment, electrical equipment and electronics, specialty and energy-related applications, as mentioned in sections 3.2, 3.3, and 5), three major disadvantages are noted: (i) high melting temperatures, which generate energetic costs to enable the processing of this polymer; (ii) poor solubility in common organic solvents (PVDF is soluble in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide, and *N*-methyl pyrrolidinone (NMP)); (iii) difficult curing of this material.^{9,10}

Hence, fluorinated copolymers based on VDF have drawn more interest.^{7,8,11} The first copolymers of VDF were patented as early as 1948,^{12} produced in aqueous medium initiated by peroxides at 20−150 °C and under pressure (even above 300 atm), then followed by various generations of more and more VDF-based copolymers. Before describing PVDF and VDF-containing copolymers, it is worth summarizing the preparation of the monomer.

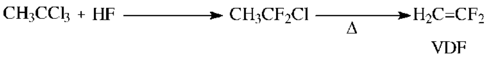
2.2. Synthesis of Vinylidene Fluoride (VDF or VF_2)

VDF is a colorless, flammable, and nearly odorless gas that boils at −82 °C; its freezing point is −144 °C. VDF's critical pressure, temperature, and density are 4434 kPa, 30.1 °C, and 417 $\mathrm{kg \cdot m^{-3}}$, respectively, while its explosive limits are 5.8−20.3 vol % in air.^{9,13} Its heat of formation is −345.2 $\mathrm{kJ \cdot mol^{-1}}$ at 25 °C, its heat of polymerization at 25 °C is −474.21 $\mathrm{kJ \cdot mol^{-1}}$, whereas its solubility in water is 6.3 $\mathrm{cm^3}$/100 g at 25 °C and 10 kPa. VDF exhibits several advantages: it is a nontoxic, environmentally friendly fluorinated gas in contrast to chlorotrifluoroethylene (CTFE)

Scheme 1



Scheme 2



$CH_3CCl_3 + HF \longrightarrow CH_3CF_2Cl \xrightarrow[\Delta]{} H_2C{=}CF_2$ (VDF)

Scheme 3

$ClCF_2CH_2Cl \xrightarrow{Zn} F_2C{=}CH_2$

and bromotrifluoroethylene (BrTFE), nonexplosive contrarily to tetrafluoroethylene (TFE) or trifluoroethylene (TrFE), and can easily homopolymerize and copolymerize under radical initiation.[9,13] In fact, acute inhalation toxicity of VDF is low. Median lethal concentration (LC_{50}) for rats was assessed: 128 000 ppm after 4 h exposure[14] and 800 000 ppm after 30 min exposure.[15] Furthermore, cumulative toxicity is low: for example, exposure of rats and mice at levels of up to 50 000 ppm for 90 days did not cause any systemic toxicity.[16] No teratogenic or reproductive effects were found in rats. Eighteen month inhalation studies on rats and mice have not detected chronic or carcinogenic effects up to 10 000 ppm of VDF.[17]

Various syntheses are possible to prepare VDF, and a nonexhaustive list is given hereafter. First, the chlorination of chlorofluorocarbon (CFC) 152 (i.e., 1,1-difluoroethane) to 1-chloro-1,1-difluoroethane (HCFC 142b),[18] followed by a dehydrochlorination at about 700−900 °C in the gas phase is the principal industrial process to VDF (Scheme 1). HCFC-142b is the preferred commercially available monomer precursor, obtained by hydrofluorination of acetylene,[19] vinylidene chloride,[20] or 1,1,1-trichloroethane.[21] The elimination can also be performed either at higher temperatures[22] in the presence of copper catalyst[23] or at lower temperatures in the presence of steam.

Second, the hydrofluorination of 1,1,1-trichloroethane (HFC-143a) yields CFC 142[24] (Scheme 2), which is subsequently dehydrochlorinated as above.

Third, the catalytic pyrolysis (at 400 °C in the presence of CrF_3, $3H_2O$) of 1,1,1-trifluoroethane requires specific conditions but produces VDF in high yield and purity.[25] Fourth, dehydrobromination of 1-bromo-1,1-difluoroethane[26] and dechlorinations of 1,2-dichloro-1,1-difluoroethane[27] and of other intermediates[13] have also been investigated as alternative routes (Scheme 3) and others well-reviewed by Dohany and Humphrey.[13]

Deuterated VDF was prepared[28,29] from trifluoroethanol-*d*$_3$, which was chemically changed into CF_3CD_2I. That iododerivative further underwent reaction with magnesium to generate $F_2C{=}CD_2$ in 44% overall yield.

2.3. Homopolymerization of Vinylidene Fluoride (VDF)

2.3.1. Radical Homopolymerization of VDF

Poly(vinylidene fluoride), PVDF or PVF_2, is usually manufactured by a radical initiated polymerization process in aqueous *emulsion* or *suspension* (involving pressures of 10−300 atm) at temperatures of 10−130 °C, regarded as heterogeneous reactions requiring a fluorinated surfactant. Chain transfer agents, buffers, or both may be used. Water-soluble initiators for the emulsion process can be persulfate salts,[30] disuccinic acid peroxide,[31] β-hydroxyalkylperoxide or alkylperoxybutyric acid.[32]

Organosoluble initiators[33] involved in the second process are diisopropylperoxydicarbonate,[33b−e] *tert*-butylperoxypivalate[33g] or *tert*-amylperoxypivalate,[33g] or di-*tert*-butyl peroxide,[33i] while water-soluble polymers such as cellulose derivatives or poly(vinyl alcohol) are used as suspending agents to reduce coalescence of polymer particles.

In addition, *solution* polymerization[34,35] has also been investigated. It is initiated by organic peroxides such as bis(perfluoropropionyl) peroxide,[34a] bis-4-*tert*-butylperoxycyclohexyldicarbonate[34b] or *tert*-butylperoxypivalate[35] in which the oxygen−oxygen bond undergoes a homolytic scission, in the presence of chlorofluorinated solvents.

Polymerization procedures, temperatures, pressure, recipe ingredients, monomer feeding strategy, and postpolymerization processing are variables that influence product characteristics and quality and are discussed in the well-documented reviews.[5,9,13]

Suspension and *emulsion* polymerized VDF exhibit dissimilar behaviors in solution. The suspension resin is readily soluble in many solvents (DMF, NMP, DMSO, dimethylacetamide), while in certain cases, the solution of the emulsion resin must be heated to reach solublity.

More “exotic” initiations have scarcely been studied. For example, *radiation*[36] or *plasma*[37] induced polymerizations of VDF have also been successfully carried out while *microwave*-stimulated polymerization gave thin polymeric PVDF films (<10 μm).[38]

Interestingly, DeSimone’s group pioneered, then extensively investigated[39] and reviewed,[40] the radical polymerization of VDF in supercritical (sc) CO_2. A British group[41] and a German team[42] have also been active in that area. This technology offers an advantage in the polymer isolation step where a clean dry polymer is produced simply by depressurization. The residual monomers and CO_2 can be recycled back to the reactor. Adequate CO_2 density for polymerization required pressure significantly higher (typically >100 bar) than conventional emulsion or suspension polymerizations. Because PVDF is not soluble in sc CO_2, a continuous precipitation polymerization of VDF was also investigated leading to the formation of polymers having bimolecular weight distributions.[43]

Regarding the kinetics of radical homopolymerization of VDF, the propagation rate to the square root of the termination rate of VDF has been assessed in solution (0.14 $L^{0.5}\cdot mol^{-0.5}\cdot s^{-0.5}$ at 74 °C)[44] and in sc CO_2 (1.3 $L^{0.5}\cdot mol^{-0.5}\cdot s^{-0.5}$ at 120 °C[39] and 2.23 $L^{0.5}\cdot mol^{-0.5}\cdot s^{-0.5}$ at 120 °C[42]).

In the course of the propagation, the contents of $-CH_2CF_2-CH_2CF_2-$ head-to-tail normal and $-CH_2CF_2-CF_2CH_2-$ head-to-head or $-CF_2CH_2-CH_2CF_2-$ tail-to-tail reversed VDF−VDF diads have been assessed by high resolution ^{19}F[45] (Figure 1) and ^1H nuclear magnetic resonance (NMR) spectroscopy. These head-to-head or tail-to-tail defects are influenced by the polymerization process conditions and temperature. In contrast to suspension polymerized VDF, PVDF obtained from the emulsion process contains a higher fraction of head-to-head defects. Commercial grades exhibit a wide range of 3−7 mol % defect structures. Recently, the structure of α PVDF and a VDF

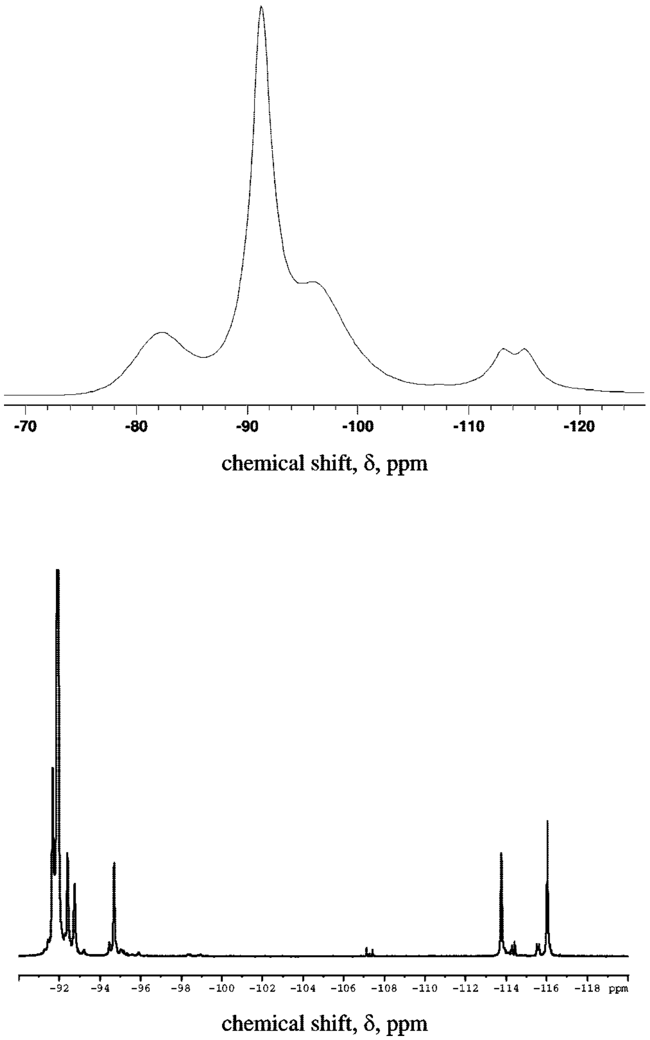


Figure 1. ^{19}F nuclear magnetic resonance spectra of PVDF: top, solid-state NMR spectrum; bottom, liquid NMR spectrum recorded in *d*-DMF.

telomer (VDFT) have been investigated by solid-state NMR using magic angle spinning (MAS) with relaxation pulse sequences.[45h] Here the degree of crystallinity, defect units, and end group content can be determined. The VDFT had the β all-trans form with similar defect unit content and a higher degree of end chains than α PVDF. It was also shown using a pre-spin-lock with radio frequency dipolar recoupling (RFDR) that the defect units are confined to the amorphous domain. Wormald's group has also recently developed a new method for NMR experiments on PVDF using "discrimination by variable amplitude multipulses" where selectivity is based on relaxation or chemical shift anisotropy and will shortly be publishing the results from a very fast MAS with back to back (BABA) dipolar recoupling experiments on PVDF to analyze the contributions to the amorphous NMR line shape.

In summary, crystallinity, which affects toughness, mechanical strength, impact resistance, and other properties of PVDF, is influenced by the defect structures.[9,13,46]

Controlled radical polymerization (CRP)[47] of VDF has been scarcely investigated and successful attempts have concerned iodine transfer polymerization (ITP)[44,48] (indeed, ITP of VDF was pioneered in the late 1970s at the Daikin Company[48]), macromolecular design through interchange of xanthate[49] (MADIX) (for which one example only has been supplied for the radical polymerization of VDF[50]), and borinates.[51] Further details on radical controlled copolymerization are supplied in section 3.3.

Nowadays, thermoplastic elastomers based on VDF (see sections 4.1.2 and 4.2.2) are currently produced at the industrial scale.

Termination of the radical polymerization of VDF proceeds exclusively through recombination.[52]

Highly regular PVDF polymer with minimized defect structure was first pioneered by Cais[53] (2.8%) for the high molecular weight PVDF, while VDF telomers (DP$_{11}$ and DP$_{20}$) were recently achieved and contained 0.73% head-to-head defects of chaining.[54] In addition, pure isogeric PVDF was achieved by reductive dechlorination of low molecular weight poly(1,1-dichloro-2,2-difluoroethylene).[55]

The synthesis of deuterated PVDF has also been reported by Cais and Kometani[29,56] with higher melting point and molecular weight and enhanced crystallinity arising from a "more perfect chain structure" than those of "hydrogenated" PVDF. In fact, the maximum residual polarization attained with deuterated PVDF homopolymer film was 1.0 mC·cm^{-2}.

2.3.2. Initiations Different from the Radical Ones

Trialkyl aluminum[57] and other low-temperature systems[29,58] have proven to be efficient "initiators" that generate low defects of chaining (<2.4%). In addition, the polymerization of VDF initiated by alkylboron compounds activated by oxygen, pioneered by Natta et al.[59] in 1965, was later investigated by Chung's group.[51] Interestingly, that system is able to control the polymerization of VDF via $^{\bullet}OBR_2$, a stable radical that acts as a counterradical (as reported in section 3.3.5).

2.4. Properties of PVDF

Among polyfluoroethylenes, PVDF is a thermoplastic that exhibits interesting properties. Physical and electrical characteristics of PVDF have been reported in various reviews[9,13] and depend upon the molecular weights, molecular weight distributions, chain configurations, crystalline form (see below), and defects of chaining.[46] Among these properties, PVDF is attractive for its piezoelectric (Kawai[60] discovered that behavior in 1969), pyroelectrical (first reported in 1971 by Bergman et al.[61] and by Nakamura and Wada[62]), and ferroelectric[63] behaviors. The β form of PVDF has even superior dielectric permittivity arising from the strong polymerization originating from C−F bonds and the spontaneous orientation of dipoles in the crystalline phases (Figure 2).

PVDF is inert to various solvents, oils, and acids and shows low permeabilities to gases and liquids. The glass transition (T_g) and melting (T_m) temperatures of the amorphous and crystalline PVDF regions are in the range of −40 to −30 and 155−192 °C, respectively, depending on the sample (e.g., the molecular weight and the amount of defects of chaining) and the testing method.

In fact, PVDF is typically 50−70% crystalline with five distinct crystal polymorphs named α, β, γ, δ, and ε, though α, β, and γ are the most frequent ones (Figure 2). This polymorphism is directly related to the slightly larger van der Waals radius of the fluorine atom (1.35 Å) versus that of the hydrogen one (1.20 Å). Indeed, these five types of crystalline phases in PVDF[64] are a rare characteristic for synthetic homopolymers. Most popular is the α phase (form II) having a trans−gauche configuration in which the

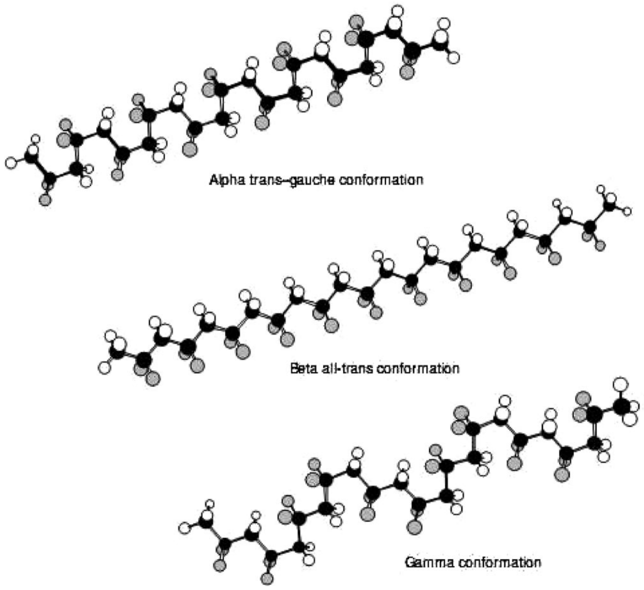


Figure 2. Main polymorphs of PVDF where the black, white, and gray spheres represent carbon, hydrogen, and fluorine atoms, respectively. Reproduced with permission from Wiley & Sons, ref 9b, copyright 2004.

polymeric chains are in nonpolar conformation (*TGTG′*), hydrogen and fluorine atoms alternating in a regular way on both sides of the chain,[65] giving a helix-type structure (Figure 2). This form α is kinetically the favorable one, while β form is the most thermodynamically stable form. The polar crystalline phase β (form I), which has zigzag (all-trans) conformation (*TTT*) of the polymeric chains, is obtained by straining, stretching, or quenching.[66] The β phase is most intriguing due to its piezo-, pyrro-, and ferroelectric properties,[64] which originate from the orientation of the strong dipole in the $-CH_2CF_2-$ base units along the polymeric chain. The intermediate polar conformation (*TTTGTTTG′*) phase γ (form III) is formed when the polymer is moderately stressed or when high-temperature annealing is applied. These different crystalline phase structures have already been characterized.[64,67,68] Amorphous PVDF regions have a density of 1.68 $g\cdot cm^{-3}$, the α and γ polymorphs of 1.92 and 1.93 $g\cdot cm^{-3}$, respectively, while that of β polymorph is 1.97 $g\cdot cm^{-3}$. The melt density of PVDF homopolymer is ca. 1.45−1.48 $g\cdot cm^{-3}$ at 230 °C and 1 bar.

These different structures (especially α and β forms) enable PVDF to exhibit dielectric properties. Indeed, under appropriate circumstances, if pressure is applied to a piezoelectric material, a voltage is generated. Piezoelectric transducers were developed at the beginning of the 20th century, notably by Langevin, and immediately found application in detecting the sound waves emanating from submerged submarines. The origin of piezoelectricity in PVDF is usually explained in terms of a "dipole model". PVDF is a semicrystalline polymer, and the crystalline phase is composed of two major contributions: α (antiparallel chain) and β (parallel chains where the dipoles align). Under the application of an electric field, the polymer chains align themselves in the field by rotating the dipoles around the axis. A net polarization occurs, which is responsible for the piezoelectric effect in PVDF. Nowadays, piezoelectric PVDF materials are ubiquitous and used in all sorts of applications, including crystal oscillators, transducers in telephone speakers, headphones, sonar arrays, mechanical actuators, etc.

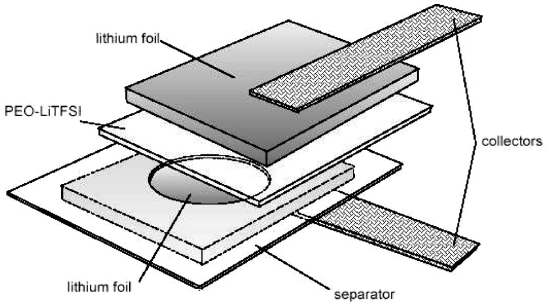


Figure 3. Lithium battery sketch (reproduced with permission from the Electrochemical Society; Bouchet, R.; Lascaud, S.; Rosso, M.; J. Electrochem. Soc. 2003, 150, A1385).

The dielectric constant and dissipation factor of PVDF at 25 °C are 8.15−10.46 and 0.005−0.026 at 1 kHz, respectively, while the Curie temperature has been assessed as 197 °C[69] and 195−197 °C.[70]

From wide-angle diffraction, Abbrent et al.[71] characterized the parameters of the orthorhombic unit cell typical of the α phase ($a = 4.96$ Å, $b = 9.64$ Å, and $c = 4.62$ Å).

Recently, Arkema tailored various homopolymers of VDF to obtain unexpected morphologies. Long chain branches (LCB) were synthesized using potassium persulfate and *n*-butyl-4,4-bis(*tert*-butylperoxy)valerate.[72,73] The number of branch points per 1000 monomer units was assessed by NMR to be in the 4.0−4.8 range, while for "reference Kynar PVDF", this number ranged between 0.8 and 3.1. It was noted that the higher the initiator concentration, the greater the number of "branch" points, which is well-characterized by multiangle light scattering and viscosimetry data. The authors have claimed that these LCB PVDFs should find new applications in melt processing.[73]

PVDF has shown organic permselectivity in the pervaporative separation of volatile organic compound/water mixtures.[74]

Thanks to its remarkable properties, PVDF has been extensively used as a component of electrolytes and Li-ion batteries (Figure 3), either as a binder for electrode materials[75] or as plasticized microporous PVDF separators for Li-ion batteries.[76]

Indeed, recent electrolytes consist of a macroporous PVDF separator, the polymeric backbone of which is swollen by the liquid electrolyte, while the porous volume is filled with the liquid electrolyte.[77]

2.5. Composites and Polymer Blends Made of PVDF

2.5.1. Composites

There is a real challenge to disperse nanofillers in fluorinated polymers, and the examples are scarce. Among them, PVDF/nanofiller or PVDF/clay nanocomposites have been investigated, and four examples are given hereafter.

First, Lui et al.[78] studied the effect of montmorillonite clay containing various quaternary alkylammonium salts for the preparation of gel PVDF n-composite electrolytes. These original electrolytes could be obtained by the addition of an appropriate amount of DMF or ethylene carbonate (EC)/propylene carbonate (PC) (acting as suitable cosolvent between PVDF and the clay), the organophilic clay, and lithium perchlorate to PVDF. The resulting materials showed better film formation, solvent-maintaining capability, and dimensional and electrochemical stabilities and enhanced ionic conductivity (reaching a value up to 10.3 mS·cm^{-1}) than electrolyte films without any added organophilic clays.

The same year, Priya and Jog[79] obtained PVDF/clay n-composites by melt intercalation (in a Brabender mixer) with organophilic bentonite clay (Cloisite 6A-treated with dimethyl dehydrogenated tallow quaternary ammonium chloride) and noted three major features: (i) PVDF in the n-composites crystallized in the β form[79a,b] (which was stable after thermal annealing achieved at 125 and 185 °C[79c]); (ii) an enhanced rate of crystallization with the addition of clay; (iii) significant improvement in the storage modulus over the temperature range of −100 to 150 °C.[79a]

Then, Dillon et al.[64] investigated the PVDF/nanoclay composites prepared by both solution casting and coprecipitation methods and using three n-clay morphologies (exfoliated, partially intercalated, and phase-separated morphology). From solution cast samples, phase separation and intercalation occurred, depending upon the organic modifiers, while complete exfoliation of the n-clays was noted in the coprecipitated n-composites.

Chung's group[80] prepared n-composites based on PVDF as an original "polymeric surfactant", which showed interfacial activity in the exfoliated fluoropolymer/clay nanocomposite. Actually, the functional group anchors the polymer chain to the clay interface. The rest of the unperturbed high molecular weight hydrophobic and oleophobic fluoropolymer chain, which dislikes the hydrophilic surfaces of the clay is claimed to exfoliate the clay layer structure, and the disorder is maintained even after mixing.

2.5.2. Polymer Blends

2.5.2.1. Introduction. The interest in polymer blends[81] lies in (i) obtaining properties different from those of parent homopolymers and copolymers, (ii) improving the physical properties (mainly mechanical), (iii) easy preparation, and (iv) a wide versatility of these blends.

Indeed, varying the blend composition induces a great variety of products endowed with a wide range of properties. However, such blends are required to be miscible or partly miscible, to enable the resulting materials to exhibit interesting properties.

Unlike most crystalline polymers, PVDF exhibits thermodynamic compatibility with other polymers,[82] and blends of PVDF with various other homopolymers were partly reviewed.[64,82] Viscometric behaviors of polymer blends based on PVDF have been also extensively investigated.[83] Among homopolymers that have led to many studies, poly(methyl methacrylate), PMMA, is miscible over a wide range of composition[84] (isotactic PMMA being more miscible with PVDF than atactic and syndiotactic ones[85]) and many investigations have revealed H-bonding between the carbonyl group of PMMA and the protons of PVDF.[86] Addition of 10−30 wt % PMMA improves the transparency of PVDF films or coatings in the UV−visible spectrum. The relationship between the optical transmission and compatibility of PVDF/PMMA blends has shown that films made of the blends containing at least 15 wt % PMMA are very transparent.

Specific PVDF/poly(methacrylate) blends have led to various interesting products for paints and coatings; one of them, Kynar, is marketed by Arkema (formerly Elf Atochem, Atofina, or Total Fina Elf).

The behavior of the PVDF/PMMA blend from solutions was revisited by Ma et al.[87] The crystallization behavior and morphology of the films cast from the mixed solvent THF/DMF revealed an enormous dependence on the DMF content. Indeed, increased DMF content in the mixed solvent enhanced the interactions between polymers and solvents and favored formation of the β crystal of PVDF but hindered formation of the α phase of PVDF.

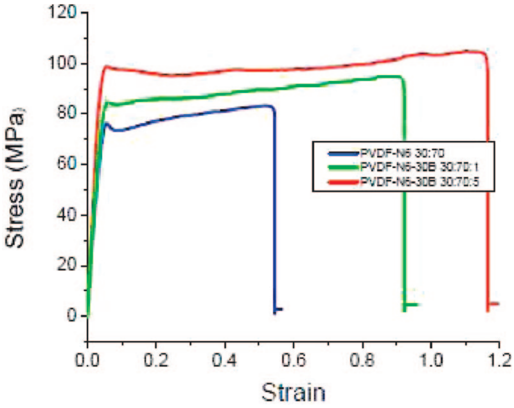


Figure 4. Tensile stress/strain curves for PVDF/nylon-6 blends with various contents of organoclays.[90] Reproduced from ref 90b with permission from the ACS Division of Polymer Chemistry.

Compatibilized blends of PVDF and thermoplastic polyurethane (TPU) have been developed using maleated PVDF (PVDF-*g*-MA), and investigations on the rheology, morphology, and mechanical properties of these blends have been achieved.[88]

Polyamide 11 (PA11)/clay blends, (PVDF)/clay blends, and ternary PVDF/PA11/clay blends were obtained by melt processing (using a high shear extruder) to prepare nanocomposites.[89] Two types of organoclays with different modified alkyl tails and different polarities were used for PA11 and PVDF nanocomposites. PA11 nanocomposites derived from an organoclay having one alkyl tail show a well-exfoliated morphology but no crystal form transformation, whereas those derived from an organoclay having two alkyl tails give a little less clay dispersion with the clear α to γ crystal form transition with the addition of the clay. In contrast, the PVDF composites derived from the two organoclays gave a poor dispersion. It was found that the clay platelets were selectively dispersed in the PA11 phase for a size larger than 200 nm, while no clay platelets were located in the PVDF phase or in PA11 nanodomains with size smaller than 200 nm.

Another approach regarding PVDF/nylon-6 (N6) 30/70 blends with various modified montmorillonite clays (Cloisite 30B and Cloisite 20A) was achieved by melt compounding.[90] Giannelis' team[90] investigated the morphological, thermal, and mechanical properties of the resulting blend nanocomposites. These authors have found that the degree of compatibilization induced by the nanoclay particles was dependent on both the location of the particles and the degree of clay dispersion. The blend nanocomposite with the best mechanical properties (Figure 4) had good dispersion of particles throughout the N6 matrix and at the PVDF/N6 interface, as sketched by Figure 5. In this blend nanocomposite, the coalescence of PVDF domains was prevented, and the crystallization of the PVDF domains was suppressed, ultimately creating a blend nanocomposite that is stiffer, stronger, and tougher than the blend without any nanoparticles (Figure 4).

On the other hand, quite a few PVDF/F-polymer blends have been published in the literature, and it is of interest to

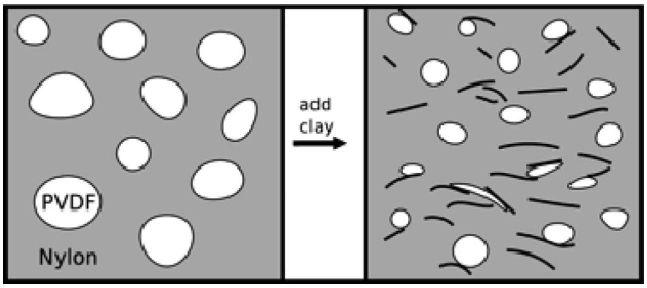


Figure 5. Cartoon showing the effect of the clay in PVDF/nylon-6 blends by melt compounding.[90] Reproduced from ref 90b with permission from the ACS Division of Polymer Chemistry.

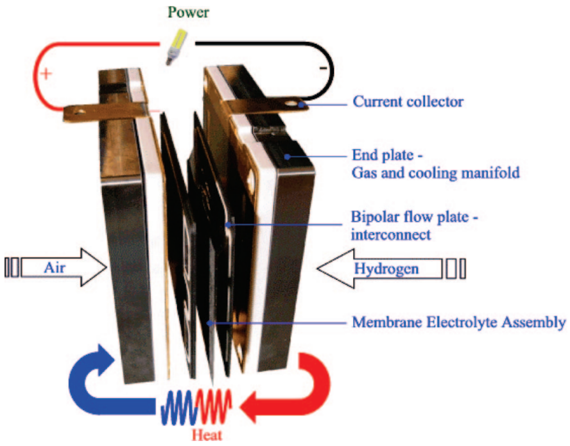


Figure 6. Schematic representation of an elementary "membrane electrode assembly", MEA, of a fuel cell.

mention Olkhov et al.'s basic survey[91] on the morphology of PVDF and its isomer the poly(ethylene-*alt*-tetrafluoroethylene) copolymer, ETFE, by thermomechanical analysis. This characterization showed that the polymers had completely amorphous "diblock" morphology. Parameters that characterize a degree of interchain interaction, such as coefficients of thermal expansion, free volume, and temperatures of polymer transformation into the glassy, high-elastic, or flow-viscous state were determined. PVDF and ETFE have similar topographic composition but different molecular mass and temperatures of phase transitions.

2.5.2.2. PVDF/Ionomer Polymer Blends. One of the most attractive applications of these blends concerns the preparation of proton conducting polymeric membranes, used as electrolytes in the so-called proton exchange membrane fuel cell (PEMFC, Figure 6). For example, Scrosati's team[92a] synthesized an original composite poly(acrylonitrile) (PAN)/PVDF hollow blend based on membrane dispersed n-Al_2O_3 ceramic filler swollen by aqueous acid solutions (phosphoric, sulfonic, or trifluoroacetic acids) as a gel-type polymer electrolyte. These acids were claimed to ensure the protonic conductivities keeping the same values (ca. 0.1 $S \cdot cm^{-1}$) from 25 to 85 °C, though MEA performances were poor (only 2 $mW \cdot cm^{-2}$ as a maximum of power density at room temperature). In a basic study, the same group[92a] also investigated by vibrational spectroscopy the structure of PVDF/polyacrylonitrile blends for such applications. By comparison of the dissociation degree and the actual amount of acid in the membrane to the conductivity, the limiting factor for the conductivity was established as the long-range mobility of protons, which is governed by the morphology of the membrane.

Another strategy suggested by Mokrini et al.[93] concerned the preparation of functional polymer blends for polymer electrolyte membrane fuel cell (PEMFC) from PVDF and a styrene−ethylene/butylene−styrene (SEBS) thermoplastic elastomer as a compatibilizer, after two different processes: (i) twin-screw extrusion and then calendring[93a] or (ii) melt blending and extruding into films.[93b] The resulting films were then reacted with sulfonic acid to enable proton conductivity. The advantage of inserting the additive is demonstrated by scanning electron microscopy (SEM). The SEM picture shows the phase separation for a blend that does not contain any compatibilizer (Figure 7a) and a significant reduction of the size of the phase when the additive was present (Figure 7b,c). SEBS is a phase-segregated material where the polystyrene blocks can be selectively functionalized offering high ionic conductivity, while PVDF ensures good dimensional stability and chemical resistance to the films. The compatibilized blend membranes prepared in the first case showed higher conductivities, 5.5×10^{-3} to 1.9×10^{-2} $S \cdot cm^{-1}$,[93a] and improved water management compared with those achieved from the second process. Water swelling decreased for compatibilized blend membranes. Adding a PMMA-*b*-poly(butyl acrylate)-*b*-PMMA block copolymer[93a] also enabled the compatibility of the blend by reducing the segregation scale and improving the blend homogeneity. These Canadian authors also studied the effect of varying the nature and concentration of the compatibilizer on the morphology and properties of a 50/50 wt % PVDF/SEBS blend.

For a similar application, Wootthikanokkhan's group[94] investigated PVDF/poly(styrene sulfonic acid) (PSSA) blends using compatibilizers such as PS-*b*-PMMA diblock and PMMA-*b*-PSSA-*b*-PMMA triblock copolymers. They studied the effects of blend ratio on the thermal and electrochemical properties of the resulting blend membranes (water uptake, proton conductivity, and methanol crossover). Interestingly, only 5% PS-*b*-PMMA diblock copolymer (for which the PMMA segment was compatible with PVDF and PS compatible with PSSA) remarkably increased the resistance to methanol crossover, the proton conductivity (though the maximum value was 3.9 $mS \cdot cm^{-1}$), and the mechanical properties (the tensile strength was 12 MPa), taking into account that blending PSSA with PVDF enabled the PSSA to reduce its degradation.[95] Further, the blends were stable up to 300 °C.

In addition, Nasef et al.[96] prepared pore-filled membranes composed of PSSA anchored in microporous PVDF films (by radical polymerization of SSA in the pores of PVDF). The variation of PSSA content induced changes in the structure of the membrane matrix. The porosity of the membranes decreased with increasing PSSA content without reaching a complete plugging of some pores in PVDF matrixes. Liquid uptake was dependent on the degree of crystallinity of the polymer electrolyte. Such a procedure was revisited by Moszczynski et al.[97] who obtained membranes, the proton conductivities of which reached 100 $mS \cdot cm^{-1}$ between 20 and 90 °C. However, and as expected, for higher temperatures, the conductivity value drops drastically because of the drying of the membranes. In addition, these membranes exhibit the drawback of aging in water since ca. 77% of the initial weight of PSSA was eluted after 32 days in water.

Another elegant and original strategy to blend PVDF and PSSA for fuel cell applications was developed in Prakash's

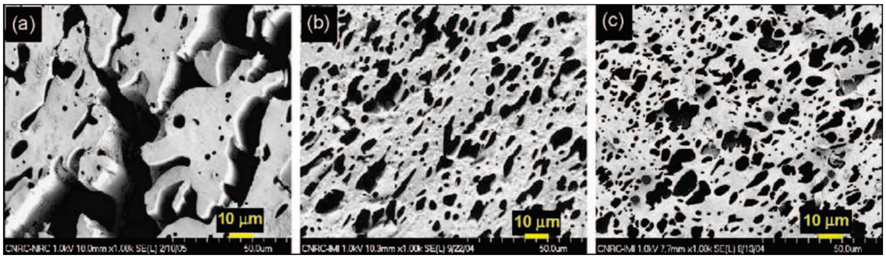
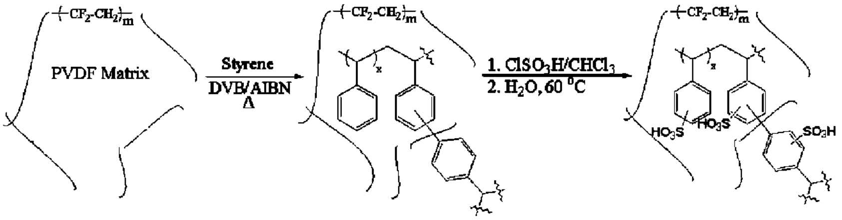


Figure 7. Scanning electron microscopic (SEM) pictures of membranes made of PVDF and SEBS without any compatibilizer (a) and with compatibilizer (b,c). Reproduced with permission from Elsevier, ref 93a, copyright 2006.

Scheme 4



group.[98] This involves the preparation of a semi-interpenetrated polymer network (sIPN) by immersing a PVDF membrane into a mixture of styrene monomer and divinyl benzene cross-linker prior to carring out the polymerization of styrene initiated by AIBN (Scheme 4).

Then, the sIPN membrane was impregnated with chlorosulfonic acid to insert sulfonic acid function on the aromatic rings for proton conductivity. The compatibility of PSSA and PVDF arose from the cross-linked structure in the sIPN, restricting the phase separation between both homopolymers. PVDF/Nafion blends led to an original fuel cell membrane with attractive electrochemical properties (Figure 8), comparable conductivity values to those of Nafion (ca. 77 $mS\cdot cm^{-1}$ at 25 °C), and a much lower methanol crossover (decrease of ca. 95% compared with that of Nafion). Such a strategy was efficiently used for direct methanol fuel cells.[99,100]

Furthermore, Goldbach et al.[101] prepared polymer electrolyte fuel cell membranes by blending Kynar PVDF and polyelectrolyte (based on aromatic sulfonic acid) (thickness 25 μm) and compared their electrochemical properties to those of Nafion112 (thickness 50 μm). They noted a lower methanol crossover and better chemical and thermal stabilities (less than 1% loss of small sulfur-containing molecules after 2000 h, in contrast to Nafion 112, which lost ca. 50%). Though the conductivity values were a bit lower (130−150 $mS\cdot cm^{-1}$ by adjusting the processing, compared with 160 $mS\cdot cm^{-1}$ for Nafion112), the obtained membranes had superior gas crossover resistance and tear properties, while the water uptake was higher (60% compared with 37% for Nafion112).

The morphologies of these novel PEMFCs were evaluated by TEM before and after incorporation of the membrane into a membrane electrode array. Nanometer-scale changes of the polymer structure and changes in the spatial distributions of fluorine, sulfur, and other elements were analyzed. The effects of microstructural and microchemical observations were correlated to the changes in fuel cell performance with

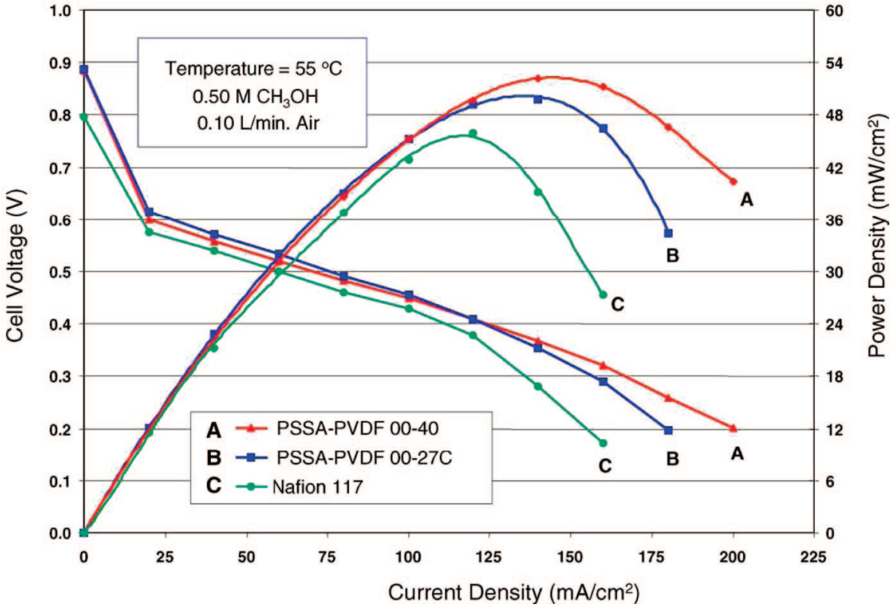
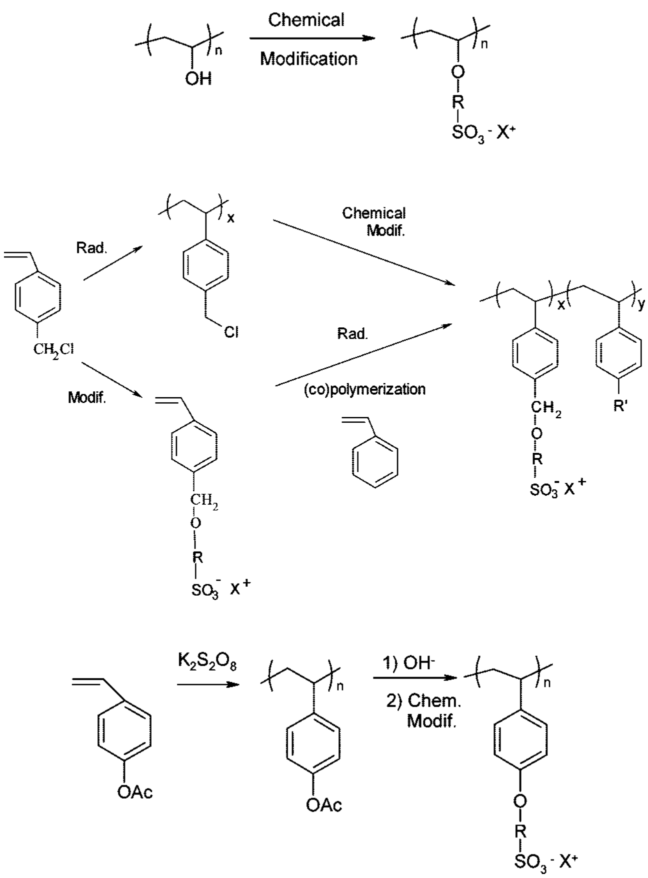


Figure 8. Polarization curve of PVDF/PSSA membrane achieved from semi-interpenetrated polymer network compared to these of Nafion. Reproduced with permission from Elsevier, ref 98, copyright 2004.

Scheme 5



time.[101] The Arkema company[102] also obtained relevant fuel cell membranes by blending Kynar PVDF with various polyelectrolytes prepared by chemical modification of poly(vinyl alcohol), poly(vinylbenzyl chloride), and poly(*para*-acetoxystyrene) as in Scheme 5.

Rather thin (25−50 μm) membranes were used for membrane electrode assemblies (MEAs).[102] These polyelectrolyte resins were blended into a polymer or copolymer matrix. Specifically, the polyelectrolyte resins are polymers or copolymers without hydrolyzable groups. Kynar PVDF is required as a tough and highly chemically resistant polymer.

For the same fuel cell membrane application, sulfonated PEEK/PVDF blends have also been investigated by several authors[103] for direct methanol fuel cells (DMFCs) since methanol crossover was 20 times lower than that of Nafion,[103b] though power density was only 30 mA·cm^{-2} at 60 °C.[103b]

Jung and Park[103c] have shown that less than 10 wt % PVDF was enough to bring mechanical stability to avoid phase separation (since for a high PVDF content, two T_g's were noted) and led to satisfactory conductivities (10^{-2} S·cm^{-1} at 60 °C) with similar fuel cell performances as those of Nafion (Figure 9).

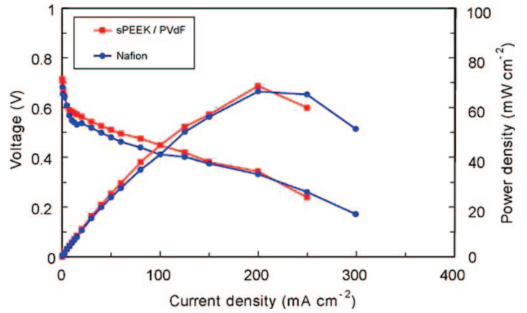


Figure 9. Electrochemical performance of a membrane composed of sulfonated PEEK (97.5 wt %)/PVDF (2.5 wt %) (■) compared with those of Nafion (●); the temperature is not given. Reproduced with permission from Elsevier, ref 103c, copyright 2007.

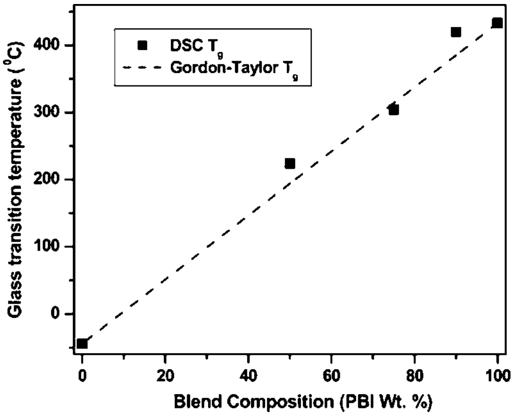


Figure 10. Variation of the glass transition temperature (T_g) of PBI/PVDF blend as a function of PBI. The solid points are the experimentally obtained T_g values from the DSC study, and the dotted line is the calculated T_g curve according to the Gordon−Taylor equation with k = 1. Reproduced with permission from ref 104. Copyright 2008 American Chemical Society.

More recently, Arunbabu et al.[104] have also studied polybenzimidazole (PBI)/PVDF blends and have shown by FTIR that hydrogen-bonding interactions occurred between the N−H bond of PBI and difluoromethylene groups of PVDF. DSC evidenced miscibility of these polymers in a wide composition range, by the presence of a unique T_g, with a value always ranging between that of PVDF (claimed at −44 °C) and that of PBI (+433 °C) (Figure 10). The experimental values were in good agreement with those predicted from the Gordon−Taylor equation, in which the adjustable fitting parameter related to the strength of the intermolecular interaction between both homopolymers was 1. Such a miscible blend was cast into a proton exchange membrane fuel cell doped with phosphoric acid (PA). Though no values of conductivity were supplied, the PA doping level of the blend membrane improved significantly as a result of the hydrophobic nature of PVDF, which suppressed water uptake.

To enhance the porosity, PVDF was prepared by the phase inversion method using poly(ethylene glycol) (PEG)[105] as an additive and *N*,*N*-dimethylformamide as the solvent. A uniform sponge structure of PVDF−PEG membranes for lithium secondary batteries was prepared with 10 wt % PEG concentration in PVDF−PEG solution. Porosity, elongation, and tensile strength of the membrane were 87%, 75%, and 275 MPa, respectively.[105]

Yang et al.[106] have investigated the effect of lithium iodide concentration on the conduction behavior of poly(ethylene oxide)/poly(vinylidene fluoride) (PEO/PVDF) polymer blend electrolyte and the performances of the corresponding dye-sensitized solar cell (DSSC). The conduction behavior of these electrolytes was investigated with varying LiI concentration (10−60 wt % in the polymer blend). The optimized conversion efficiency was obtained at a salt content of 28.9 wt % in the "polymer-in-salt" region, with an ionic conductivity of 1.06 × 10^{-3} S·cm^{-1}. Based on these facts, the

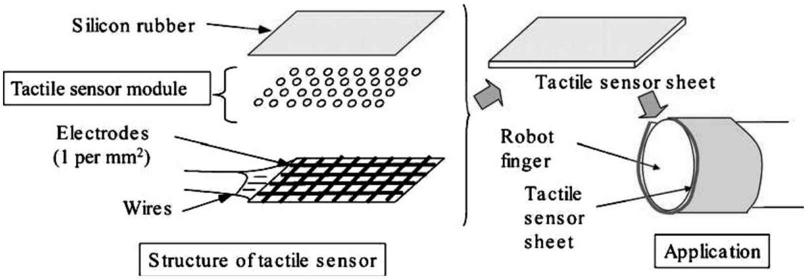


Figure 11. Tactile sensor (the tactile sensor sheet is made of PVDF) for robotic applications. Reproduced with permission from ref 150b. Copyright 2008 Elsevier.

changes of conduction behavior and the changes of I^{3-} and I^- concentrations in the electrolytes were suggested to contribute to the final performance variation of the corresponding DSSC with varying LiI concentration.

Another interesting topic related to blends made of PVDF deals with artificial muscles. Indeed, to develop artificial muscles with improved performance, electroactive polymer actuators are searched, and among various examples, Lu et al.[108] have prepared a new one by employing an ionic networking membrane of poly(styrene-*alt*-maleimide) (PSMI)-incorporated PVDF in the presence of platinum particles. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that smaller and uniform platinum particles were formed on the surface of the actuator fabricated through the electroless-plating technique, as well as within its polymer matrix. Under constant voltage excitation, the tip displacement of the actuator constructed with that ionic network membrane was several times larger than that of its Nafion counterpart of similar thickness without straightening-back. Under the stimulus of alternating-current voltage,[108] this actuator displayed an excellent harmonic performance, and the measured mechanical displacement was comparable to that of the Nafion-based actuator (a tactile sensor is sketched in Figure 11), with an inherent large ionic-exchange capacity and unique hydrophilic nanochannels of the ionic networking membrane, hence finding niche applications in biomimetic motion.

2.6. Behavior of PVDF in Solution

Regarding the behavior in solution of VDF-containing polymers, little data is given in the literature,[109−111] except the Mark−Houwink relationships to determine molecular weights of PVDF.[112,113] The intrinsic viscosity−molecular weight empirical relationship according to Mark−Houwink−Sakurada was first suggested by Lutinger and Weill[114] ($K = 4.5 \times 10^{-2}$ mL·g^{-1} and $\alpha = 0.70$ at 25 °C in DMF).

To our knowledge, the most pertinent studies have been achieved by Zimbo and Theodore[110] and by Maccone et al.[111] who determined key molecular weight parameters by size exclusion chromatography, such as average molecular weights and molecular weight distributions. The latter team also investigated the branching of PVDF from the transfer to the polymer and then the cross-linking in the presence of a fluorodiolefin.[111]

2.7. Cross-Linking of PVDF

Cross-linking of polymers usually enables enhancement of their properties. In the case of PVDF, various methods involving different cross-linking agents have been investigated as reported recently:[5,10] aliphatic diamines, bisphenols, peroxide/triallyl (iso)cyanurate systems, PVDF-containing cure site monomers (CSMs), or electron beam irradiation. Indeed, PVDF has been used in the last 30 years in nuclear radiation environments because, unlike most plastics, it cross-links rather than degrades, thus retaining mechanical integrety.

2.8. Processing of PVDF

PVDF is available in a wide range of melt viscosities as powders and pellets to fulfill typical fabrication requirements.[5,9] It can be molded in conventional compression, transfer, and injection-molding equipment.[109] As a crystalline polymer, it shows relatively high mold shrinkage of ca. 3%. Further data on PVDF processing can be found in the comprehensive reviews written by Seiler,[9a] Humprey and Sanayed,[9b] or Dohany.[13]

As mentioned above, Hedhli et al.[72,73] have evidenced by rheology possible branching in PVDF arising from hydrogen abstraction of a methylene group surrounded by two CF_2 groups. Indeed, these authors claimed that long chain branching (LCB) naturally occurs in emulsion polymerization of VDF.

PVDF is available commercially in a wide range of melt flow rates and with various additives to enhance processing or end use properties. PVDF is not hazardous under typical melt processing conditions. A variety of forms are available: latex and fine powders from emulsion processes, and granules from either suspension or emulsion processes.

All common extrusion and molding techniques can be used to process PVDF into shapes. Typical molding temperatures in the cylinder and nozzle are 180−240 °C for injection types and 50−90 °C for molds.

Certain additives such as titanates or silicates catalyze the thermal decomposition of molten PVDF at temperatures lower than typical for the natural resin, leading to dangerously high pressures in the equipment because of byproduct gases. Generally, metal oxides catalyze degradation at high processing temperature, for example, oxides of titanium, manganese, and iron.

2.9. Conclusion

PVDF is an exceptional polymer endowed with remarkable properties, involved in many high-tech applications. When the term PVDF is used to search the Chemical Abstract databases from 1992, there are approximatively 500 citations per year, about half of which are patents, showing a growing industrial interest. The worldwide PVDF market in 2000 was about 21 000 tons.[9] PVDF usage is expected to grow at an average of ca. 6% for all fluoropolymers in the first decade

Table 1. Main Commercially Available Fluoroelastomers[a]

	HFP	PMVE	CTFE	P
VDF	Daiel G 801 and others (Daikin) Dyneon elastomer (3M/Dyneon) Tecnoflon N/FOR (Solvay Solexis) SKF-26 (Russia) Viton A (DPE)		Dyneon elastomer (3M/Dyneon) SKF-32 (Russia) Voltalef (Arkema North America)	
TFE		Daiel perfluoro (Daikin) Dyneon elastomer (3M/Dyneon) Kalrez (DPE) Tecnoflon PFR (Solvay Solexis)		Aflas (Asahi Glass) Viton Extreme TB (DPE)
VDF + TFE	Daiel G 901 and others (Daikin) Dyneon elastomer (3M/Dyneon) Tecnoflon P/T/TN/FOR (Solvay Solexis) Viton B/F/GF/GBL (DPE) Tecnoflon BR (Solvay Solexis)[b]	Daiel LT (Daikin) Dyneon elastomer (3M/Dyneon) Tecnoflon PL (Solvay Solexis) Viton GLT/GFLT (DPE) Tecnoflon VPL (Solvay Solexis)[c]		Aflas (Asahi Glass)

[a] DPE, DuPont Performance Elastomers; CTFE, chlorotrifluoroethylene ($F_2C{=}CFCl$); HFP, hexafluoropropene ($F_2C{=}CFCF_3$); HPFP, 1-hydropentafluoropropene ($FHC{=}CF{-}CF_3$); P, propene ($H_2C{=}CHCH_3$); PMVE, perfluoromethyl vinyl ether ($F_2C{=}CFOCF_3$); TFE, tetrafluoroethylene ($F_2C{=}CF_2$); VDF, vinylidene fluoride (or 1,1-difluoroethylene) ($F_2C{=}CH_2$); X, cure site monomer ($XCY{=}CZ{-}R{-}G$; G, function). [b] Further comprising recurring units derived from hydrogenated olefin. [c] Further comprising recurring units derived from particular perfluorovinylethers having catenary oxygen atoms in the pendant chain.

of this 21st century. Processing, morphology, properties, and end-use performances are affected by branching, cross-linking, differences in the content of defect of structures, and other chain irregularities.

3. Copolymerization of Vinylidene Fluoride

3.1. Introduction

Copolymerization is the most general and powerful method to perform effective systematic changes in polymer properties, and is widely used in the production of commercial polymers and in basic investigations of structure−property relationships. As a result, copolymerization usually modifies the symmetry of the polymeric chain and modulates both intramolecular and intermolecular forces so that properties such as melting point, glass transition temperature, crystallinity, stability, elasticity, permeability, and chemical reactivity may be varied within wide limits.

It is well-known that copolymerization of fluoroalkenes is carried out by a radical method.

In this section, most VDF copolymers are random (section 3.2), but in later sections, useful data will be reported on the formation of alternating poly(VDF-*alt*-M) copolymers and then on the well-defined VDF-containing fluoropolymers (e.g. block and graft copolymers).

Four types of VDF-based fluoropolymers[4,6−8] are manufactured: the earliest types of fluorocarbon elastomers are those prepared from VDF and HFP (type-A);[13,26] later, the B types were developed, which contain VDF, HFP, and TFE base units;[6,8,115] fluoroelastomers designated as type-C were prepared to improve solvent resistance; they contain a higher fluorine content and cure-site monomer (CSM) such as bromotrifluoroethylene in addition to VDF, TFE, and HFP; the most recent ones are called type-D fluoroelastomers endowed with low-temperature resistance and containing perfluoroalkyl vinyl ether instead of HFP (Table 1).

3.2. Random Copolymers by Conventional Radical Copolymerization

Nowadays, copolymers based on VDF and chlorotrifluoroethylene (CTFE) or hexafluoropropene (HFP) represent the most important production among thermoplastic copolymers of VDF, while such a positive fate was reached for poly(VDF-*co*-HFP) elastomers produced by most industries of fluoropolymers.

3.2.1. Poly(VDF-co-chlorotrifluoroethylene) Copolymers

The first copolymers based on VDF and chlorotrifluoroethylene (CTFE) were produced for military interests in 1955.[116] Poly(VDF-*co*-CTFE) copolymers are statistic, with $[(CH_2CF_2)_x(CF_2CFCl)_y]_n$ chemical structure and are widely used in the current industry. In the mid-1950s, these materials were also the first commercially available fluoroelastomers (from the Kellog Company under the Kel F trademark) with vulcanizate properties superior to any other existing materials. Nowadays, according to the properties and applications required, various poly(VDF-*co*-CTFE) copolymers are proposed, in which the amount of CTFE is crucial. On the one hand, this amount may influence the glass transtion temperature (T_g) of poly(VDF-*co*-CTFE) copolymers, the assessment of which was investigated for the first time by Mandelkern et al.[117] in 1957: according to the composition, it ranges between −40 (T_g of PVDF) and 45 °C (T_g of PCTFE).

On the other hand, poly(VDF-*co*-CTFE) copolymers containing small VDF amounts are semicrystalline copolymers with a hexagonal structure,[118] while those composed of 25−70 mol % VDF are amorphous, though it has also been more recently noted[119] that poly(VDF-*co*-CTFE) copolymers containing more than 16.6 mol % CTFE units had an amorphous state (Figure 12). VDF-based fluoroelastomers have remarkable resistance to flames, chemicals, solvents, heat, and oxidation. These materials can be cured by bis-nucleophiles such as bis-phenols or diamines or by peroxides.[10]

VDF percentages higher than 70% lead to thermoplastics with a monoclinic crystalline structure,[120] and these copolymers are called flexible PVDF.[121]

The synthesis of poly(VDF-*co*-CTFE) copolymers can be carried out in emulsion[122] or in suspension.[123]

The microstructure of poly(VDF-*co*-CTFE) copolymers was assessed for the first time by Murasheva et al.[124] in 1979 from a careful ^{19}F liquid-state NMR characterization and was

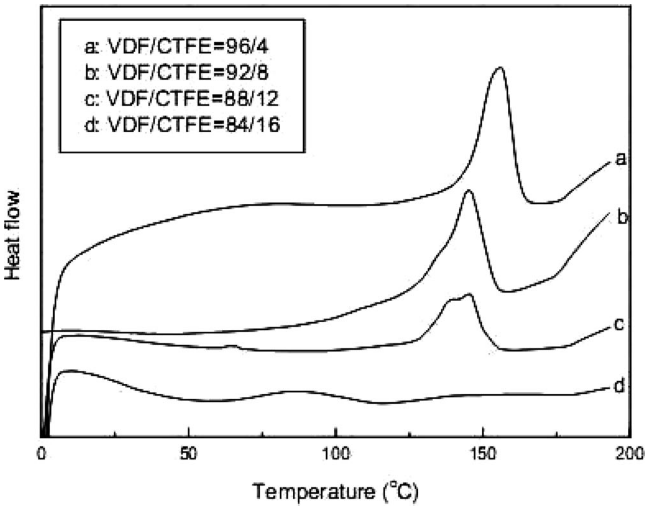
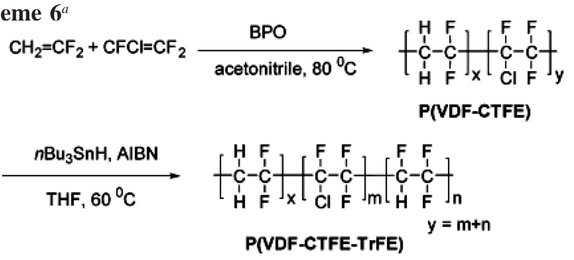


Figure 12. Differential scanning calorimetry thermograms of poly(VDF-*co*-CTFE) copolymers containing various amounts of CTFE. Reproduced with permission from ref 138. Copyright 2007 the Electrochemical Society.

Scheme 6[a]



[a] Reproduced with permission from ref 126a. Copyright 2006 American Chemical Society.

revisited by Chung's team[125] in 2002 (who surprisingly did not quote these Russian pioneers). Isbester et al. reported ^{19}F solid-state NMR high-speed magic-angle spinning analysis.[45e]

As reported above for PVDF, poly(VDF-*co*-CTFE) copolymers are also endowed with piezoelectrical properties, discovered in 1982, and recently, a renewed interest has been pointed out by various authors.[125−128] Indeed, ferroelectric PVDF and its copolymers are the most interesting dielectric polymers due to strong polarization originating from C−F bonds and spontaneous orientation of dipoles in the crystalline phases.[63b] For example, poly(VDF-*co*-CTFE) copolymer has a dielectric permittivity of 13.[127]

A high electromechanical response was noted in poly(VDF-*co*-CTFE) copolymers containing 9 and 12 mol % CTFE.[129] The one containing 12 mol % showed an eletrostrictive strain response of more than 15%. When compared with other PVDF-based electroactive polymers (EAPs), poly(VDF-*co*-CTFE) copolymer exhibits a higher strain response but requires a higher driving electric field. Advantageously, this copolymer is less expensive and commercially available.

Poly(VDF-*co*-CTFE) copolymer-based nanocomposites[130] have been prepared by mixing that fluorinated copolymer with carbon nanotubes (CNTs) or C_{60} using a solution cast method. The volume fraction of CNTs or C_{60} was varied from 0.1% to 1.0%. The influence of CNTs and C_{60} on the crystallization behavior of poly(VDF-*co*-CTFE) copolymers was determined by XRD and DSC, and the authors showed that CNTs or C_{60} increased the β-phase and the crystallinity.

To enhance dielectric properties of poly(VDF-*co*-CTFE) copolymers, various teams have selectively reduced the chlorine atom of CTFE units. This reduction was first pioneered by Cais and Kometani[131] in 1984, then in collaboration with Lovinger's group,[132] and recently revisited by Lu et al.[126] to lead to poly(VDF-*ter*-CTFE-*ter*-TrFE) terpolymers (Scheme 6).

Lu et al.[126] nicely characterized the microstructures of these terpolymers by ^{19}F NMR, and they noted head-to-head VDF−TrFE diads in these "reduced" poly(VDF-*co*-CTFE) copolymers in contrast to head-to-tail VDF−TrFE diads produced from direct radical copolymerization of VDF with TrFE.[128] Although this strategy to get poly(VDF-*co*-CTFE) copolymer required one more step than the direct radical copolymerization of VDF with TrFE (see section 3.2.2), it has the advantage not to use hazardous TrFE (dangerous to transport and store).[133]

Lu et al.[126] also noted that the ferroelectric fluoropolymers exhibited high dielectric constants. Tuning the structure of the copolymers enabled that American team to establish a "polymer structure thermal and dielectric properties" correlation, which provided insights into factors governing the responses in these organic electroactive materials. Actually, 47 samples of poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers were synthesized and led to a wide range of materials having various Curie temperatures[126] (ranging from 22 to 106 °C, while that of PVDF is 197 °C[70] or 195−197 °C[71]) and room-temperature dielectric constants varying from 11 to 50 at 1 kHz. Indeed, a high RT dielectric constant of 50 and a low dielectric loss (tgδ < 0.05)[126] were reached for poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymer containing 78.8, 7.2, and 14.0 mol % of the respective fluoroalkenes. Such dielectric values are higher than those of terpolymers prepared by direct radical terpolymerization of VDF with CTFE and TrFE,[134] for which the dielectrical constant is 37.5.[135]

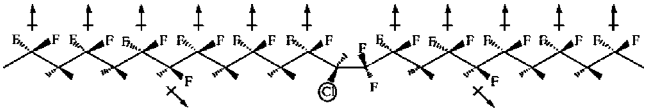
The same American team[136] also investigated the direct radical terpolymerization of VDF with CTFE and TrFE and established the relationship between the composition of these terpolymers and the dielectric permittivity. They noted that for the same VDF content in the terpolymer, the higher the TrFE content, the higher the T_m and the lower the dielectric permittivity. Indeed, for a large energy storage capacity, both high dielectric permittivity and electrical breakdown strength are required. They could assess the permittivity of poly(VDF-*ter*-CTFE-*ter*-TrFE) terpolymers of 50 (measured at 1 kHz and at ambient temperature).[137]

In addition, Wang's team[138] has found that these terpolymers exhibit high electric energy density and can be used as potential ferroelectric capacitors endowed with fast discharge speed and high efficiency.

An original synthetic strategy for a similar application has also been used by Chung's group[119,139] who investigated the controlled radical copolymerization of VDF with CTFE (and $F_2C{=}CF{-}R{-}Si(OR)_3$) at room temperature in the presence of borane/oxygen system. In fact, the borinate generated *in situ* enabled control of the radical copolymerization (more details are given in section 3.3.5). Resulting poly(VDF-*co*-CTFE) copolymers reached molecular weights greater than 20 000 g·mol^{-1} with narrow molecular weight distributions and always showed a CTFE mole percent higher than that of the feed.

From the same syntheses, Zhang and Chung[128] also carried out the selective reduction of chlorine atoms in CTFE units leading to original poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers. The consecutive VDF units provide strong polarization

Scheme 7[a]



[a] Reproduced with permission from ref 128. Copyright 2007 American Chemical Society.

and the randomly distributed TrFE units (cocrystallizable with VDF units) direct the VDF sequence to all-trans (polar) conformation. In addition, the small amount of bulky chlorine atoms in CTFE units act as the kinks to reduce the crystalline size without significantly reducing the overall crystallinity (Scheme 7).

Hence, these poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers exhibit potential ferroelectric properties such as diffuse phase transition and high dielectric constant at ambient temperature: the highest RT dielectric constant of 60 at 1 kHz was obtained for a terpolymer composed of 65.5 mol % VDF, 26.7 mol % TrFE, and 7.7 mol % CTFE at the Curie temperature of 20−40 °C,[128] compared with poly(VDF-*co*-CTFE) copolymers (see Figure 13). These poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers have shown high dielectric relaxation (large frequency dependence) for potential high pulsed capacitors with high energy density (releasing an energy density higher than 13 $J \cdot cm^{-3}$), low energy loss, and also no residual polarization at zero electric field. The authors noted similar bulky CTFE effects in these terpolymers with the decrease of melting and Curie temperatures (down to 18.8 °C).[136]

From these controlled structures and molecular weight poly(VDF-*co*-CTFE) copolymers, the same team showed another interesting application, fuel cell membranes,[128] two types of which are presented hereafter.

The first type deals with poly(VDF-*co*-CTFE) copolymer/Nafion/inorganic filler blend for which the highest conductivity was 25 $mS \cdot cm^{-1}$ at 120 °C for 70% relative humidity (RH) when $H_3OZr_2(PO_4)_3$ particles were used in 20% (the Nafion content was 60%). This is an interesting value since it is known that perfluorosulfonic acid polymers (e.g., Nafion-type) lose their electrochemical performances (including conductivity) when temperature is higher than 85 °C at relative humidity (RH) <100%.

The second family involving first a similar methodology to obtain poly(VDF-*ter*-CTFE-*ter*-M) terpolymers precursors (Scheme 8) did not contain any Nafion. Indeed, the sulfonic acid functions were added from a straightforward reaction [via sulfonated silicon dioxide or 2-(4-sulfonic phenyl) ethyl triethoxysilane, CSPETMS].

In certain conditions, the borinate end group could be modified into a triethoxysilane end group, which led to a tris(trialkoxysilane) poly(VDF-*co*-CTFE) copolymer capable to react with CSPETMS via hydrolysis and condensation.[139] After hydrolysis of SO_2Cl into a sulfonic acid group, composite membranes were produced as illustred by Scheme 9.

Satisfactory membrane conductivities (ionic exchange capacity was 2.25 $mmol \cdot g^{-1}$) were obtained (Figure 14).[139]

In addition, termination by radical coupling led to telechelic (or α,ω-difunctional PVDF) bis(trialkoxysilane). These original end-functionalized fluoropolymers are effective surfactants[80] that showed a high interfacial activity in the exfoliated F-polymer/clay nanocomposite. The trialkoxysilane was able to anchor the polymeric chain to the clay interface, while the hydrolytic polymer exfoliated the clay layer structure.[80]

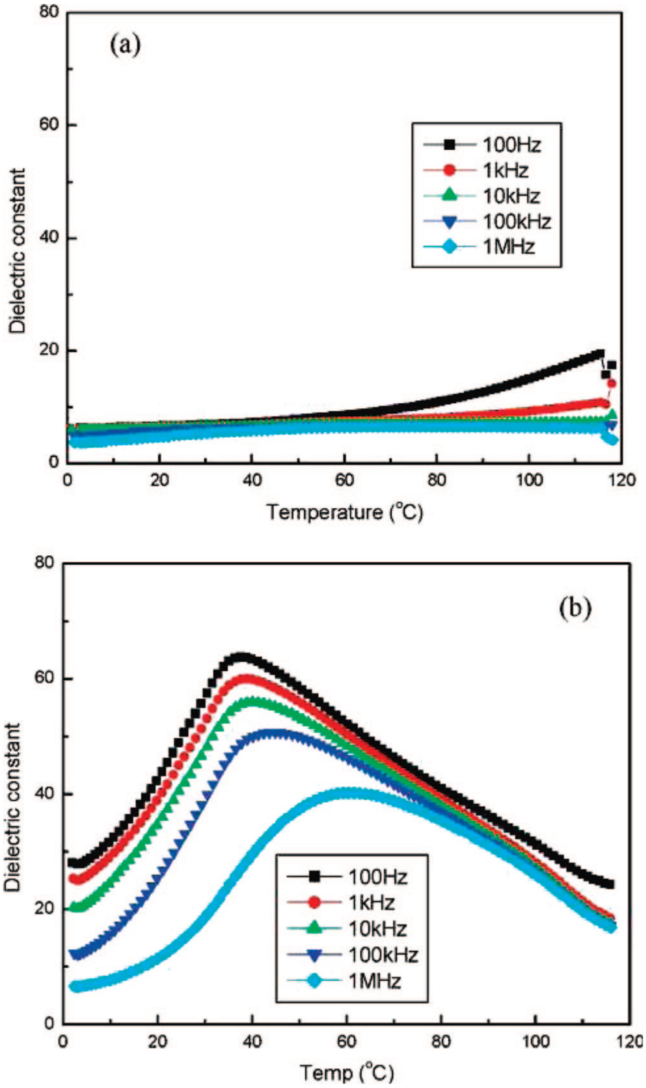
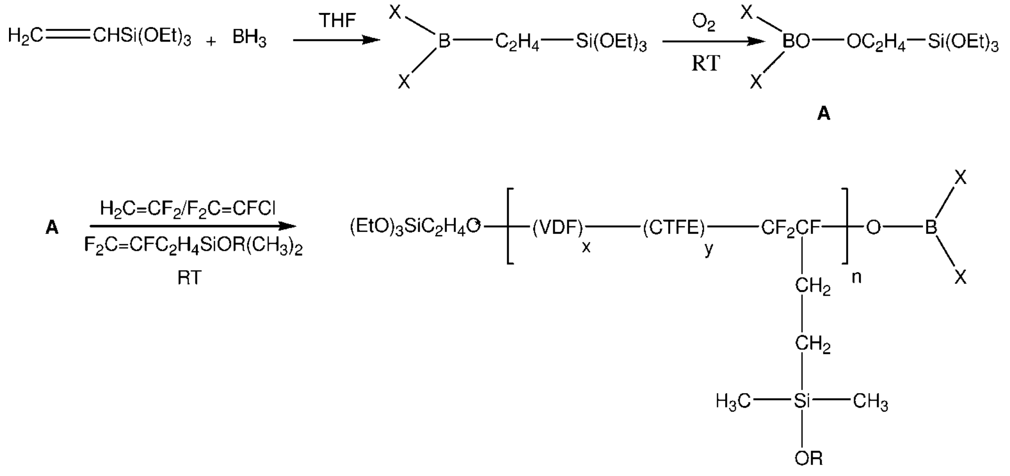


Figure 13. Dielectric constant of (a) poly(VDF-*co*-CTFE) (92/8 mol %) copolymer (melting temperature, T_m= 145.0 °C; Curie temperature, T_c, not assessed) and (b) poly(VDF-*ter*-TrFE-*ter*-CTFE) (65.6/26.7/7.7 mol %) terpolymer (T_m= 123.6 °C and T_c= 23.8 °C). Reproduced with permission from ref 128. Copyright 2007 American Chemical Society.

A different application related to very large electro-optic effects has been observed in relaxor ferroelectric poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymer.[140] By addition of a small amount of zinc sulfide (ZnS) nanoparticles, the refractive index of the nanocomposites can be tuned between about 1.4 and 1.5 while retaining large electro-optic effects and high transparency.[140] Tunable long-period fiber gratings have been fabricated with the nanocomposite as the second cladding, and over 50 nm of resonant wavelength shift has been achieved under a change of electric field of 30 $V \cdot \mu m^{-1}$, which is much larger than other reported E-O tuning ranges. This corresponds to a pure refractive index change of the nanocomposite of $\Delta n/n \approx 0.4\%$.

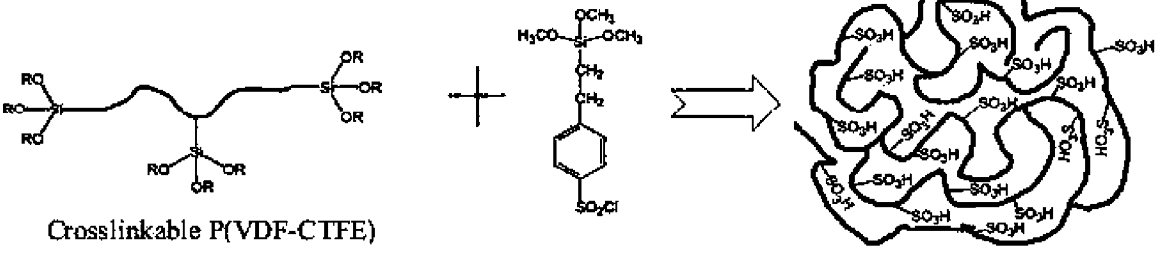
Another interesting optical application involving original thermoplastic elastomers was achieved by the Daikin Company[141] from iodine transfer copolymerization of VDF and CTFE in the presence of IC_4F_8I as the chain transfer agent.

Scheme 8[a]



[a] X can be H or $C_2H_4Si(OEt)_3$.

Scheme 9. ([a])



[a] Reproduced with permission from ref 139. Copyright 2007 Electrochemical Society.

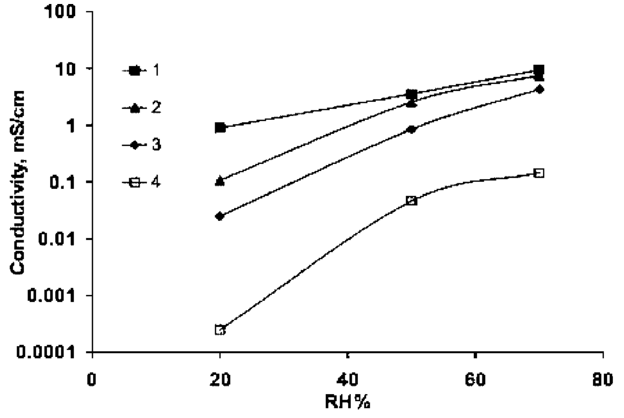


Figure 14. Conductivity of new composite materials compared with Nafion at 120 °C and different relative humidity (RH): (1) Nafion115; (2) 40% poly(VDF-*co*-CTFE) copolymer/60% sulfonated silicon dioxide; (3) poly(VDF-*co*-CTFE)-*g*-SPETMS; (4) 30% poly(VDF-*co*-CTFE)/30% Nafion/40% MS). Reproduced with permission from ref 139. Copyright 2007 Electrochemical Society.

This led to I-poly(VDF-*co*-CTFE)-I (Scheme 10) where the contents of VDF and CTFE in the elastomeric block were 55 and 45 mol %, respectively, with a T_g value of −7 °C. This soft telechelic diiodide was able to reinitiate the radical copolymerization of ethylene (E) and CTFE (or E and tetrafluoroethylene) to insert thermoplastic or "hard" sequences. Hence, original triblock hard−soft−hard thermoplastic elastomers were produced (Scheme 10); the melting points of the hard blocks containing either poly(E-*alt*-CTFE) or poly(E-*alt*-TFE) copolymers were 247 or 252 °C, respectively. These TPEs were used for artificial lenses.[141]

Moreover, another interesting strategy to synthesize TPEs lies on a macroinitiator terpolymer (MacroPerCa) based on VDF, CTFE, and a peroxide functional allyl monomer (TBPAC), subsequently grafted to PVDF to form a tough, flexible graft thermoplastic material, as marketed by the Central Glass Company under the Cefral trademark[142] (Scheme 11).

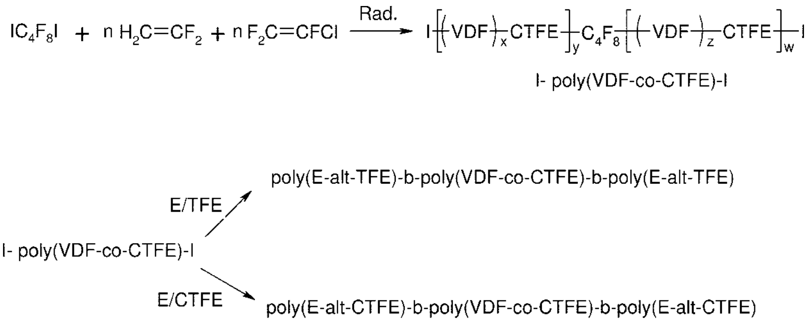
In conclusion, poly(VDF-*co*-CTFE) copolymers have found valuable applications as nanocomposites, fuel cell membranes, surfactants, optical devices, capacitors, electroactive polymers or actuators (thanks to their piezoelectrical properties), and thermoplastic elastomers. The piezo- or pyroelectric properties have been enhanced when a chlorine atom was selectively reduced, hence leading to original and very interesting poly(VDF-*ter*-CTFE-*ter*-TrFE) terpolymers. Further relevant electric properties are also shown in the section below from copolymers based on VDF and trifluoroethylene.

3.2.2. Poly(VDF-co-trifluoroethylene) Copolymers

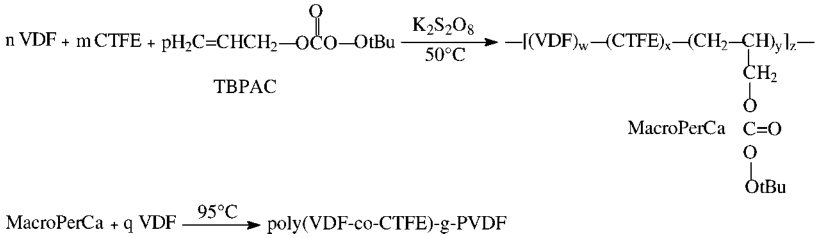
VDF can copolymerize in all proportions with trifluoroethylene (TrFE)[143−146] leading to random semicrystalline thermoplastic copolymers, whatever the composition in contrast to poly(VDF-*co*-CTFE) and poly(VDF-*co*-HFP) copolymers. Nowadays, only poly(VDF-*co*-TrFE) copolymers containing a TrFE amount ranging from 17 to 50 mol % have a slight commercial development limited to few tons per year.

Their microstructures were characterized by ^{19}F nuclear magnetic resonance (NMR) spectroscopy for the first time in 1979 by Yagi and Tatemoto,[143] then reviewed by Harris et al.[45d] who, reported an extensive survey on their structure

Scheme 10



Scheme 11



and morphology, and more recently, ^{19}F MAS and ^{1}H−^{19}F CP/MAS NMR spectra of poly(VDF-*co*-TrFE) copolymer containing 75 mol % VDF[144] (showing that the VDF−TrFE head-to-tail sequence is the most stable part in the copolymeric chain). At low temperature, the structural change between the crystalline forms with increasing TrFE content is detected clearly. At room temperature, the morphology of VDF-rich copolymers is readily analyzed, two components having the same ^{1}H and ^{19}F ratios. On the other hand, below 70 mol % VDF, both components have different ^{1}H and ^{19}F ratios, which implies segregation between TrFE-rich and VDF-rich sequences.[45d]

In their very interesting chapter, Harris et al.[45d] reported the microstructure of a poly(VDF-*co*-TrFE) copolymer of 71:29 composition by ^{19}F NMR. They showed that there is 5 mol % diads in the oligo(TFE) blocks and 2.5 mol % head-to-head defects in the oligo(VDF) blocks.

Actually, a poly(VDF-*co*-TrFE) copolymer of composition 70:30 has a T_g of 0 °C.

Yagi and Tatemoto[143] assessed the reactivity ratios of both comonomers from solution copolymerizations, as follows: $r_{VDF} = 0.70$ and $r_{TrFE} = 0.50$ at 22 °C,.

While expensive because of the price and hazards of TrFE,[133] these copolymers have found applications in various fields thanks to their piezo-, ferro-, and pyroelectric properties[145] since the incorporation of TrFE into PVDF induces the appearance of a ferroelectric-to-paraelectric (F−P) phase transition below the melting temperature of the polymer crystals.[146] This F−P phase transition (called Curie transition) is associated with a crystalline phase change from polar (β) phase to nonpolar (α) phase and the copolymer conformation changes from all-trans to trans−gauche.[146c]

As expected, Curie temperature (T_c) lowers with increasing TrFE content in the PVDF chain. However, it reaches the lowest point (ca. 96 °C) after incorporating ca. 20 mol % TrFE units, which makes a dramatic difference from that of poly(VDF-*co*-TrFE) copolymers prepared by direct copolymerization for which the T_c value at similar copolymer composition is higher than 130 °C and continuously decreases before reaching a constant value of 65 °C.[146b−d]

Ferroelectric poly(VDF-*co*-TrFE) copolymers were inflated into three-dimensional periodic opal lattices with nanosilica opal diameter of 180−300 nm to form periodic composite structures. Further, this method was efficient to prepare inverse copolymer opals where the copolymer could nearly completely fill the voids in the silica opal.[147]

In addition, Ohigashi et al.[148] established that the remanent polarization of poly(VDF-*co*-TrFE) copolymers was 100 mC·m^{-2} in 1995, while Fang et al.[149] reported an intriguing phenomenon of polarization enhancement for poly(VDF-*co*-TrFE) 75/25 mol % copolymer films under cyclic electric field in 2008. The copolymer film, initially subjected to electric cycling at a comparatively low field magnitude, led to an increase of the remanent polarization with increasing field cycles. These authors also examined the morphology and microstructure changes during the electric cycling. They suggested that the polymer chains in the interfacial layers between the crystalline and amorphous regions gradually increased in the ordering degree, which contributed to polarization enhancement during the electric cycling.

However, these remanent polarization values seem lower than that of a VDF telomer[150] containing 14 or 17 VDF units (thus having a lower molecular weight than PVDF). Among organic ferroelectrics, it has the largest reported remanent polarization. In addition, the piezoelectric coefficient of oligo(VDF) was greater than that of poly(VDF-*co*-TrFE) copolymer. A film composed of oligo(VDF) was thin and uniform and was evaluated as a prototype sensor device for medical tactile sensors (Figure 11).

As a matter of fact, the incorporation of a small percentage of CTFE (or $F_2C{=}CHCl$) units in the poly(VDF-*co*-CTFE) copolymers is very effective in altering the Curie temperature[125] and the activation energy of the ferro−paraelectric phase transition, without significant reduction of the overall crystallinity and dielectric constant.

Dielectric and electroactive strain behaviors of poly(VDF-*ter*-CTFE-*ter*-TrFE) terpolymers containing different CTFE contents from room temperature down to cryogenic temperatures have been investigated by Yu et al.[151] Increase in CTFE concentration slightly shifted the temperature where the maximum dielectric constant occurred at lower temperature, whereas high electroactive strain (ca. 1%) was noted for all compositions. Furthermore, high stress level was

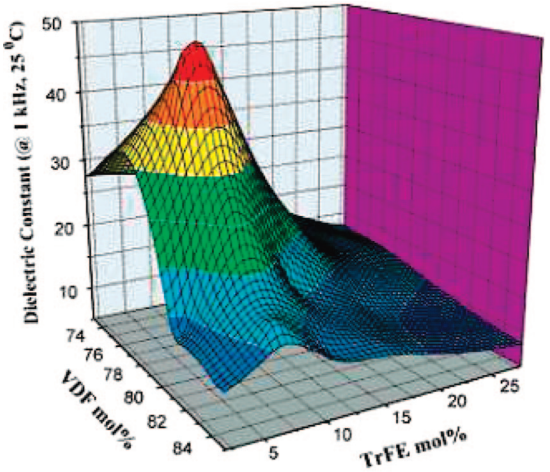


Figure 15. A three-dimensional plot of room-temperature dielectric constants at 1 kHz for the P(VDF−CTFE−TrFE) terpolymers. Reproduced with permission from ref 126a). Copyright 2006 American Chemical Society.

decreased at cryogenic temperatures hence leading to promising space technology applications.

In addition, Lu et al.[126a] have assessed the dielectric constant of the copolymers versus the content of both comonomers and showed a maximum value of 47 at 1 kHz at 25 °C (Figure 15), though the maximum residual polarization attained with a poly(VDF-*co*-TrFE) copolymer film containing 80 mol % VDF (the crystallinity of which was 50%) was 3.0 $mC \cdot cm^{-2}$.

As shown for PVDF, nanocomposites based on poly(VDF-*co*-TrFE) copolymers have enhanced electrical properties thanks to polyaniline conductive nanofibers.[152] These polyaniline (PANI) nanofibers doped by protonic acids have a high dispersion stability in poly(VDF-*co*-TrFE) copolymer and lead to percolative nanocomposites. A near 50-fold rise in the dielectric constant of the ferroelectric polymer matrix has been observed. Percolation thresholds of the nanocomposites are relevant to doping levels of PANI nanofibers and can be as low as 2.9 wt % for fully doped materials. The interface between conductive nanofiber and polymer matrix plays a crucial role in the dielectric enhancement of the nanocomposites in the vicinity of the percolation threshold. Compared with other dopants, perfluorosulfonic acid resin is better at improving the performance of nanofibers. Noteworthy, these nanocomposites can be utilized for potential applications as high energy density capacitors, thin-film transistors, and nonvolatile ferroelectric memories.

In another topic, Poulsen et al.[153] have successfully prepared Langmuir−Blodgett films based on poly(VDF-*co*-TrFE) copolymers.

In conclusion, poly(VDF-*co*-TrFE) copolymers are semicrystalline whatever the compositions and have demonstrated exceptional dielectric properties, which enable them to find interesting applications as capacitors, electroactive polymers or actuators (even under cryogenic conditions), and nanocomposites.

3.2.3. Poly(VDF-co-hexafluoropropylene) Copolymers

3.2.3.1. History and Characteristics of Poly(VDF-*co*-HFP) Copolymers. In the 1940s and 1950s, Handford (working for M.G. Kellogg) remembered the earlier work on VDF copolymers carried out by Ford at DuPont and produced a very stable elastomer of VDF and CTFE (under the Kel-F trade name). Subsequently, the 3M Company bought the rights. The DuPont company reacted, and under the Direction of Schroeder, this company developed original poly(VDF-*co*-HFP) copolymers, a family of elastomers under the Viton trade name. This pushed the scientists at DuPont to focus on a variety of elastomers based on VDF and HFP (Viton A) and based on VDF, HFP, and tetrafluoroethylene (TFE) (Viton B). In fact, after examining the research samples on Viton A samples, the Air Force claimed that they were superior materials to anything they had. These polymers have better thermal stability and inertness to chemicals and a lower swelling to oils and petroleum than the TFE copolymers.[154] Viton B was developed and found to be even more resistant to temperature and solvents. Both these F-elastomers, which had service temperatures of about 200 °C, were commercialized in 1957. Viton elastomers are still produced though a part of the DuPont de Nemours Company became DuPont Dow Elastomers LLC, from the joint venture with Dow Chemicals and DuPont formed in 1996, and have been called DuPont Performance Elastomers since mid-2005. Then, Fluorel copolymers became available from 3M, which has been called Dyneon since 1999. Poly(VDF-*co*-HFP) copolymers have also led to various kinds of products according to the content of hexafluoropropylene. At less than 15−19 mol % HFP, the resulting copolymers show thermoplastic properties[3,5−8,155,156] (Figure 16), while those containing a higher HFP content behave as elastomers.[3,5−8,156] Ajroldi et al.[157] have demonstrated that a composition of 20−21 mol % HFP represents the best compromise between the requirements of a low T_g and a fully amorphous elastomer. From both academic and applied points of view, Apostolo et al.[158] have carried out interesting investigations on the kinetics of emulsion copolymerization of VDF and HFP, monitoring all the parameters of the experimental conditions and using an appropriate model.

Thermoplastic poly(VDF-*co*-HFP) copolymers are currently produced by Arkema or Solvay under the Kynar or Solef trade names, respectively, while elastomeric poly(VDF-*co*-HFP) copolymers are marketed by Daikin, DuPont Performance Elastomers, 3M/Dyneon, Solexis. and the S.V. Lebedev Synthetic Rubber Institute (VNIISK) called Daiel, Viton, Dyneon Copolymers, Tecnoflon, and Fluorelast, respectively. In addition, the 3F company in China and KCCE, Kirovochepetsk, in Russia are presently producing these elastomers.

In 1960, Ferguson[45a] pioneered the ^{19}F NMR solution-state spectroscopy of poly(VDF-*co*-HFP) copolymers, which has been later deeply investigated by Pianca et al.[159] Later on, ^{19}F NMR magic angle spinning spectra of poly(VDF-*co*-HFP) copolymers were recorded by Isbester et al.,[45e] while on the other hand, Harris et al.[45d] have supplied very interesting ^{19}F high-resolution solid-state (magic angle spinning) NMR spectra of a commercially available Viton copolymer providing peak decomposition and structural assignment as well as relaxation time associated with all the resonance peaks.

In addition, Moggi's group[160] have correlated the microstructures of these poly(VDF-*co*-HFP) copolymers with their T_g's and melting temperatures, and their crystallinity (assessed by DSC and by X-ray diffraction, respectively). They observed that the presence of a small amount of HFP in these poly(VDF-*co*-HFP) copolymers did not affect the polymorphism of PVDF. Later on, Tarascon et al.[161] revisited the thermal behaviors of various copolymers containing different contents of VDF and HFP, showing, as expected, that the

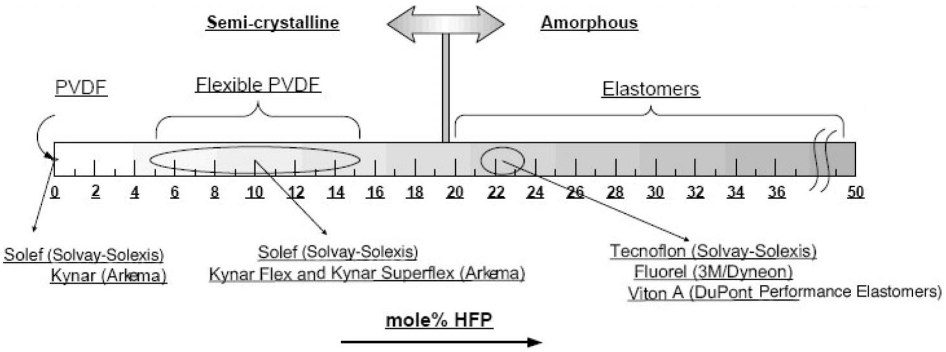


Figure 16. Semicrystalline or amorphous poly(VDF-*co*-HFP) copolymers according to the content of HFP in the copolymer (reproduced with permission from ref 39. Copyright 2007 American Chemical Society.

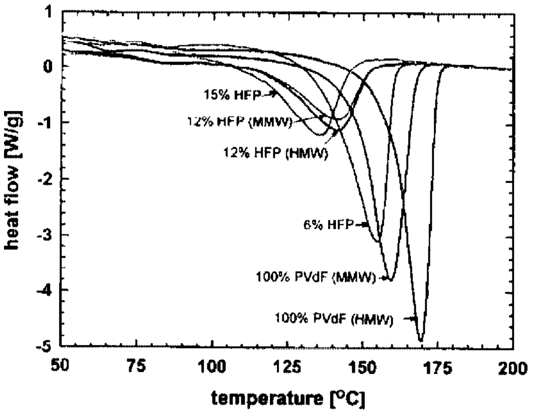


Figure 17. Differential scanning calorimetry thermograms of poly(VDF-*co*-HFP) copolymers with different HFP contents (HMW and MMW stand for high molecular weight and medium molecular weight, respectively). Reproduced with permission from ref 161. Copyright 1996 Elsevier.

higher the content of HFP in thermoplastic, the lower the melting point of the copolymer (Figure 17).

Furthermore, an interesting comparison of the T_g values of fluoroelastomers containing VDF was realized by Van Cleef[11] showing that their T_gs could not be lower than −29 °C.

Interestingly, DeSimone et al.[39,40,156] and Howdle's team[41] have carried out original radical copolymerizations of VDF and HFP in supercritical CO_2 medium which enabled them to solubilize the resulting poly(VDF-*co*-HFP) copolymers. Depending on the VDF content, these copolymers exhibited either thermoplastic or elastomeric morphologies (Figure 16).

Even more recently, Asandei et al.[162] investigated the UV-irradiated copolymerization of VDF with HFP, simultaneously initiated by *tert*-butyl peroxide (DTBP) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (BTBDMH). For a given total reaction time, a continuous increase in conversion was observed with increasing irradiation time and faster rates were observed for tetrafunctional BTBDMH than for difunctional DTBP. The molecular weights and polydispersity indices remained relatively constant. The authors claimed that UV irradiation was essential for the generation of initiator-derived radicals at room temperature but did not induce pure photopolymerization in the absence of the initiator.[162] Further work was also investigated under various temperatures ranging from 25 to 90 °C in different solvents. While many conventional thermal or redox systems failed to initiate in this temperature range, oxygen-centered radicals initiated the copolymerization even at room temperature, especially under UV irradiation. The trend in initiator efficiency (*tert*-Bu peroxybenzoate < dicumyl peroxide < di-*tert*-Bu peroxide) paralleled the increase in nucleophilicity of these radicals. The authors also observed that the solvent effect (acetonitrile = DMSO ≫ trifluorotoluene) correlated with the solvent polarity.[162b]

3.2.3.2. Properties and Applications. Poly(VDF-*co*-HFP) copolymers can be either thermoplastic or elastomers according to the HFP content, and their cross-linking enables production of various items tolerant of hostile environments,[6−9] such as gaskets, O-rings, or diaphragms for aerospace, automotive, or oil industries. Exotic copolymers also exhibit certain dielectric properties, yet lower than those of poly(VDF-*co*-TrFE) copolymers. For example, similarly as above, the room-temperature terpolymerization of VDF with HFP and methacryloxypropylheptacyclo-pentyl-T8-silsesquioxane (MP-POSS), readily initiated by DTBP under UV radiation, leads to polymers having potential applications as high dielectrical constant materials.[162c]

As for dielectrical properties, Wolak et al.[163] have investigated the effect of introducing a multilayer microstructure on the dielectric properties of polymer materials in 32- and 256-layer films with alternating polycarbonate (PC) and poly(VDF-*co*-HFP) layers.[163] The permittivity, dielectric loss, dielectric strength, and energy density have been measured as a function of the relative PC/copolymer volume concentrations. Permittivity follows an effective medium model, while the dielectric strength is typically higher than that predicted by a volume fraction based weighted average of the components. Energy densities as high as 14 J·cm^3, about 60% greater than those of the component polymers, are measured for 50/50 wt % PC/copolmer films.

Other areas such as polymer blends have been explored, and Wang and Tang[164] blended poly(VDF-*co*-HFP) copolymers with poly(vinyl pyridine). They demonstrated the miscibility from the assessment of a unique T_g for each composition. In addition, poly(VDF-*co*-HFP) copolymers/ionomer blends have led to deeper investigations, as summarized below.

3.2.3.3. Poly(VDF-*co*-HFP) Copolymers Involved in Energy-Related Applications. In fact, poly(VDF-*co*-HFP) copolymers have also found various applications in the energy area (membranes for fuel cells, rechargeable lithium ion batteries, dye-sensitized solar cells). Nonexhaustive examples are listed below.

3.2.3.3.1. Polymer Electrolyte Membrane for Fuel Cell (PEMFC). The advantage to involve these copolymers in fuel cell membranes arises from the high molecular weight poly(VDF-*co*-HFP) copolymers that supply the mechanical strength and, as mentioned above for PVDF, can also be blended with various proton conducting systems. Fortunately,

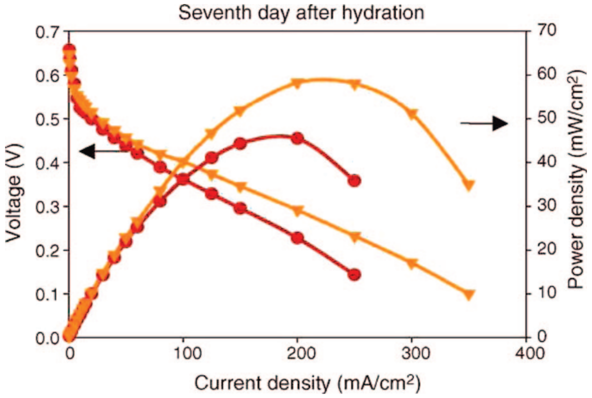


Figure 18. Polarization curves of coated Nafion (orange) and virgin Nafion 117 (brown) at 30 °C. Reproduced with permission from Elsevier, ref 167, copyright 2006.

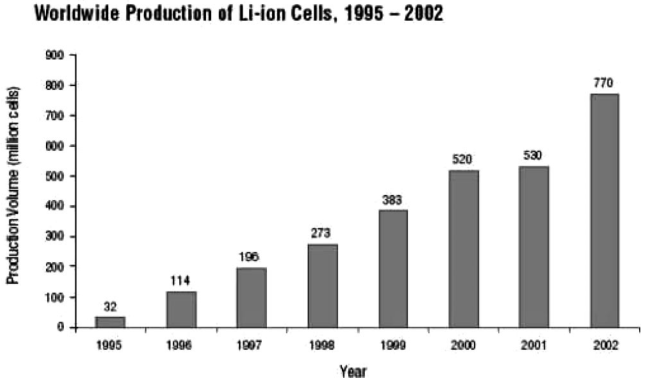


Figure 19. Evolution of lithium ion cells versus years.

these membranes strongly resist acidic media, in which poly(VDF-*co*-HFP) copolymers are stable, in contrast to alkaline ones where they undergo dehydrofluorination.[165]

Song et al.[166] have conceived membranes made of Nafion and poly(VDF-*co*-HFP) copolymers, both components showing a high miscibility up to 60% Nafion fraction. Advantageously, the hydrophobic VDF-containing copolymers reduced water uptake of the resulting membranes, though conductivity values were lower than that of Nafion115. MAEs were prepared from these membranes (35 μm thick), doped with sulfuric acid and hot pressed between catalyzed carbon paper ELAT electrodes. A 25 cm^2 single cell was installed and delivered a maximum power of 440 mW$\cdot$cm^{-2} at 900 mA$\cdot$cm^{-2} under H_2/O_2 flows. It was comparable to the performance of Nafion115 under the same operating conditions.

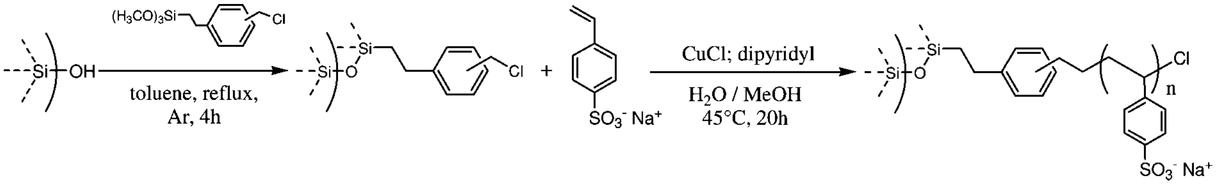
Cho et al.[167] have elaborated membranes from miscible poly(VDF-*co*-HFP) copolymer (15 mol % HFP and M_n = 380 000 g$\cdot$mol^{-1})/Nafion 117 blends. A pretreated Nafion 117 membrane was immersed into a poly(VDF-*co*-HFP) copolymer/Nafion solution in DMF to coat it with a poly(VDF-*co*-HFP) layer (ca. 1 μm). Objectives were (i) to enhance electrode/membrane compatibility of a DMFC and (ii) to reduce the methanol crossover from anode to cathode. Interestingly, the coated Nafion exhibited better performance in DMFC than the uncoated one, as evidenced by the polarization curves (Figure 18).

In 2008, Niepceron et al.[168] elaborated composite membranes showing potential applications as PEMFCs composed of a poly(VDF-*co*-HFP) copolymer (16 wt % HFP, molecular weight of 350 000 g$\cdot$mol^{-1}, and T_m = 135 °C) embedded with polystyrene sulfonic acid-grafted silica particles (7 nm diameter and 390 m$^2\cdot$g^{-1} of specific surface). These membranes were prepared in three steps (Scheme 12): (i) condensation of trimethoxysilyl chloromethyl styryl onto the surface of the silica particles via the hydroxyl groups leading to original particles containing benzyl chloride end groups; (ii) these end groups could initiate the atom transfer radical polymerization (ATRP) of sodium styrene sulfonate via the "grafting from" procedure yielding hydrophobic polymer (average particle size of 370 nm, molecular weight of 54 000 g$\cdot$mol^{-1}, PDI > 1.5, and ionic exchange capacity of 3.0 ± 0.4 mequiv$\cdot$g^{-1}); (iii) extrusion or casting of the resulting membranes to favor a homogeneous dispersion of the particles in the fluorinated matrix, which brought the mechanical properties. Depending on the process, the authors observed various morphologies of the membranes, from particle aggregates to cocontinuous domains, by confocal fluorescence microscopy. They noted that the percolation threshold was achieved for ca. 30 wt % loading. Niepceron et al.[168] showed that the ohmic resistance versus the thickness of the composite membranes was not a linear relationship but sedimentation (inhomogeneous dispersed particles) occurred from 60 μm and the polarization curve gave the best results for a membrane of 30 μm. Finally, a satisfactory balance between the proton conductivity (σ = 95 ± 6 mS$\cdot$cm^{-1} at 20 °C) and reasonable water uptake was achieved from a loading of 40−60 wt %.

On the other hand, Scrosati's team[169] incorporated original ionic liquids, by neutralizing tertiary amines with *N,N*-bis(trifluoromethanesulfonyl)imide into poly(VDF-*co*-HFP) copolymer matrix for a high-temperature polymer electrolyte fuel cell membrane endowed with an ionic conductivity of 10^{-2} S$\cdot$cm^{-1} at 140 °C.

3.2.3.3.2. Rechargeable Lithium-Ion Batteries. Another application claimed by various authors[75,161,170−172] stems from the interesting properties of poly(VDF-*co*-HFP) copolymers as a host for liquid electrolytes in rechargeable lithium batteries. Several examples are suggested hereafter. There is an increasing interest and use for lithium ion batteries as evidenced by the linear evolution of production volume of Li-ion cells versus years (Figure 19). In 1975, Feuillade and Perche[173] pioneered the use of several gelled copolymer electrolytes based on commercially available matrices such as polyacrylonitrile, poly(vinyl butyral), poly(vinyl pyrrolidinone), and poly(VDF-*co*-HFP) copolymers as electrolytes of Li/CuS batteries. On the other hand, because the liquid electrolyte uptake sometimes decreases the mechanical strength of poly(VDF-*co*-HFP) gelled electrolyte, Wang et

Scheme 12



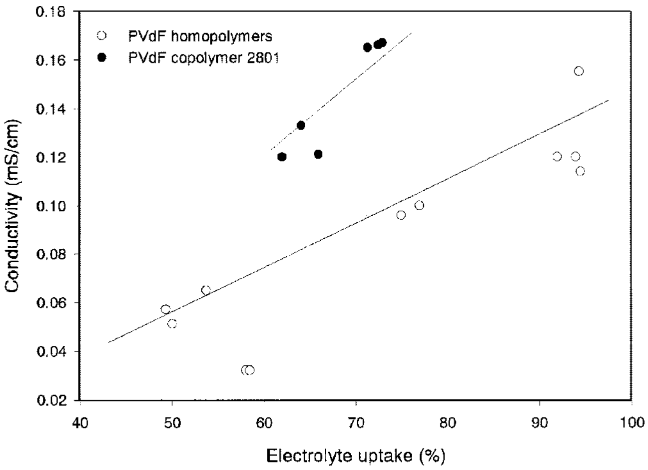


Figure 20. Conductivity as a function of the electrolyte uptake for low-porous PVDF and poly(VDF-*co*-HFP) copolymers (PVDF copolymer 2801) membranes. Reproduced with permission from Elseveir, ref 170b, copyright 2000.

al.[174] have reported the use of a microporous polyolefin to improve mechanical properties.

A new strategy to increase the ionic conductivity of polymeric gel electrolytes has been proposed, either by embebbing the liquid electrolyte in the pores[175] or by insert nanoparticles[176] or ionic liquids.[177] Indeed, Tarascon's team[161,171] showed that poly(VDF-*co*-HFP) copolymers can uptake more electrolyte solution than PVDF because of their lower degree of crystallinity. Interestingly, the group of Watanabe[170b] has observed lower conductivity values of PVDF than poly(VDF-*co*-HFP) copolymer containing 12 mol % HFP and 6% head-to-head defects (i.e., $-CH_2CF_2-CF_2CH_2-$ diads, see section 2.3.1) of chaining versus the electrolyte uptake (Figure 20).

Further data on the swelling behavior of copolymers based on VDF, their kinetics, safety concerns, electrochemical properties of VDF-based separators and battery performances have been well documented by Sanchez et al.[75]

More recent investigations[176] on poly(VDF-*co*-HFP)/silica composites have shown the beneficial effect of SiO_2 in (i) providing better mechanical properties to the conducting membranes and (ii) increasing the porosity of the dry copolymers. Consequently, the volume of the liquid phase in the produced gel becomes higher and the conductivity increases.

More recently, Ye et al.[177] have used 1-methyl-3-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (P_{13}TFSI) as ionic liquid and obtained dimensionally stable, elastic, flexible, non-volatile polymer-gel electrolytes with high electrochemical stabilities, high ionic conductivities, and other desirable properties. They were synthesized by dissolving Li imide salt (LiTFSI) in P_{13}TFSI ionic liquid and then mixing the electrolyte solution with poly(VDF-*co*-HFP) copolymer.

In addition, to improve the discharge capacity in lithium ion microbatteries, a thick-film cathode was fabricated by a screen printing using $LiCoO_2$ pastes.[178] An all solid-state microbattery could be assembled using sputtered LiPON electrolyte, an evaporated Li anode, and printed $LiCoO_2$ cathode films without delamination or electrical problems. This delamination was overcome by using a poly(VDF-*co*-HFP) gel electrolyte, which enhanced the contact area and adhesion force between cathode and electrolyte and could increase the discharge capacity from 7 μA·h·cm^{-2} to 164 μA·h·cm^{-2} (~110 mA·h·g^{-1}). Interestingly, the authors claimed that the cell could be fabricated in a leakage-free process, hence resolving safety problems for a microbattery.

Another process to improve the efficiency of the lithium ion batteries in which poly(VDF-*co*-HFP) copolymers were used as the separator and the binder for electrodes has been achieved by cross-linking these copolymers in the presence of an aliphatic diamine as cross-linking agent.[179] Such a strategy offers mechanically resistant membranes with improved thermal and chemical stabilities and makes the binder insoluble in the electrolyte. Hence, the resulting secondary batteries[179] showed reversible capacity retention higher than 80% even after 50 cycles.

An interesting approach to obtain an original homogeneous blend of poly(ethylene oxide) (PEO) and poly(VDF-*co*-HFP) copolymer has been proposed by Cheng et al.[180] who synthesized a semi-IPN by dissolving a poly(VDF-*co*-HFP) copolymer with an α,ω-dimethacrylate PEO, followed by a free-radical copolymerization. The solvent evaporation generated some porosity. The resulting membrane was swollen by 1 M $LiPF_6$ in ethylene carbonate−dimethylcarbonate, and the liquid uptake decreased with the content of PEO network, though the conductivities of the swollen membranes reached 1.5 mS·cm^{-1} at 25 °C.

Such a strategy has also been investigated by Korean authors[181] who noted an enhancement of the thermal stability of poly(VDF-*co*-HFP) copolymer gel polymer electrolyte (GPE) by cross-linking with α,ω-diacrylate PEO. The resulting semi-IPN structure reduced the crystallization of the fluorinated copolymer and showed better affinity with organic liquid electrolyte in a cell composed of $LiCoO_2$/GPE/Li foil.

Commercially available Nafion 117 membrane was lithiated[182] (after classical treatment, the Nafion grains were immersed into 1 M LiOH solution) and mixed with poly(VDF-*co*-HFP) copolymer containing 12 wt % HFP and fumed nanosilica (12 nm). Afterward, the mixtures were cast as polymer electrolyte films. The ionic conductivities, which rose rapidly to 10^{-4} S·cm^{-1}, depended on the Li^+ ion content and on the addition of SiO_2. Wang et al.[182] suggested that the high conductivity (Figure 21) could be attributed to these nanoparticles, which have a drastic influence on the morphology.

In addition, these authors also proposed a model (Figure 22) suggesting an interaction between the ionic groups and the polymer backbone in the Nafion−Li/poly(VDF-*co*-HFP) copolymer blend electrolyte.

3.2.3.3.3. Solar Cells. Another original topic of energy-related applications concerns dye-sensitized solar cells (DSSC).[183] Microporous polymer electrolytes based on poly(VDF-*co*-HFP) hybrid with different amounts of either silica nanoparticles (to solidify 3-methoxypropionitrile-based liquid electrolytes)[183a] or TiO_2 nanoparticles[183b] were prepared. The microporous polymer electrolyte with TiO_2 nanoparticles exhibited better ionic conductivity compared with the original poly(VDF-*co*-HFP) copolymer electrolyte with an optimal ionic conductivity of 0.8 mS·cm^{-1} obtained with 30 wt % TiO_2 nanoparticles. When assembled with 30 wt % TiO_2 nanoparticle-modified quasi-solid-state electrolyte, the dye-sensitized TiO_2 nanocrystalline solar cell exhibited a light-to-electricity conversion efficiency of 2.465% at light intensity of 42.6 mW·cm^{-2}, which is much better than the performance of original poly(VDF-*co*-HFP) microporous polymer electrolyte DSSC.[183b]

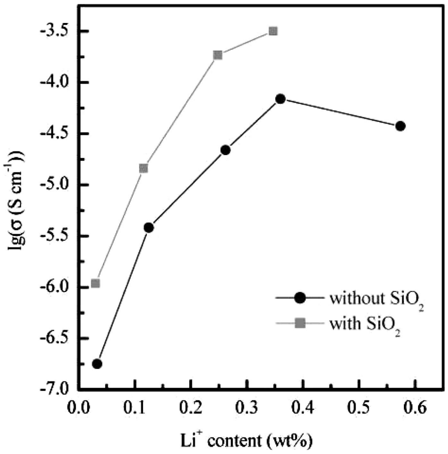


Figure 21. The Li^+ content of gel polymer electrolyte without SiO_2 (●) and with SiO_2 (■) dependence on the ionic conductivity. Reproduced with permission from ref 182. Copyright 2004 American Chemical Society.

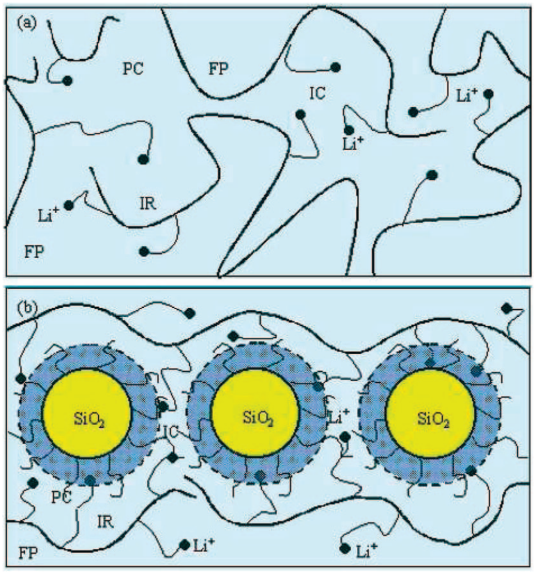


Figure 22. The two models proposed for the interaction between polymer and polycarbonate in the Nafion−Li/PVDF−HFP blend polymer electrolyte membrane (a) without SiO_2 and (b) with SiO_2. The fluorocarbon phase (FP), interfacial region (IR), and ionic clusters (IC) are shown. Reproduced with permission from ref 182. Copyright 2004 American Chemical Society.

In conclusion, a wide range of poly(VDF-*co*-HFP) copolymers may be produced, and according to their HFP percentages, they can behave as thermoplastics, elastomers, or thermoplastic elastomers. They exhibit a high thermostability and, when cross-linked, show a high insolubility, enhanced mechanical properties, and resistance to oils, fuels, and chemicals. Hence, they can withstand a hostile environment. However, the glass transition temperatures of these cross-linked copolymers are a bit high for potential applications at low temperatures or for items undergoing cryogenic conditions. Nevertheless, these copolymers have already been involved in various applications, and in the last five years, increasing academic and industrial research has suggested them for various uses in the field of energy (PEMFCs, Li ion batteries, solar cells, etc.).

3.2.3.4. Poly(VDF-*ter*-HFP-*ter*-comonomer) Terpolymers. Various examples of poly(VDF-*ter*-HFP-*ter*-comonomer) terpolymers are given hereafter, the most important in volume and applications is when the comonomer is tetrafluoroethylene (TFE). Depending on VDF, HFP, and TFE contents, poly(VDF-*ter*-TFE-*ter*-HFP) terpolymers can be elastomers, thermoplastics, or thermoplastic elastomers (marketed by DuPont Performance Elastomers, Solvay Solexis, 3M/Dyneon, or Daikin under the Viton B, Tecnoflon, THV (or Dyneon terpolymers), or Dai-el trademarks, respectively (Table 1). Somewhat exhaustive interesting reviews or book have been prepared by Hull et al.[115] or by Moore.[5]

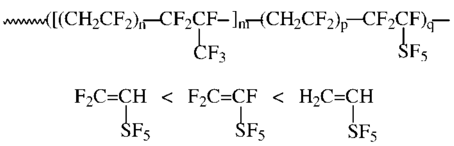
Elastomeric terpolymers of VDF, TFE, and HFP provide gum stocks for high-performance fluoroelastomers, while for various amounts of these three fluorolefins, thermoplastic elastomers can be produced, as well-reported by Hull et al.[115] Indeed, depending on the respective amounts of monomers, the elastomeric behavior (the region of the triangle the summits of which are VDF, HFP, and TFE encompasses a composition of 20−70% VDF, 20−60% HFP, and 0−40% TFE][6−8] may fall into a thermoplastic elastomer (composition of 15−20% or 70−80% VDF, 13−25% or 80−85% HFP, and 15−30% or 80−85% TFE) nicely explained by Logothesis[6] or Hull et al.[115] and also by the 3M company.[184] Melting points of the thermoplastics range between 170 and 220 °C. For a structural point of view, it is required that the microstructure of the elastomers contains about one HFP unit for every 2−4 of the other monomer units to prevent any crystallization of the terpolymer and to ensure an amorphous macromolecule. Although no adjacent HFP units were found in the microstructure[159] (its reactivity ratio was 0), a more recent telomerization of HFP gave evidence of the presence of two consecutive HFP units when the reaction was carried out at higher temperatures[185] in the presence of α,*ω*-diiodoperfluorobutane. In addition, careful liquid state ^{19}F NMR spectroscopy of these poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers was achieved by Dec et al.[186] while ^{19}F NMR magic angle spinning spectra of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers were recorded for the first time by Isbester et al.[45e]

THV medical devices are coated with terpolymers of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride (THV).[187] The mole fractions of TFE, HFP, and VDF can be in the ranges from about 0.005 to about 0.85, 0.005 to 0.85, and 0.005 to 0.990, respectively. Elastomers or TPEs have found applications as fuel hoses.[5,115] Moreover, the THV coating on the implantable medical devices is advantageously biocompatible.[187]

Basic research has also been published about these terpolymers. A first recent example, reported by Emmons et al.,[188] deals with the high-pressure Raman spectroscopy and X-ray diffraction of THV 500, for which changes in interatomic spacing and shifts of the vibrational bands were compared with those of PTFE, showing the effects of copolymerization and reduced crystallinity.

A second example, reported by two German laboratories,[189] displays designed terpolymerizations of VDF with HFP and TFE to produce various samples of two different morphologies: straight linear topology or model poly(VDF-*ter*-TFE-*ter*-HFP) terpolymers with an interesting controlled amount of long chain branching (LCB). The absolute molar mass distributions of the linear THV terpolymers were assessed by size exclusion chromatography coupled with multiangle light scattering.[189a] The presence of the LCB was evidenced by the reduced radius of gyration in the high molar mass region[189a] and by dynamic mechanical measurements.[189b] These branched terpolymers behaved in a complex thermorheological way. Indeed, their zero-shear-

Scheme 13



$$\sim[(CH_2CF_2)_n-CF_2CF(CF_3)-]_m-(CH_2CF_2)_p-CF_2CF(SF_5)_q-$$

$$F_2C=CH(SF_5) < F_2C=CF(SF_5) < H_2C=CH(SF_5)$$

rate viscosities were significantly higher than those of linear terpolymers with equivalent molecular weights.[189b] Based on further rheological properties in solution and in the molten state, the authors demonstrated that the linear behavior of the melts could favorably be used to get an insight into the molecular architecture of THV terpolymers.

Several termonomers other than tetrafluoroethylene (TFE) have also been incorporated successfully to lead to poly(VDF-*ter*-HFP-*ter*-M) terpolymers where M represents CTFE,[190] α-trifluoromethacrylic acid,[191] hexafluoroacetone,[192] fluorinated ketones such as $O=C(R_F)_2$,[193] $F_2C=CFO-Ar-X$ ($X = Br$[194] or SO_2Cl[195]), and methacryloxypropylheptacyclopentyl-T8-silsesquioxane (MP-POSS)[162c] as reported in section 3.2.3.2.

Lannuzel et al.[190] inserted CTFE as a termonomer in the suspension radical terpolymerization of VDF with HFP, which led to a thermoplastic containing 95.0 mol % VDF, 1.6 mol % CTFE, and 3.4 mol % HFP having a melt flow index of 2.26 (21.6 kg) and a melting temperature (T_m) of 141 °C.

The above other trifluorovinyloxy aryl termonomers behave as HFP or PMVE: they do not homopolymerize under radical conditions or copolymerize with HFP but terpolymerize in the presence of VDF and HFP. This is also the behavior of $Y_2C=CYSF_5$[196] ($Y = H$ or F) reported in the radical terpolymerization of VDF and HFP with pentafluorosulfanyl derivatives, which led to original SF_5-containing materials. Molar masses and thermal properties were also assessed.[197] The overall structures of the obtained copolymers and the increasing order of reactivity in terpolymerization with VDF and HFP (though the radical copolymerization with VDF was smoother than those involving PMVE, HFP and PPVE) were as displayed in Scheme 13.

3.2.4. Poly(VDF-co-tetrafluoroethylene) Copolymers

Poly(VDF-*co*-TFE) copolymers are statistic, as most VDF-containing copolymers.

Radical copolymerizations of VDF and tetrafluoroethylene (TFE) have been carried out in emulsion[198-201] or under "exotic" plasma initiation.[202] Several kinetics of radical copolymerization[200,201] have been investigated leading to the reactivity ratios of both comonomers $r_{VDF} = 0.11$[200] or 0.32[201] and $r_{TFE} = 1.06$[200] or 0.28[201] at 25 °C (Table 2).

Deeper studies on their microstructures by ^{19}F NMR spectroscopy have also been realized[203] just like the mechanism of this copolymerization. Actually, a Russian team[204] pointed out chain transfer and chain termination of primary and growing macroradicals, along with branched structures, linked to their compositions and structures.

Regarding the properties, poly(VDF-*co*-TFE) copolymers have received increasing attention since the first discovery reported by Lovinger[205] in 1983 of these ferroelectric materials and the assessment of their Curie transitions. Earlier, Lando and Doll[206] noted that these copolymers were able to crystallize from the melt with the unit cell of the ferroelectric β phase, provided that they contained at least 7 mol % TFE. Piezoelectricity and pyroelectricity in poly(VDF-*co*-TFE) copolymers have been investigated by several authors.[207] Lovinger et al.[208] synthesized poly(VDF-*co*-TFE) copolymers over a full compositional range and their crystalline structures were studied at ambient temperature, as well as during heating to the melting point and subsequent cooling. The room-temperature structure changes from α-PVDF (for compositions with >93 mol % VDF) to β-PVDF (for 71−92 mol % VDF), to β-PVDF and PTFE-like (for 35−71 mol % VDF), and eventually to PTFE (for <34 mol % VDF). Between 72 and 82 mol % VDF, discrete and reversible Curie transitions have been observed, the same type as these authors already noted in poly(VDF-*co*-TrFE) copolymers that exhibit the same kind of paraelectric structures. In addition, the authors observed that the ferroelectric-to-paraelectric transition increased linearly with VDF content up to 81−82 mol %, where it was aborted by melting.

The maximum residual polarization attained for a poly(VDF-*co*-TFE) copolymer containing 80 mol % VDF (the crystallinity of which was estimated to be 50% by XRD) is $3.0\ mC \cdot cm^{-2}$.[45d]

Various applications of copolymers based on VDF and TFE and even other comonomers (i.e., vinyl esters) have been developed by Dupont Performance Elastomers,[209] which synthesized original elastomers based on VDF and TFE, while transparent films were obtained by the Kureha Chemical Industry[210] (≥85% transparency to parallel light for 30 μm films). Further, terpolymers based on VDF, TFE, and comonomers have also been synthesized and few examples involving ethylene, propylene, 3-ketofluoroglutaroyl halides, and perfluoromethyl vinyl ether (PMVE) are given hereafter. First, suspension terpolymerization of VDF with TFE and ethylene (E), which has been carried out by the same Japanese company, leads to dielectric materials (dielectric constant ≥4.0 and dielectric loss (tgδ < 0.5%)) endowed with excellent heat resistance.[211]

In poly(VDF-*ter*-HFP-*ter*-TrFE) terpolymers, various authors[6-8,10] claimed that a HFP unit surrounded by two VDF units or by VDF and TFE units was a useful structure curable by dinucleophiles, since the $-CF_2CF(CF_3)CH_2CF_2-$ diad could be dehydrofluorinated, leading to a reactive inner double bond. This double bond was also created to enable the addition of amino compounds (according to a Michael reaction).[10,179] Interestingly, an elegant strategy developed at the Asahi Glass Company,[212] to improve the well-known Aflas elastomers (based on alternating poly(TFE-*alt*-P) copolymer) dealt with the replacement of HFP by propylene (P), which made the resulting poly(VDF-*ter*-TFE-*ter*-P) terpolymers resistant to dehydrofluorination. This can be explained by the less electron-withdrawing CH_3 group than CF_3, which contributes to a lower acidity of the adjacent methylene and methine functionality. As a result, this terpolymer has been cross-linked with difficulty in the presence of conventional nucleophilic cure systems.[212]

Such poly(VDF-*ter*-TFE-*ter*-P) elastomers have found valuable applications in lithium-ion batteries[213] after coupling the electrode particles and cross-linking, which improves their mechanical properties. A stable specific capacity of ca. $800\ mA \cdot h \cdot g^{-1}$ has been achieved. Yuan et al.[200a] investigated the emulsion terpolymerization of VDF with TFE and perfluoromethyl vinyl ether (PMVE) and showed that the emulsion terpolymerization rate (R) depended on the stirring rate, on the concentrations of both the surfactant (S) and the initiator (I), and on the total gaseous pressure (P), as follows:

Table 2. Monomer Reactivity Ratios for the Copolymerization of VDF (Monomer A) with Other Fluoroalkenes (Monomer B)

monomer B	r_A	r_B	r_Ar_B	$1/r_A$	ref
$H_2C=CH_2$	0.05	8.5	0.42	20.00	299
$H_2C=CHOCOCH_3$	−0.40	1.67	−0.67	−2.5	280
	0.50	2.0	1.00	2.0	270
$H_2C=CHCF_3$	0.28	2.35	0.66	3.57	223
$H_2C=C(CF_3)CO_2H$	0.33	0	0	3.03	191
$H_2C=C(CF_3)OAc$	0.16	7.6	1.22	6.25	270
$FCH=CH_2$	0.17	4.2−5.5	0.71−0.94	5.88	300
	0.20−0.43	3.8−4.9	0.76−2.11	2.33−5.00	301
$H_2C=CFCF_2OR_F$	0.38	2.41	0.92	2.63	302
$F_2C=CHCF_3$	9.0	0.06	0.54	0.11	216
$F_2C=CHC_6F_{13}$	12.0	0.90	10.80	0.08	220
$F_2C=CHBr$	1.2	0.4	0.48	0.83	228h
$F_2C=CFH$	0.70	0.50	0.35	1.43	143
$CFCl=CF_2$	0.73	0.75	0.55	1.37	303
	0.17	0.52	0.09	5.88	13a
$CFBr=CF_2$	0.43	1.46	0.63	2.33	229a, 303
$CF_3-CF=CF_2$	6.70	0	0	0.15	304
	5.0	0	0	0.20	6
	2.45	0	0	0.40	305
	2.90	0.12	0.35	0.34	306
	5.13	0	0	0.19	41
	3.6	0	0	0.28	307
	3.6−4.6	0	0	0.22−0.28	156
	3.2	0	0	0.31	39
	3.3	0	0	0.86	308
$F_2C=CFOCF_3$	3.40	0	0	0.29	235
	1.06	0.11	0	0.94	200b
	2.53	0	0	0.39	244
$F_2C=CFOC_3F_7$	1.15	0	0	0.86	235
$F_2C=CFO(HFP)OC_2F_4SO_2F$	0.57	0.07	0.04	1.75	247
$CF_2=CFCH_2OH$	0.83	0.11	0.09	1.02	309
$CF_2=CF(CH_2)_2Br$	0.96	0.09	0.09	1.00	230c
$CF_2=CF(CH_2)_3OAc$	0.17	3.26	0.59	5.56	264
$F_2C=CF(CH_2)_3SAc$	0.60	0.41	0.25	4.07	265
$CF_2=CFCO_2CH_3$	0.30	0	0	3.33	276
$F_2C=C(CF_3)COF$	7.60	0.02	0.15	0.13	310
$F_2C=C(CF_3)OCOC_6H_5$	0.77	0.11	0.08	1.30	311
$CF_2=CF_2$	0.23	3.73	0.86	4.35	303
	0.32	0.28	0.09	3.13	201

$$R = 5.78 \times 10^{-3}[S]^{0.58}[I]^{0.4067}P^{1.540} \text{ at } 60\ °C$$

This group has also provided valuable data on the microstructure of the terpolymers by ^{19}F NMR and studied interesting kinetics of that terpolymerization.[200b]

From an industrial point of view, Viton GLT, marketed by DuPont Performance Elastomers, is a terpolymer based on VDF, PMVE, and traces of TFE that possesses remarkable properties. For similar applications, Daikin, 3M/Dyneon, and Solvay Solexis have also developed Daiel, Dyneon, and TecnoflonPL, respectively (Table 1). More recently, Hung and Tang[209] successfully incorporated PMVE and a vinyl ester (which could be further saponified) to produce original F-elastomers.

Finally, the solvent terpolymerization of VDF with TFE and 3-ketotetrafluoroglutaroyl fluoride, initiated by perfluoropropionyl peroxide, has been successfully achieved.[193] The resulting terpolymers, showing high molecular weights (the intrinsic viscosity was 2.37 $dL \cdot g^{-1}$), were pressed at 190 °C to provide a strong, flexible, cold-drawable film that creases without cracking.

3.2.5. Poly(VDF-co-pentafluoropropene) Copolymers

The main target to synthesize copolymers of VDF and 2-hydropentafluoropropene (PFP, $CF_3CH=CF_2$), produced by 3M[214] or Montedison,[215] was to compete with poly(VDF-*co*-HFP) copolymers, leading to original fluoroelastomers. But their lower thermostability could not allow these materials to find effective development. Nevertheless, a little basic research has been achieved:[216] the kinetics of copolymerization enabled a Russian team to assess the reactivity ratios of both comonomers (Table 2) showing that VDF is more reactive than its pentafluorinated partner ($r_{VDF} = 9.0$ and $r_{PFP} = 0.06$[216]). Indeed, quite a few fluorinated comonomers have been successfully used in radical copolymerization with PFP, such as CTFE, HFP, TFP, VDF, and perfluoromethyl vinyl ether (PMVE); under the same conditions, PMVE has led to higher yields. Recent work in our laboratory[217] has proposed the following decreasing order of reactivity of PFP in copolymers based on various F-alkenes: CTFE > HFP > TFP > VDF > PMVE. However, the obtained yields had a reversed tendency: HFP < CTFE < PMVE < VDF < TFP.

Ter- or tetrapolymers containing 23−65% VDF, 25−75% $F_2C=CFOR_F$, 0.3−0.5% 2-hydropentafluoropropene, and optionally 0−30% TFE have been prepared by Bowers and Schmiegel.[218] These copolymers exhibit excellent low-temperature properties and processability when cured with polyhydroxy compounds or amines. Recent developments involving various M termonomers[219] (such as CTFE, HFP, *tert*-butyl α-trifluoromethacrylate, (MAF−TBE), and PMVE) have led to original poly(VDF-*ter*-PFP-*ter*-M) terpolymers yielding a new generation of elastomers endowed with low glass transition temperatures (ca. −45 °C). Indeed, the increasing order of yields of these terpolymers is as follows: poly(VDF-*ter*-PFP-*ter*-HFP) > poly(VDF-*ter*-PFP-*ter*-

MAF−TBE) > poly(VDF-*ter*-PFP-*ter*-PMVE) > poly(VDF-*ter*-PFP-*ter*-TFP) terpolymers.

A longer 2*H*-perfluoroalkene, such as $F_2C{=}CHC_6F_{13}$[220] has also been synthesized from the dehydroiodination of $ICF_2CH_2C_6F_{13}$, which is the monoadduct telomer obtained from the radical telomerization of VDF with $C_6F_{13}I$.[221] The kinetics of copolymerization has led to the reactivity ratios $r_{VDF}= 12.0$ and $r_{F_2C=CHC_6F_{13}} = 0.90$ at 74 °C.[220]

3.2.6. Poly(VDF-co-3,3,3-trifluoropropene) and Poly(VDF-co-1,1,1,2-tetrafluoropropene) Copolymers

The Shin Etsu Company[222] has claimed the suspension copolymerization of VDF and 3,3,3-trifluoropropene (TFP). In both examples of the patent, the feed TFP is very low (1−1.2 mol %). The resulting copolymers have good flexibility, weather and corrosion resistance, electrical properties, and processability. A 93.2:6.8 VDF/TFP copolymer had torsional rigidity 2900 kg·cm^2 vs 7000 for VDF homopolymer. Recent investigations[223] have reported that TFP copolymerizes with VDF in all proportions. Unexpectedly, TFP is more incorporated in the copolymer than VDF, and their reactivity ratios have been assessed: $r_{VDF} = 0.28$ and $r_{TFP}= 2.35$ at 75 °C[223b] (Table 2). In addition to the above subsection, poly(VDF-*ter*-TFP-*ter*-PFP) terpolymers were also claimed in a patent as original fluoroelastomers.[219]

Recently, Honeywell International Inc.[224] has successfully produced moisture and oxygen barrier materials from poly(VDF-*co*-2,3,3,3-tetrafluoropropene) copolymers, which have never been reported in the literature.

3.2.7. Poly(VDF-co-bromofluoroalkenes) Copolymers

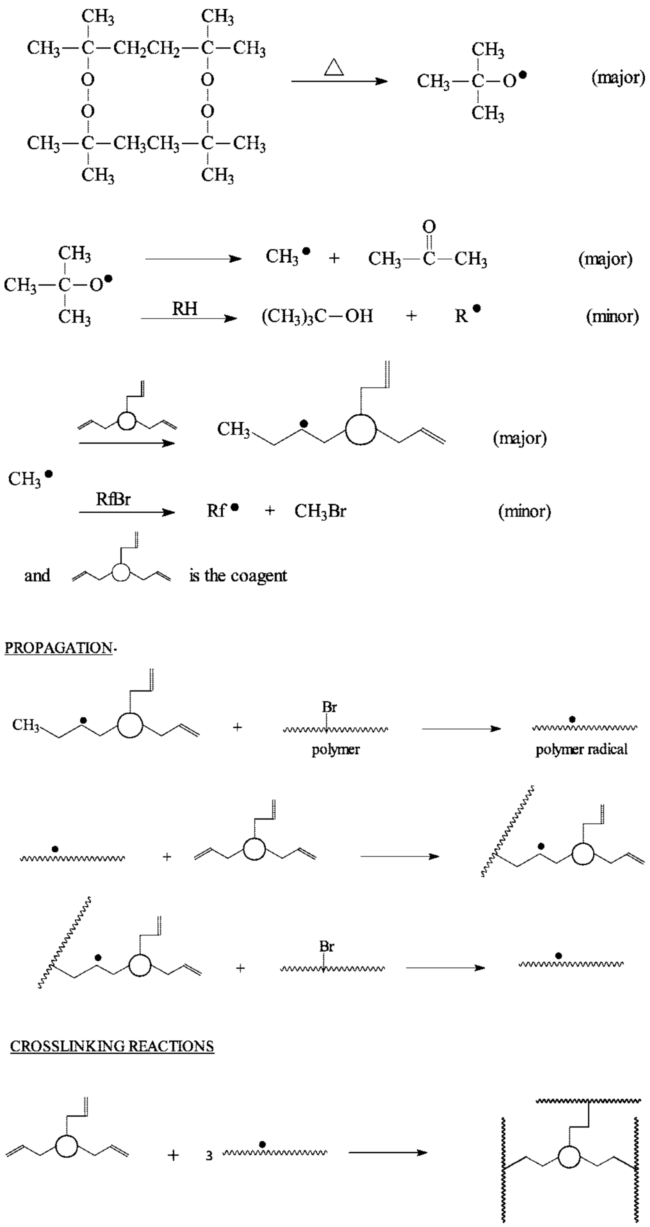
Comonomers bearing bromine end atom have already been involved in co-, ter-, or tetrapolymerization with VDF and have led to interesting cross-linkable copolymers, terpolymers, or tetrapolymers containing VDF units. Among them, eight have already led to various developments: $H_2C{=}CHCF_2Br$,[225] $H_2C{=}CHC_2F_4Br$,[226] $H_2C{=}CHC_6F_{12}Br$,[227] $F_2C{=}CHBr$,[228] $F_2C{=}CFBr$,[229] $F_2C{=}CFC_2H_4Br$,[230] $F_2C{=}CFOC_2F_4Br$,[231] and $F_2C{=}CFCF_2Br$.[225] Most of these monomers behave as cure site monomers (CSM) for fluoropolymers capable of giving a vulcanized product with a good compression set or melt-processable thermoplastic fluoropolymers, where only a small amount of halogen-containing CSM is included in the copolymerization through peroxide vulcanization. This procedure induces good mechanical properties for different applications. Several patents describe such fluoroelastomers and their process for peroxide vulcanization. Peroxide vulcanization of the compounded rubber (containing triallyl isocyanurate) gives vulcanizates endowed with improved mechanical properties (especially modulus, tensile strength, elongation, and compression set) as in Scheme 14.

Another potential thermoplastic application from graft copolymers containing VDF is to achieve the synthesis of original trifluorovinyl macromonomer containing an oligo(VDF) chain bearing a bromine side group for cross-linking,[232] as in Scheme 15.

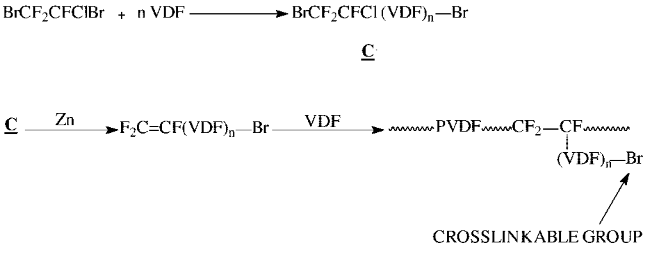
3.2.8. Poly(VDF-co-hexafluoroacetone)[192] and poly(VDF-co-3-ketofluoroalkylglutaroyl halide) Copolymers

Copolymers of VDF with hexafluoroacetone[192a] were first produced by the DuPont Company in the late 1960s. These thermoplastics are crystalline and attractive for their electrical properties, as claimed by Central Glass.[192b−d]

Scheme 14. Crosslinking Mechanism of Poly(VDF-*co*-bromomonomer) Copolymer in the Presence of Peroxide/Triallyl(iso)cyanurate System[6,10]

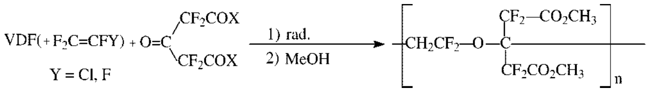


Scheme 15. Synthesis of Original Trifluorovinyl Macromonomer Containing Oligo(VDF) Bearing a Bromine Side Group for Cross-Linking



Almost 30 years ago, the radical copolymerization of VDF with 3-ketofluoroalkylglutaroyl halides (or terpolymers based on VDF and HFP or VDF and TFE with these carbonyl-containing comonomers), initiated by perfluoropropionylperoxide, led to original co- (or ter-) polymers bearing *gem*-

Scheme 16



Scheme 17

$(CH_2CF_2)_x[CF_2CF(OCF_3)]_y(C_2F_4)_z$ with x=4 ; y=1 and z= trace

diCF_2COX (with X = F, Cl, or even OCH_3 after esterification with methanol)[193] as shown in Scheme 16.

Advantageously, zinc acetate was added and the mixture was press-heated at 190 °C to give tough, flexible films as shape memory material endowed with no further shrinkage.

3.2.9. Poly(VDF-co-perfluoroalkyl vinyl ether (PAVE)) Copolymers

3.2.9.1. Introduction. Although perfluoroalkyl vinyl ethers are expensive monomers, their use in radical copolymerization with either TFE or VDF enabled a decrease of the crystallinity of PTFE and PVDF and even in that latter polymer obtainment of elastomers (see section on HFP). The challenge in this area is still to reach T_g's lower than −40 °C for low-temperature resistance applications. Hence, the synthesis of softer copolymers, for example, including perfluoroalkoxy alkyl vinyl ethers (PAAVEs), has been persued and exceptionally low T_g's have been reached. Further, abundant literature sources report that under radical conditions, functional perfluoroalkyl vinyl ethers (PAVEs) or perfluoroalkoxy alkyl vinyl ethers (PAAVEs) can copolymerize with TFE, leading to proton exchange membranes for fuel cells, PEMFC (Figure 6).[233] In contrast to these thermoplastic copolymers, those obtained from the copolymerizations of PAVE (or even better in the case of PAAVE) with VDF exhibit interesting elastomeric properties when the mole percent of VDF is lower than 85%, although little development has been achieved. Indeed, the ether group(s) brought by the PAVE (or PAAVE) comonomer enables the macromolecule to exhibit a low glass-transition temperature, and in certain cases, elastomers resistant to low temperature endowed with good thermal stability have been obtained, as summarized in subsequent sections.

3.2.9.2. Copolymerization of VDF with Nonfunctional PAVEs. The first radical copolymerization of VDF with perfluorovinyl methyl ether (PMVE) was pioneered by Albin and Gallagher[234] in the 1960s from an emulsion process, yielding copolymers with a temperature of flexibility (close to the glass-transition temperature, T_g) ranging from −28 to −24 °C. This reaction evidenced the poor reactivity of PMVE, which did not homopolymerize ($r_{PMVE} = 0$; $r_{VDF} = 3.4$ at 74 °C[235] or $r_{PMVE} = 0.11$; $r_{VDF} = 1.06$;[200b] Table 2). However, adding traces of TFE led to commercially available Viton GLT (from DuPont Performance Elastomers) endowed with outstanding properties.[4,6−8] This terpolymer exhibits a repeating unit structure (Scheme 17).

In 1966, the NASA[236] published a report describing similar interest, dealing with exotic copolymerizations of VDF with $F_2C{=}CFOC_nF_{2n+1}$ ($n = 1, 2, 3$) in drastic conditions (initiated by AIBN at high pressure ($P > 1000$ atm)). The authors obtained fluoroelastomers, the T_g's of which ranged from −25 to −20 °C.

PMVE or perfluoro-*n*-propyl vinyl ether (PPVE) was shown to readily copolymerize with VDF in solution, initiated by peroxides yielding poly(VDF-*co*-PMVE) and poly(VDF-*co*-PPVE) copolymers with interesting elastomeric behaviors since T_g's were as low as −44 °C.[235,237]

Scheme 18

$$\text{VDF} + F_2C{=}CFOCF_2CF(CF_3)OC_3F_7 \longrightarrow \text{poly (VDF-co-PAAVE)}$$

Perfluoroalkoxy alkyl vinyl ethers (PAAVEs) were also copolymerized with VDF in emulsion leading to poly(VDF-*co*-PAAVE) fluoroelastomers[238] endowed with T_g's ranging between −36 and −29 °C (Scheme 18).

These copolymers showed excellent low-temperature resistance, alcohol resistance, and high thermostability (up to 380 °C). In certain cases, these authors carried out ternary polymerization of aforementioned comonomers with either perfluoro-*n*-propyl vinyl ether or 2-bromo-perfluoroethylvinyl ether, which enabled cross-linking in a further step.

Furthermore, the Daikin Company[239] patented a comonomer with three ether bridges such as $F_2C{=}CF[OCF_2CF(CF_3)]_2OC_3F_7$ and its solution copolymerization (in 1,2,2-trifluorotrichloroethane), initiated by a chlorofluorinated perester. The T_g's of the resulting copolymers could reach −44 °C. In addition, the challenge to lower the T_g's (as low as −119 °C) could be reached by the 3M company,[240] which claimed synthesis of original copolymers based on VDF and PAAVE that contained perfluoropolyethers.

More recently, iodine transfer copolymerization of VDF and PMVE have been successfully achieved in the presence of 1,4-diiodoperfluorobutane as the chain transfer agent.[241] This radical copolymerization is regarded as controlled (or pseudoliving) (section 3.3). The resulting poly(VDF-*co*-PMVE) copolymers of $M_n < 3000$ g·mol^{-1} have T_g values of ca. −60 °C for satisfactory thermal stability. These fluorinated diiodides led to original telechelic dihydroxy, diazido, diacrylate, bis(triethoxysilane), and bis(methyldiethoxysilane) poly(VDF-*co*-PMVE) copolymers, as precursors of novel cross-linked elastomers.[242]

A deeper investigation in our group has recently consisted of assessing the reactivity ratios, r_{VDF} and r_{PMVE}, in the radical copolymerization of VDF and PMVE in emulsion. This can be deduced from plotting ln[VDF]/[VDF]$_0$ versus ln[PMVE]/[PMVE]$_0$; r_{VDF} can be determined from the value of the slope of the straight line of ln[VDF]/[VDF]$_0$ versus ln[PMVE]/[PMVE]$_0$ (Figure 23), according to Jaacks' law.[243] From the consumption of PMVE and VDF in the course of the reaction, it is possible to assess their reactivity ratios: $r_{VDF} = 2.53$ and $r_{PMVE} = 0$ at 80 °C in aqueous solution,[244] which are rather close ($r_{VDF} = 3.40$ and $r_{PMVE} = 0$ at 74 °C[235]) to those achived in an organic medium. This shows again that PMVE does not homopropagate. These values confirm that

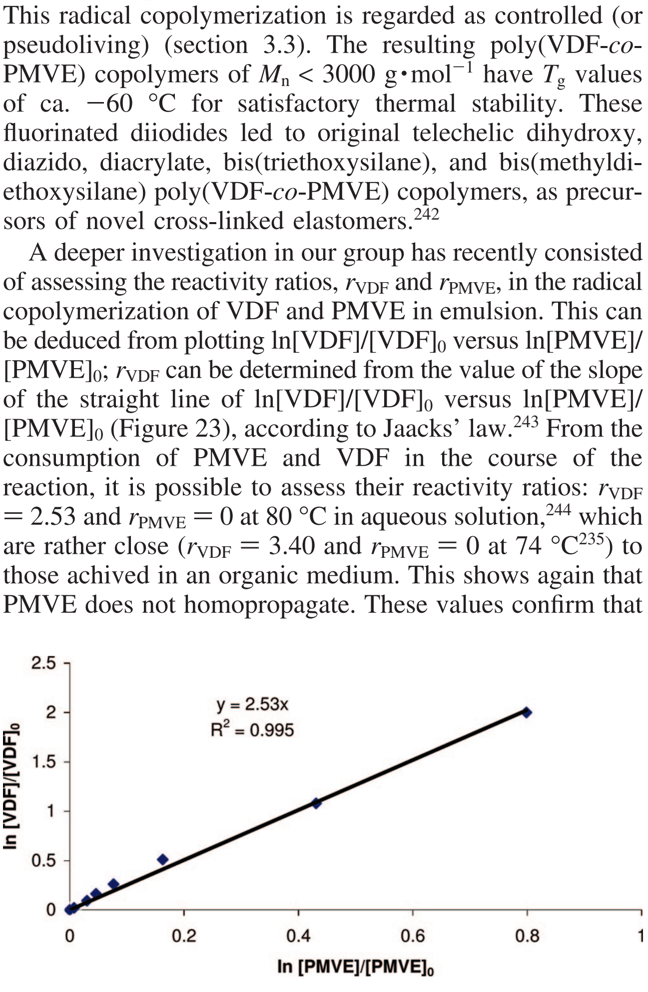
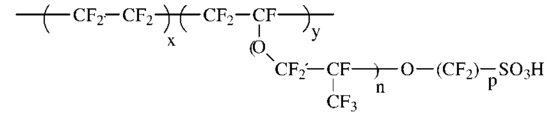


Figure 23. Evolution of ln[VDF]/[VDF]$_0$ versus ln[PMVE]/[PMVE]$_0$ for the radical copolymerization of VDF and PMVE in emulsion in the presence of IC_4F_8I. Feed composition is VDF/PMVE (mol %) 90/10 in aqueous medium.

Scheme 19[a]



[a] Where x ranges from 5 to 14 for $y = 1$; n can be 0, 1, or 2, and $p = 2-4$.

the content of VDF in the copolymers is always higher than that in the feed, whatever the initial comonomer concentrations.

3.2.9.3. Radical Copolymerization of VDF with Functional PAVEs or PAAVEs. Many studies report the radical copolymerization of TFE with functional perfluoroalkoxyalkyl vinyl ethers. This is mainly the case for those containing a sulfonyl fluoride useful for chlor-alkaly and fuel cell membrane applications.[233] Hence, novel materials for fuel cell membranes such as Nafion, Flemion, Hyflon Ion, Fumion, and more recently 3MMembrane[245] are currently marketed by DuPont, Ashai Glass Co., Solvay Solexis, Fumatec, and 3M companies, respectively (Scheme 19).

In contrast to these studies, a few investigations deal with VDF[246−248] instead of TFE.

Functional perfluoroalkoxyalkyl vinyl ethers and mainly those containing a sulfonyl fluoride or their derivatives have also been successfully copolymerized with VDF in various processes.

First, Ezzel and Carl[249] encompassed copolymers of VDF and perfluorovinyl ethoxy sulfonyl fluoride. Then, Connolly and Gresham[250] disclosed the copolymerization of VDF with perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PFSVE) and the terpolymerization involving HFP, in an emulsion process, but using a small amount of functional comonomer so that only 0.2−5.0 mol % was present in the copolymer. Investigations in partnership with Hydro-Quebec led to a wider range of fluorinated copolymers[247,248] or terpolymers (involving HFP).[251]

In addition, Feiring et al.[246] have also investigated the emulsion copolymerization of VDF with various functional comonomers such as $F_2C=CFOCF_2CF(CF_3)OC_2F_4R$ where R represents $NHSO_2CF_3$ (also reported by DesMarteau[252]), $SO_2CLi(SO_2CF_3)_2$, $SO_2NLiSO_2CF_3$, and SO_2F (PFSVE).[246] In the case of the last system, the copolymers have a T_g of −20 °C and no weight loss was noted up to 375 °C. These copolymers with pendant groups containing fluorosulfonyl methide or fluorosulfonyl imide derivatives are original fluorinated ionomers that have been claimed to be used in applications such as batteries, fuel cells, electrolysis cells, ion exchange membranes, sensors, and electrochromic windows, in electrochemical capacitors, and for modified electrodes.

Recently, the radical terpolymerization of VDF with PFSVE and 4-bromo-3,3,4,4-tetrafluorobut-1-ene (BDFO) has led to interesting terpolymers that could be cross-linked via the bromine atom in the presence of ROOR peroxides and triallyl isocyanurate (TAIC), as in Scheme 20.[253]

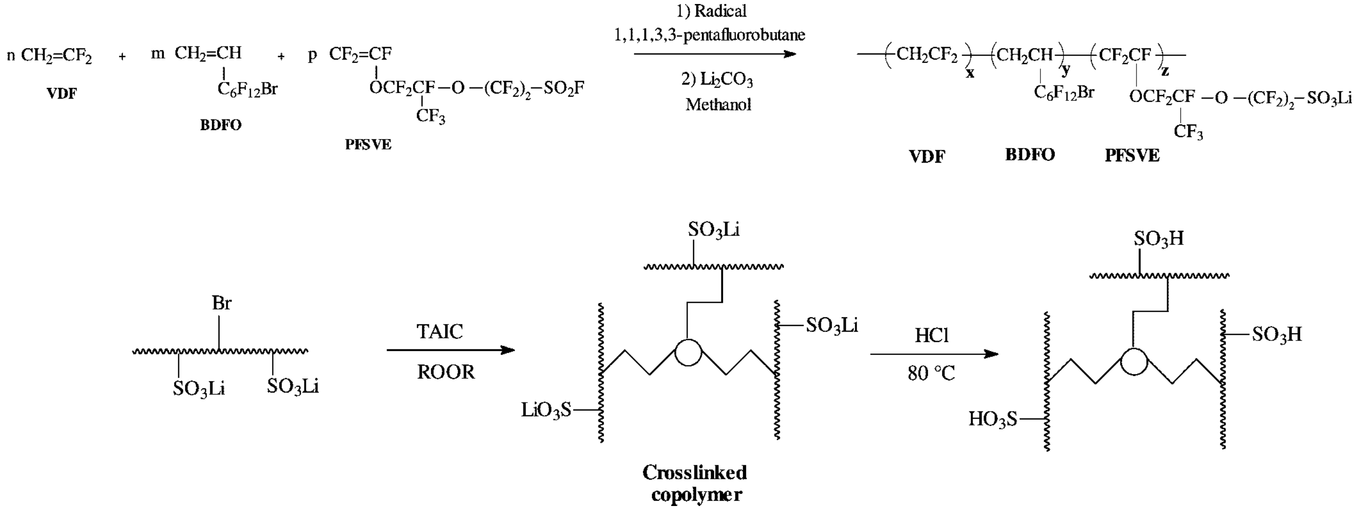
3.2.10. Poly(VDF-co-functional perfluorovinyl monomer) Copolymers

These above perfluorovinyl ethers propagate with difficulty in radical homopolymerization (though only hydroxy terminated perfluorovinyl ethers homopolymerize under ionic conditions.[254] In contrast, several attempts of copolymerizations of VDF with $F_2C=CF-R-G$ (where G and R represent a functional group and a hydrogenated spacer, respectively) have shown that these monomers easily homopolymerize. Such original monomers enable the resulting copolymers to be efficiently cross-linkable via routes different from those usually involved (by means of diamines, bisphenols, peroxides or radiation[5,10]).

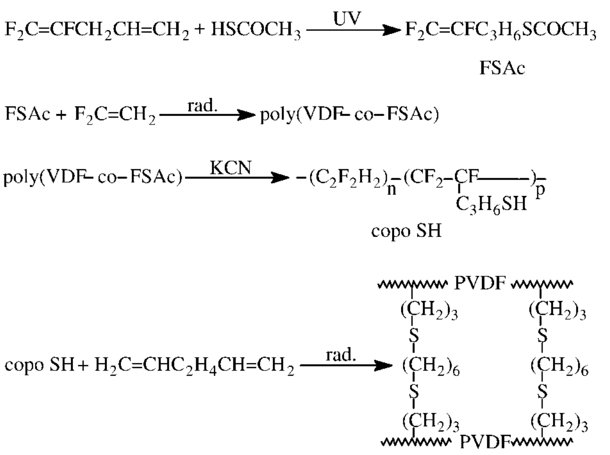
Pioneering work has been carried out by the Daikin Company[255] from various functional monomers such as $F_2C=CF(CF_2)_n(CH_2)_mOH$ where $n = 0$, 1, 2 and $m = 1-3$.

The synthesis of the monomers was reported in the same patent, while the optimization of $F_2C=CF(CH_2)_nOR$ (where $n = 1$ or 3 and R = H or Ac) was later on extensively described.[256] Other functional trifluorovinyl monomers have also been prepared, bearing either an ω-insaturation[257−259] or a carboxylic,[260,261] a nitrile,[262] an amide,[258] a sultone,[257] an epoxide,[263] a hydroxyl,[255,256,260,264] or a thioacetoxy group.[265,266] More exotic routes to trifluorovinyl end groups in metallic complexes have also been reviewed.[267] Radical copolymerizations of VDF with $F_2C=CF(CH_2)_3OR$[255,264] (according to the nature and the amount of the functional monomer, the T_g values ranged from −23 to −8 °C[255]) or with $F_2C=CF(CH_2)_3SCOR$[265,266] have been investigated, leading to original elastomers.[266] These elastomers even could be cross-linked in the presence of telechelic diene via the "thiol−ene" process, displayed in Scheme 21.

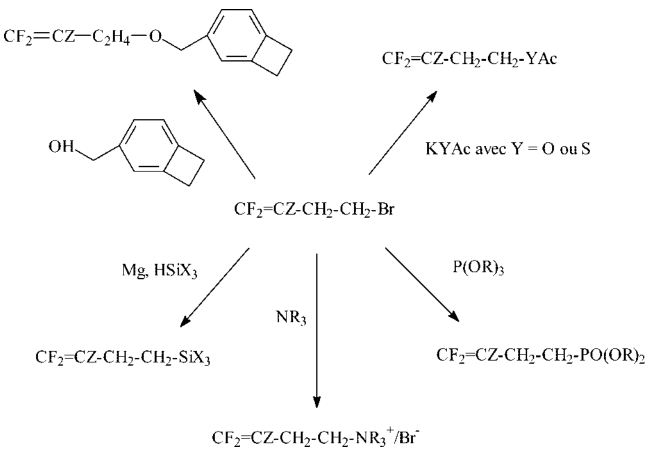
Scheme 20



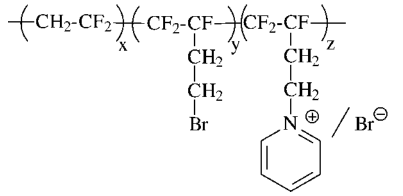
Scheme 21



Scheme 22



Scheme 23



Another interesting strategy to involve a "cure site monomer" in the radical copolymerization in solution has been achieved from $F_2C{=}CF(CH_2)_3Si(OR)_3$ (with R = Et or Me) comonomers.[268] The resulting copolymers were cross-linked in the presence of acidic water, after hydrolysis and condensation.

As mentioned in the preceding subsection, further fluorinated monomers bearing a bromine end group potentially enable the cross-linking of the resulting copolymers. This is the case of $CF_2{=}CF{-}CH_2{-}CH_2{-}Br$, C_4Br,[230c] the bromine atom of which can also be chemically changed into other functional groups (acetate, thioacetate, phosphonate,[269] trialkoxysilane[268] (Scheme 22), which either could allow cross-linking or could be hydrolyzed into phosphonic acid[269]). A recent study on the radical copolymerization of VDF with C_4Br, followed by a chemical modification (via Arbuzov) has led to original poly(VDF-*co*-C_4P) copolymers (where C_4P stands for $CF_2{=}CF{-}CH_2{-}CH_2{-}P(O)(OH)_2$ unit) for which the phosphonic acid enables protonic exchange for PEMFC.[269]

In the same way, poly(VDF-*co*-$CF_2{=}CF{-}CH_2{-}CH_2{-}Br$) copolymers have been synthesized and could be modified into original copolymers bearing a quaternary ammonium function (Scheme 23).[270]

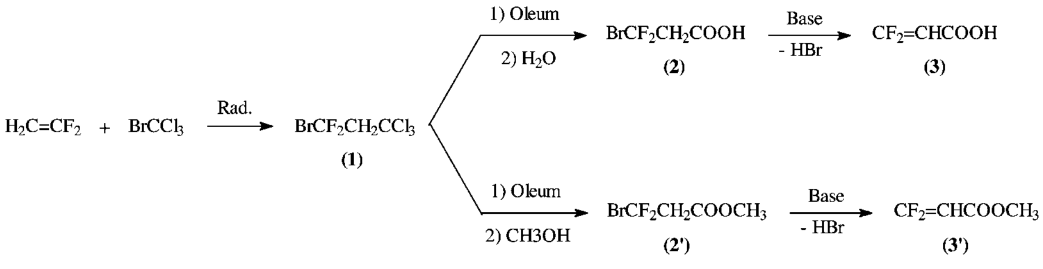
3.2.11. Radical Copolymerization of VDF with Fluoroacrylates

According to Q and e values of acrylate ($Q_{\text{acryate}} = 0.5-0.9$ and $e = 0.22-1.1$),[271] the radical copolymerization of VDF with an acrylate does not occur[270] since it leads to a homopoly(acrylate). A similar behavior has also been noted when VDF reacted with an α-fluoro acrylate,[270] although a Japanese patent surprisingly claims that such an emulsion copolymerization is possible.[272a] In addition, random poly(VDF-*co*-(meth)acrylate) copolymers have recently been achieved from the surprising suspension copolymerization of VDF with various types of (meth)acrylates[272b] (at least 40 mol % of these hydrophilic monomers were incorporated in the copolymers). These copolymers were claimed to be used for binders for batteries and for the manufacture of hydrophilic membranes.

Amazingly, though the radical copolymerization of VDF with an α,β-difluoroacrylate has not been yet investigated,[270] it is worth investigating the synthesis of a difluoroacrylate which does not possess any fluorine atom in α-position to the ester function. This original monomer (**3** or **3′**) is synthesized by the radical addition of bromotrichloromethane onto VDF leading to 1,1,1-trichloro-3-bromo-3,3-difluoropropane monoadduct (**1**), the trichloromethyl group of which was oxidized into **2** or **2′**, followed by a dehydrobromination, as shown in Scheme 24:[273]

Interestingly, the radical copolymerization of VDF with a β,β-difluoroacrylate (**3′**) has successfully been achieved.[270] For example, starting from a molar feed content (VDF/β,β-difluoroacrylate) of 90/10, the resulting copolymer contained 86 mol % of VDF. Figure 24 represents the ^{19}F NMR spectrum of the produced copolymer, showing the characteristic signals of VDF centered at −93, −115, and −117 ppm assigned to $-CH_2\mathit{CF}_2-CH_2CF_2$, $-CH_2\mathit{CF}_2-\mathit{CF}_2CH_2$, respectively. More interesting are both AB systems centered at about −110 (symbolized by * in Figure 24) and −116 ppm (represented by o in Figure 24), assigned to the difluoromethylene signals in the $-CH_2\underline{\mathit{CF}_2}-\underline{\mathit{CF}_2}CH(CO_2R)-$

Scheme 24



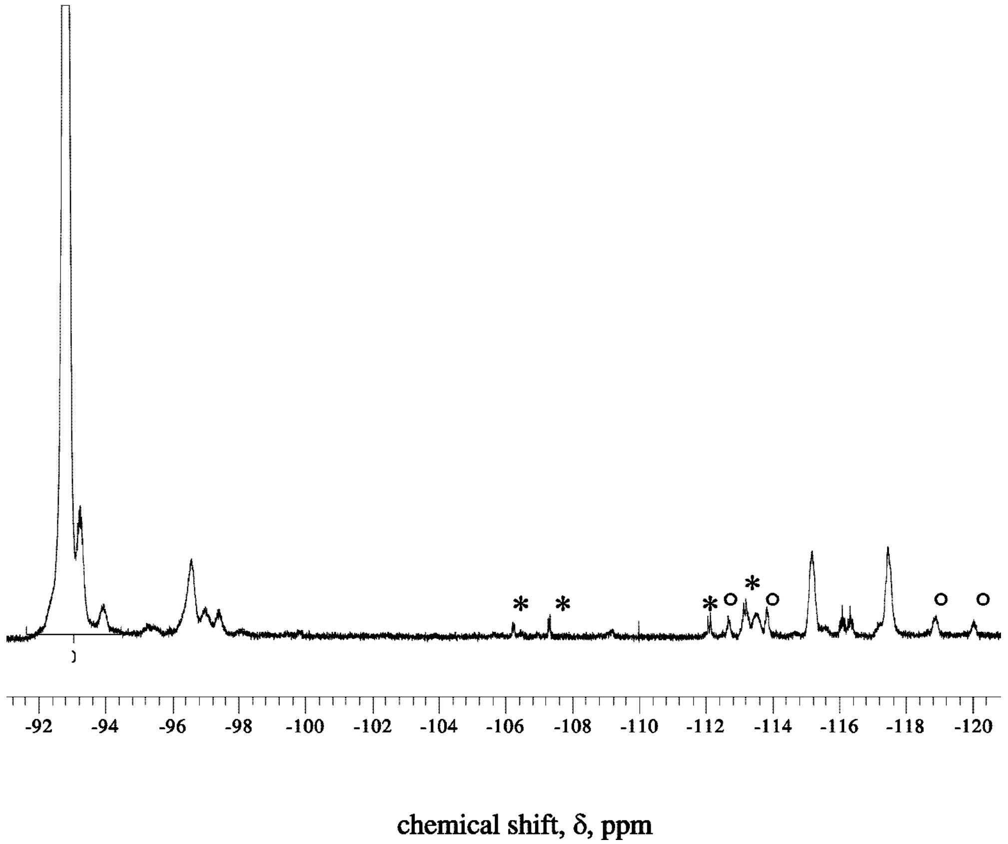
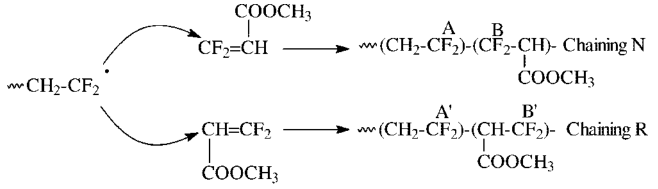


Figure 24. ^{19}F-NMR spectrum of the poly(VDF-*co*-methyl-*β*,*β*-difluoroacrylate) copolymer (90 mol % VDF in the feed; 86 mol % VDF in copolymer); symbols O and * represent the AB and A′B′ systems, respectively.

Scheme 25



diad arising from the presence of the asymmetric carbon atom and the bulky ester linked to it.

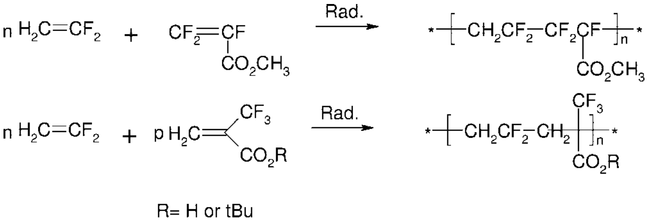
Surprisingly, the macroradical terminated by the $CH_2CF_2^{\bullet}$ group is also able to react onto the more hindered site of *β*,*β*-difluoroacrylate leading to a reversed chaining (Chaining R)[270] (Scheme 25).

The evidence of this mechanism could be highlighted from the presence of two complex signals centered at −96.5 ppm assigned to both CF_2 groups in the $-CH_2\mathit{CF_2}-CH(CO_2R)\mathit{CF_2}-CH_2CF_2-$ triad.

Only two monomers bearing three fluorine atoms linked to the ethylenic carbon atoms of a fluorinated acrylate, α,*β*,*β*-trifluoroacrylate and α-trifluoromethacrylate, are known not to homopolymerize[274] under radical conditions (when initiated by AIBN or dibenzoyl peroxide). However, both methyl α,*β*,*β*-trifluoroacrylate[275,276] and α-trifluoromethacrylic acid (MAF)[191] (Scheme 26) or *tert*-butyl α-trifluoromethacrylate (MAFTBE) have led to alternating copolymers successfully when the reaction was carried out in solution (Figure 25).

As in Figure 26, the chemical shift of the central difluoromethyl group adjacent to both methylene groups in the VDF−MAF[191] or VDF−MAFTBE diads shows a characteristic signal centered at −95 ppm.

Scheme 26



3.2.12. Radical Copolymerization of VDF with Other Monomers

In addition, the radical copolymerization of VDF with α-trifluoromethyl vinyl acetate (TFMVAc) has scarcely been investigated. This reaction was pioneered by the Polaroid Company[277] (and then, its kinetics was studied by our team[270]). Unexpectedly, TFMVAc is more reactive than VDF[270] (when it was initiated by *tert*-butyl peroxypivalate[270]) though its radical homopolymerization initiated by dibenzoyl peroxide[278] led to low molecular weight oligomers in poor yields. The limiting parameter arises from the slow propagation rate.[278,279] The higher reactivity of TFMVAc was evidenced by two features. (i) First, the ^{19}F NMR spectra of the various poly(VDF-*co*-TFMVAc) copolymers revealed the presence of three chemical shifts assigned to the CF_3 group of TFMVAc in the following triads: −66 to −67 ppm, $-[CH_2C(CF_3)OAc]-[CH_2C(CF_3)OAc]-[CH_2C(CF_3)OAc]-$; ca. −70 ppm, $-[CH_2C(CF_3)OAc]-[CH_2C(CF_3)OAc]-CH_2CF_2-$; −72.9 ppm, $-CH_2CF_2-[CH_2C(CF_3)OAc]-CH_2CF_2-$. (ii) Second, assessing the reactivity ratios led to $r_{VDF} = 0.16 \pm 0.10$ and $r_{TMFVAc} = 7.6 \pm 1.2$ at 55 °C,[270] showing a poor reactivity of VDF.

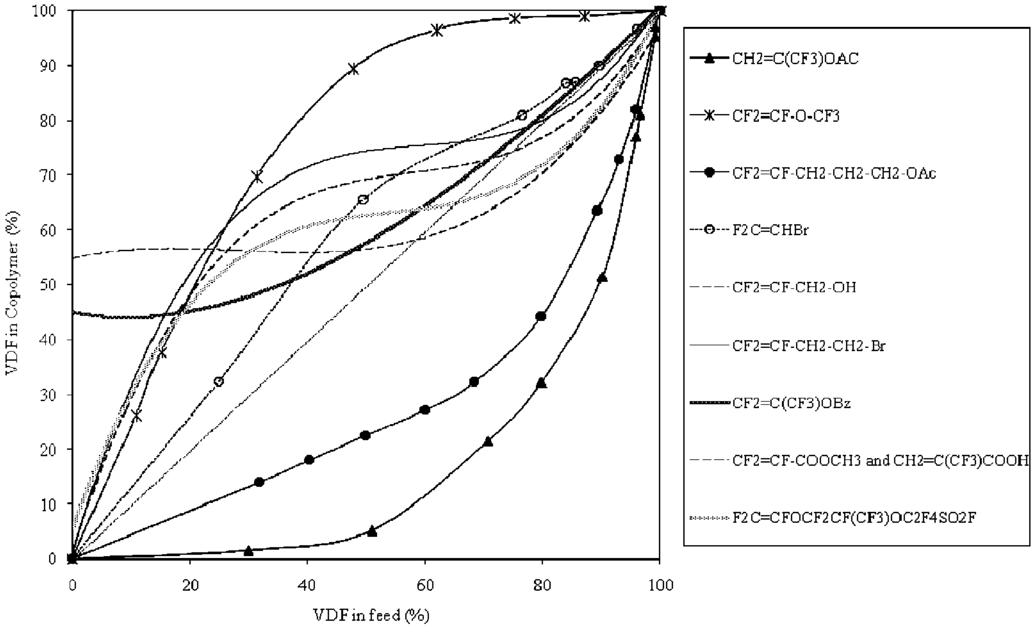


Figure 25. Monomer-polymer copolymerization curves from the radical copolymerization of VDF with various comonomers (the various lines represent the theoretical curves).

An atypic radical copolymerization of vinyl acetate (VAc) with VDF has been investigated either in supercritical CO_2,[280] in suspension,[281] or in solution,[270,282] showing that VAc is more incorporated than VDF (Table 2). VAc has three limitations: (i) it is too reactive and forms PVAc chains; (ii) it does not possess any fluorinated atom on the double bond and thus the resulting copolymers cannot have the same thermal stability as that of PVDF; (iii) it is known that a proton located in the α position of the double bond induces the transfer reaction to the polymer.[283]

In contrast, the radical copolymerization of VDF with hydrogenated vinyl ethers (VEs) has never been mentioned in the literature, contrarily to the production of alternated copolymers based on CTFE and VEs (Lumiflon) or TFE and VEs (Zeffle) marketed by Asahi Glass Co and Daikin, respectively.[4]

Furthermore, VDF was also involved in radical copolymerization with monomers bearing cyano groups[284] showing that neither acrylonitrile nor methacrylonitrile nor vinylidene cyanide copolymerized successfully with VDF leading to homopolymers based in these cyanomonomers exclusively.

A few allylic monomers have been incorporated in the copolymerization of VDF. The Kureha[285] Company claimed that the allyl glycidyl ether led to copolymers containing a small amount of that oxirane-containing monomer, and the resulting copolymer (the melting point of which is 160−175 °C) was used for lithium battery applications, after a cross-linking reaction via the epoxide side groups.

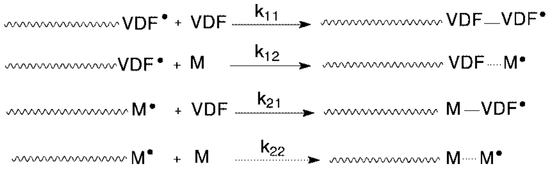
The same strategy was also attempted by Kappler, Perillon, et al.[286−288] who were able to incorporate more allyl glycidyl ether (ca. 4.3 mol %)[286] from its radical copolymerizations with VDF or with VDF and TFE. In addition, these authors used other hydrogenated functional allylic comonomers such as monoallyl-1,2-cyclohexanedicarboxylate,[288] allyl diol,[289] and ω-functionalized C_nF_{2n+1} end groups[290]). The three former monomers produced terpolymers ($M_n = 7800-9000$ g·mol^{-1}), which were cross-linked either with *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)adipamide (for a CO_2H content of 0.67 mequiv·g^{-1} [288]), melamine,[291] Lewis acid (such as $Ph_3S^+SbF_6^-$ [286]), isophorone diisocyanate,[290] or HDI-based polyisocyanate.[289a] These cross-linking steps were required to induce a high solvent resistance (to MEK especially), and the main application of these materials was for formulations of original coatings (CX 2000 from Elf Atochem) to compete with Lumiflon paints from the Asahi Glass Chemical Company. To complete that area, Tournut[292,293] published two very interesting reviews on the radical copolymerizations of VDF with functional hydrogenated comonomers for paint applications.

Another exotic and surprising copolymerization of VDF was that involving a vinyl monomer bearing a fluorinated substituent $H_2C{=}CHC_nF_{2n+1}$ ($n > 4$) as claimed in Shin Etsu's patents.[222]

Recently, the Solvay Company[294] has developed new maleimized PVDF copolymers containing small amounts (<1 mol %) of maleic anhydride comonomer, under the Priex trademark. Recently, that company has transferred the Priex technology to Addcomp Company. Similar copolymers based on VDF (or containing various other fluoroalkenes (FA)) have also been achieved by Arkema[295] under the Kynar ADX trade name by extrusion of PVDF or poly(VDF-*co*-FA) copolymers in the presence of a small amount of maleic anhydride (see section 4.5). These resins preserve the same excellent melt and solvent processability and feature equivalent thermal, UV, and chemical resistance, high mechanical performance, and high permeation barrier properties as Kynar and Kynar Flex resins do. Their applications are in diverse fields such as transport fuel lines, battery binders, and rubber and metal coatings, though the maleic anhydride content was lower than 2 wt %.

Interestingly, the radical copolymerization of VDF with hexafluoroisobutylene (HFIB) led to an alternating poly(VDF-*alt*-HFIB) copolymer, commercially available by the Allied Company (nowadays by Honeywell International Inc.).[296,297] This is the only industrial alternating copolymer based on VDF. It has exceptional properties (high crystallinity and high melting point of $T_m = 327$ °C, and $T_g = 132$ °C), arising from both CF_3 side groups ensuring a good protection of the backbone. The history of that product has been reviewed.[298]

Scheme 27. Various Equations and Rates of Propagation in the Radical Copolymerization of VDF (1) with M (2) Comonomer



Scheme 28

$$r_{VDF} = k_{11} / k_{12} \text{ and } r_M = k_{22} / k_{21}$$

3.2.13. Kinetics of Radical Copolymerization of VDF with Comonomers

Radical copolymerization enables classification of the comonomers according to their reactivities, and it is worth investigating the kinetics of copolymerization of VDF with various comonomers (Table 2) to compare their reactivity toward VDF.

Usually, four main equations of propagation of macroradicals onto either VDF or the comonomer are under competition (Scheme 27).

The intrinsic reactivity of both comonomers can be obtained from the assessment of their reactivity ratios, *r*, which become the ratios of the propagation rates (Scheme 28).

Concerning a theoretical point of view, the kinetics of radical copolymerizations of various VDF/M monomer couples have also been studied, showing that the reactivity ratio of VDF could be lower than those of certain functional comonomers[201,224,230,264,270,299−304] (Table 2). The reactivity ratios measured in the copolymerizations of VDF with monomers bearing various substituents are gathered in Table 2. A value of *r* less than 1 indicates a tendency of the radicals to cross-propagate rather than to homopolymerize. Figure 25 represents the monomer−polymer composition curve for the radical copolymerization of VDF with various comonomers and shows different profiles ranging from random to alternating copolymerizations.

Indeed, a reactivity series of fluorinated monomers about VDF can be supplied using the traditional method for the determination of relative reactivity of a macroradical to several monomers. It is common to compare the values $1/r_1 = k_{12}/k_{11}$ as the ratio of rate constants of crossed propagation to that of propagation (k_{11}). Thus, the higher the $1/r$ value, the more the radical is able to react with the second monomer. Table 2 allows one to suggest the following series of relative reactivities of monomers to VDF$^•$ radical-terminated polymers:[235,264,265,276,299−311] $F_2C{=}CHC_6F_{13}$ < $F_2C{=}CHCF_3$ < $F_2C{=}C(CF_3)COF$ < HFP < PMVE < BDFE < PPVE < VDF < TrFE < $F_2C{=}CFCH_2CH_2Br$ < $F_2C{=}CFCH_2OH$ < $F_2C{=}C(CF_3)OCOC_6H_5$ < $F_2C{=}CFO(HFP)OC_2F_4SO_2F$ < CTFE (recent value) < TrFE < BrTFE < $H_2C{=}CFCF_2OR_F$ < $H_2C{=}C(CF_3)CO_2H$ < $F_2C{=}CFCO_2CH_3$ < TFE < $F_2C{=}CFC_3H_6SCOCH_3$ < $F_2C{=}CFC_3H_6OAc$ < $H_2C{=}CHF \approx$ CTFE (old value) < TFP < ethylene, although numerous kinetics still deserve to be investigated involving VDF.

3.2.14. Radical Copolymerizaton of VDF with Aromatic Monomers

To the best of our knowledge, the radical copolymerization of VDF with aromatic monomers has scarcely been reported. This is mainly due to the lack of copolymerizability since the *Q* value of aromatics ($Q_{styrene} = 1$) are higher than that of VDF ($Q_{VDF} = 0.036$,[310] 0.008,[201] or 0.015[271]). However, a few aromatic terpolymers based on VDF have been synthesized. Trifluorovinyloxy aromatic brominated[194] or sulfonyl chloride[195] were chosen as monomeric precursors of copolymers as electrolytes for fuel cell membranes but the poor reactivity of these aromatic monomers (sometimes

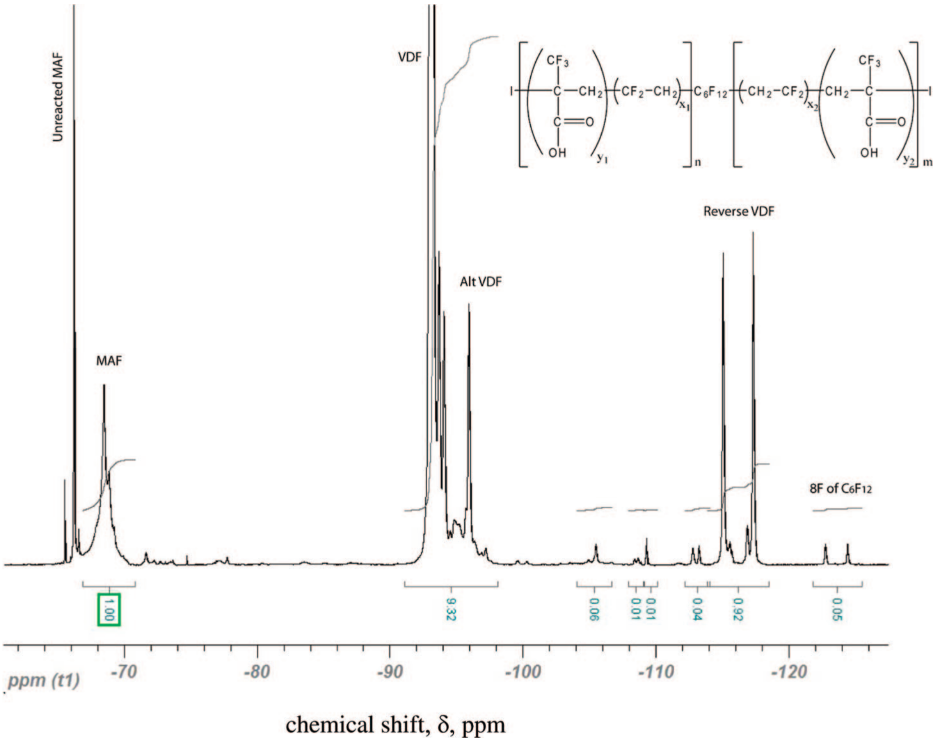
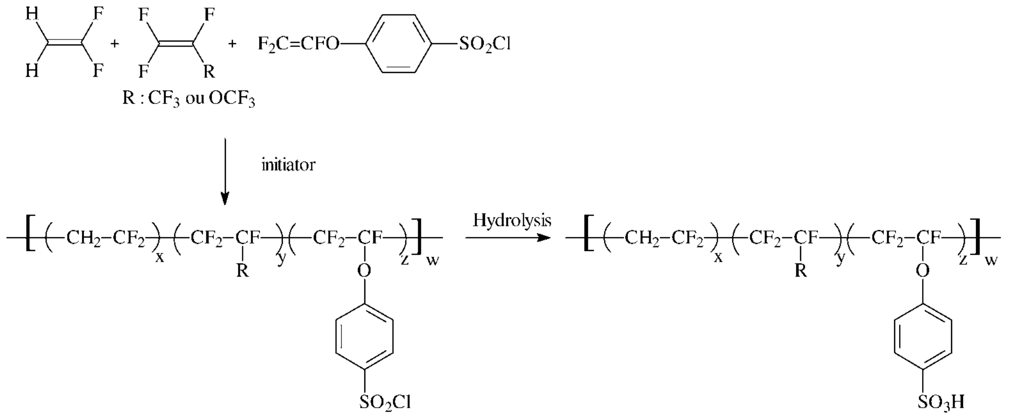


Figure 26. ^{19}F NMR spectrum of poly(VDF-*co*-MAF) copolymer recorded in DMSO (NS = 1024, D1 = 2s); feed mol % VDF/α-trifluoromethacrylic acid (MAF) = 90/10; in copolymer mol % 94/6; MW= 57 350 g·mol^{-1}.

Scheme 29



leading to a certain inhibition) and β-scission that occurred from the trifluorovinyloxy end radical in the course of the polymerization led to low ionic exchange capacities and poor conductivities. The straightforward synthesis of the preparation of terpolymers bearing sulfonic acid for fuel cell membranes is in Scheme 29.

3.2.15. Conclusion

Random copolymers containing VDF units and aliphatic comonomers are numerous, while those based on aromatic comonomers are scarce. The nature and the number of substituents born by the ethylenic carbon atoms induce great polar and steric effects on their reactivity toward VDF. The use of a cure site monomer is original and obviously various companies have taken advantage to produce new generations of fluorinated copolymers with improved performances. Although an increasing number of studies on the upstream preparation of functional fluoromonomers for fuel cell membranes has been noted, it is obvious that almost no study reports the use of VDF-containing copolymers for alkaline fuel cell membranes because of dehydrofluorination reactions of VDF-containing copolymers in basic media.[165] In addition, many efforts have been made in the past decade to find out suitable functional comonomers as cure site monomers for thermoplastics or elastomers.

3.3. Random Copolymers Synthesized by Controlled Radical Polymerization (CRP)[47−51,312]

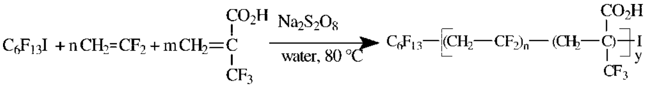
3.3.1. Introduction

Controlled radical polymerization (CRP) has drawn much interest since the mid-1990s.[47−51] Many surveys deal with the CRP of hydrogenated monomers from nitroxide-mediated polymerization (NMP), from atom transfer radical polymerization (ATRP), or from reversible addition−fragmentation transfer (RAFT). In contrast, the CRP of fluoroalkenes is scarce: ATRP of pentafluorostyrene[313] or the ATR copolymerization of 1*H*,1*H*,2*H*-perfluorooct-1-ene with methyl acrylate,[314] the use of borinate,[51,80,125,128,138] the macromolecular design by interchange of xanthate[5,49,50] (MADIX), and the iodine transfer polymerization.[4,48,312] This last pioneered method of CRP was developed by Tatemoto in the late 1970s.[4,48]

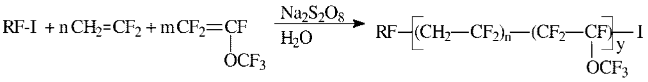
3.3.2. Controlled Poly(VDF-co-α-trifluoromethacrylic acid) Copolymers

A few examples in these three latter systems are given hereafter, starting from the iodine transfer copolymerization of VDF with α-trifluoromethacrylic acid (MAF). That reaction was successfully achieved in emulsion,[315] initiated by a persulfate, in the presence of $C_6F_{13}I$ or $IC_nF_{2n}I$ ($n = 4$ or 6) as the chain transfer agents (CTAs) but without any surfactant.[315] Indeed, the carboxylic acid enabled the self-emulsion of the process (Scheme 30).

Scheme 30



Scheme 31



The molecular weights of the resulting copolymers could be targeted from $([VDF]_0 + [MAF]_0)/[(I)R_FI]_0$ initial molar ratios. They reached values up to 220,000 $g\cdot mol^{-1}$ in the absence of $IC_6F_{12}I$ as the CTA. As an example, the ^{19}F NMR spectrum (Figure 26) enables assessment of the mole percent of both comonomers and the molecular weights from the integrals of the characteristic signals centered at −92, −95, −115, and −118 ppm assigned to VDF and at −69 ppm for MAF, and thanks to the eight fluorine atoms of the CTA centered in the −122 to −125 ppm range. In addition, the copolymers obtained exhibit small sizes of particles (ca. 100 nm).[315b]

3.3.3. Controlled Poly(VDF-co-perfluoromethylvinylether) Copolymers

A recent investigation deals with the iodine transfer copolymerization of VDF and PMVE achieved in emulsion in the presence of $C_6F_{13}I$ or 1,4-diiodoperfluorobutane as the chain transfer agent[241,244] but in the absence of surfactant (Scheme 31).

That radical copolymerization is regarded as controlled or pseudoliving. The microstructure of these α,ω-diiodopoly(VDF-*co*-PMVE) copolymers, well-evidenced by ^{19}F NMR spectroscopy (Figure 27), revealed VDF-I end groups and the absence of VDF reversed chaining. For average molar masses lower than 2500 g/mol, 100% $-CH_2CF_2I$ extremities were observed, while some $-CF_2CH_2-I$ end groups were noted for $M_n > 2600$ $g\cdot mol^{-1}$. The nature of the CTA ($C_6F_{13}I$ or $IC_nF_{2n}I$) did not affect the yield of the copolymerization versus the PMVE feed mole percent (Figure 28). As expected, the T_g values were low (ca. −60 °C) and these copolymers exhibit satisfactory thermal stability. Interestingly, these fluorinated diiodo derivatives led

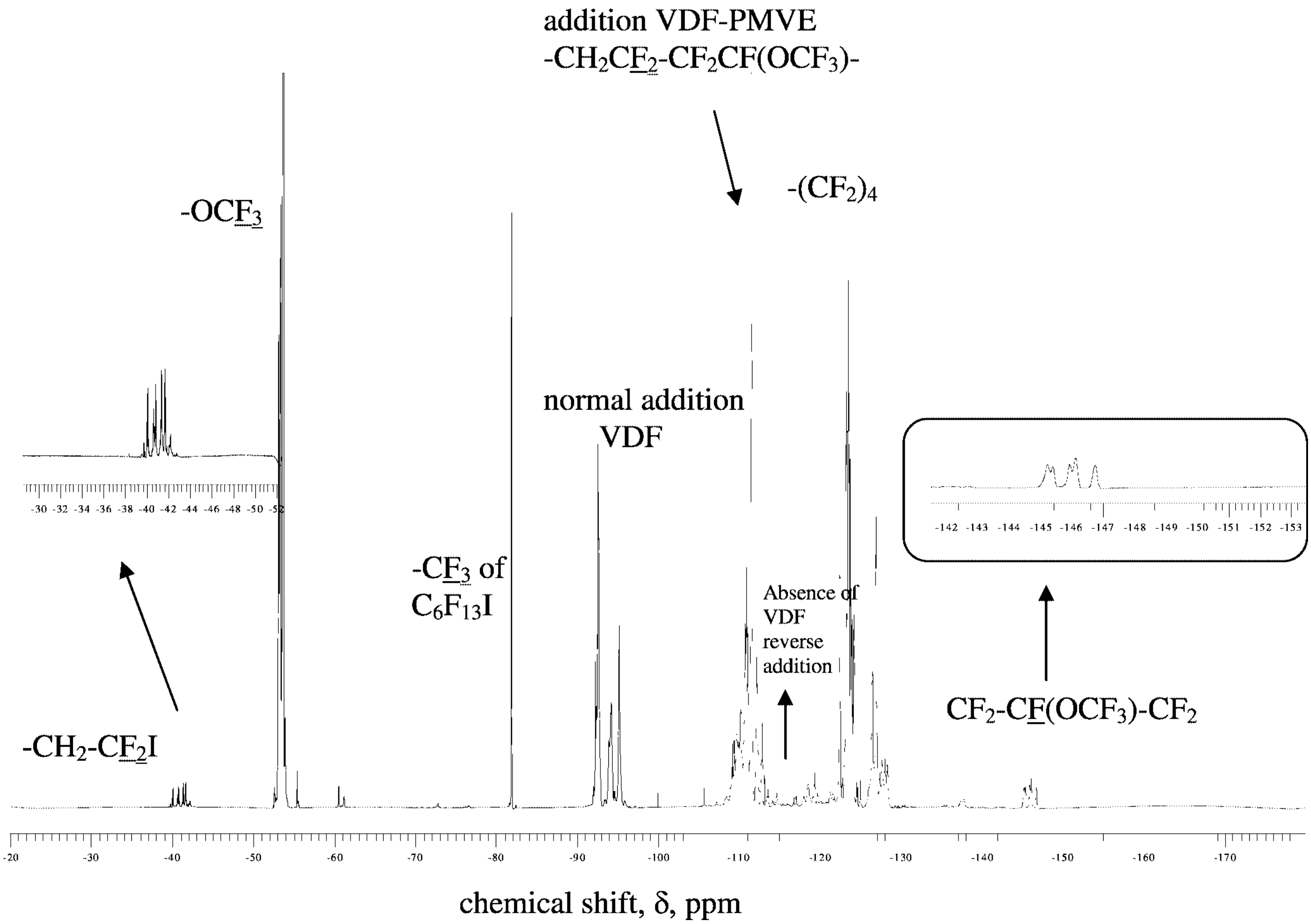


Figure 27. ^{19}F NMR spectrum of poly(VDF-*co*-PMVE) copolymer (recorded in d_6 acetone) obtained by iodine transfer copolymerization of VDF and PMVE in the presence of $C_6F_{13}I$ (feed 50/50 VDF/PMVE mol/mol, and 60/40 in the copolymer).

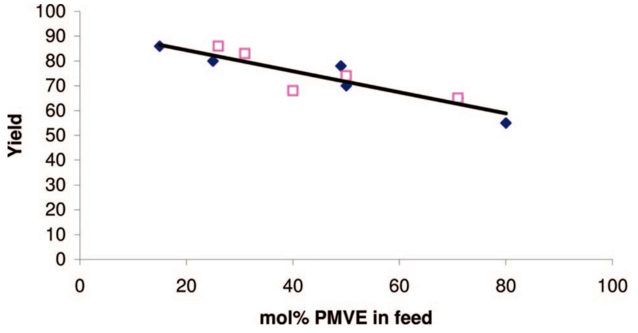


Figure 28. Evolution of yield (in %) of ITP copolymerization of VDF and PMVE in the presence of $C_6F_{13}I$ (□) or IC_4F_8I (◆) versus mole percent PMVE in feed.

to original telechelic diazido,[242a] dihydroxy,[242b] diacrylate[242b] or bis(trialkoxysilane)[242c] poly(VDF-*co*-PMVE) copolymers, as precursors of novel cross-linked elastomers.[242]

In addition, the kinetics of copolymerization enabled assessment of the reactivity ratios of both comonomers: $r_{VDF} = 2.53$ and $r_{PMVE} = 0$ at 80 °C[244] in emulsion copolymerization.

3.3.4. Controlled Poly(VDF-ter-HFP-ter-$F_2C{=}CFSF_5$) Terpolymers

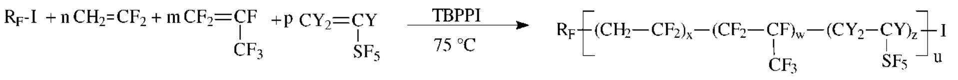
A similar strategy was also achieved for the terpolymerization of VDF with HFP and 1,1,2-trifluoro-2-pentafluorosulfanylethylene (Scheme 32 where Y represents a fluorine atom). This reaction involves $C_6F_{13}I$ as the CTA and is initiated by *tert*-butyl peroxypivalate.[197] Original terpolymers were produced, and as expected, the CTA concentration influences both the molar mass values (narrow polydispersity indices were obtained, Figure 29A) and the thermal properties of the resulting terpolymers.[197] The control of that reaction was evidenced by the linear dependence of the average molar masses on the monomer conversion (Figure 29B).

3.3.5. Poly(VDF-co-Comonomer) Copolymers Controlled by Borinates

A more recent technique, developed at Pennsylvania State University[51,78,128,138] that requires a borinate as the counter-radical, already used for hydrogenated monomers (e.g., acrylics), was successfully applied for the controlled radical copolymerization of VDF with vinyl silanes or fluoroalkenes such as CTFE, HFP, or TrFE.

BR_3 borane reacts with oxygen to generate $RO\text{-}OBR_2$ in which the oxygen−oxygen bond undergoes a homolytic cleavage to produce $RO^{\bullet}$ radical and $^{\bullet}OBR_2$ borinate (Scheme 33). In fact, $RO^{\bullet}$ is efficient oxygen centered radical able to initiate the homopolymerization of VDF (or the copolymerization of VDF with various other comonomers). In contrast, $^{\bullet}OBR_2$ radical is too stabilized

Scheme 32



$$R_F\text{-}I + n\,CH_2{=}CF_2 + m\,CF_2{=}\underset{CF_3}{CF} + p\,CY_2{=}\underset{SF_5}{CY} \xrightarrow[75\ °C]{TBPPI} R_F\text{-}\left[(CH_2-CF_2)_x-(CF_2-\underset{CF_3}{CF})_w-(CY_2-\underset{SF_5}{CY})_z\right]_u\text{-}I$$

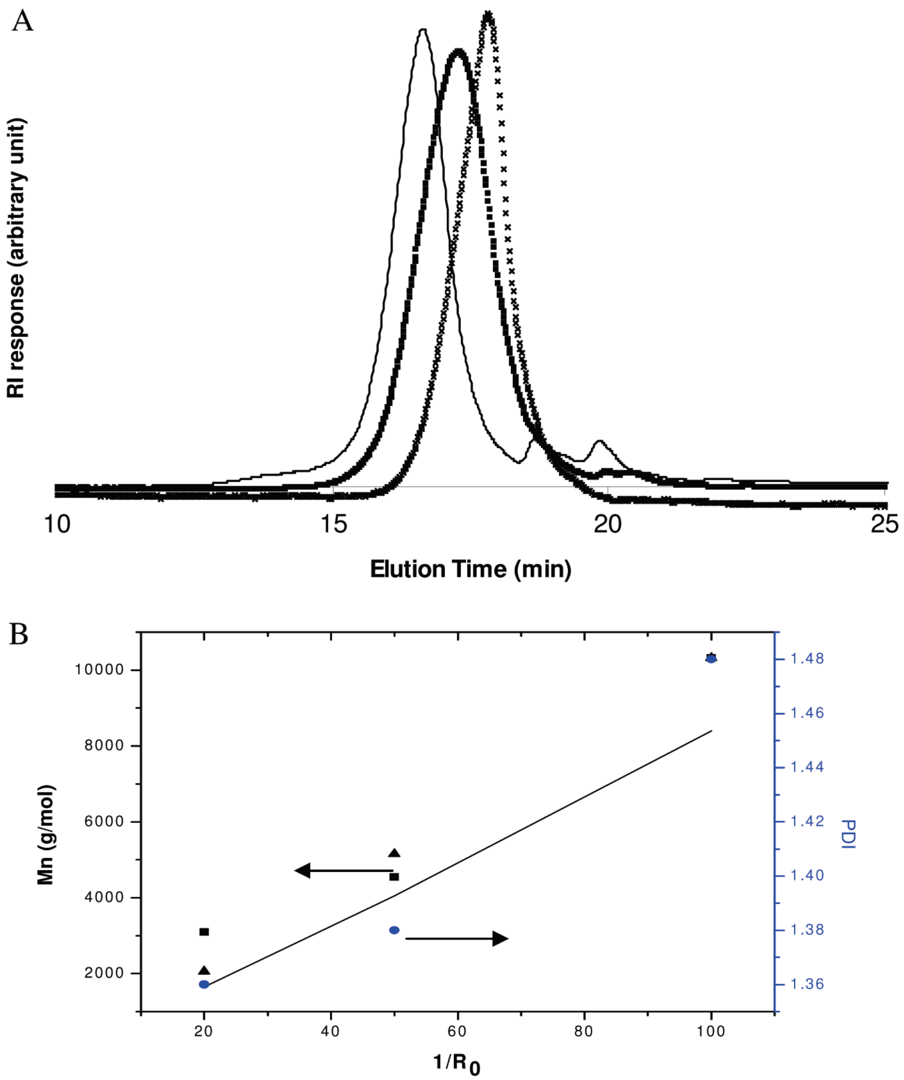
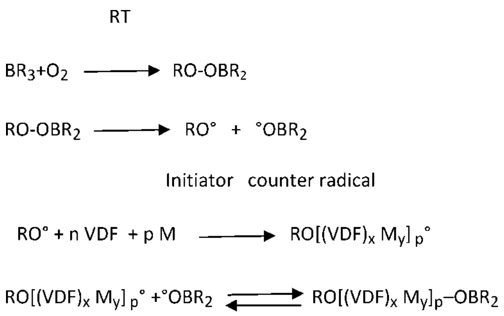


Figure 29. (A) SEC chromatograms of poly(VDF-*ter*-HFP-*ter*-$F_2C{=}CFSF_5$) terpolymers obtained by iodine transfer polymerization of VDF, HFP, and $F_2C{=}CFSF_5$: (×) $[C_6F_{13}I]_0/([VDF]_0 + [HFP]_0 + [F_2C{=}CFSF_5]_0) = R_0 = 0.05$); (■) $R_0 = 0.01$; (—) $R_0 = 0.005$. (B) Evolution of molecular weight (M_n, ■ and ▲ assessed by SEC and ^{19}F NMR, respectively) and polydispersity index (PDI, ●) versus $1/R_0$ ($R_0 = [C_6F_{13}I]/[M]$ where M represent the monomer concentrations. Experimental conditions were as follows: $[\text{initiator}]_0/[\text{VDF + HFP + SF5 monomer}]_0 = 0.01$ in 1,1,1,3,3-pentafluorobutane at 75 °C for 6 h. The straight full line represents the theoretical curve. Reproduced with permission from ref 197. Copyright 2008 American Chemical Society.

Scheme 33



and, consequently, is not able to initiate any polymerization. This stability arises from the back-donating effect of the free electron born by the oxygen atom to the empty orbital of boron atom. However, $^\bullet OBR_2$ is an efficient counterradical, which quenches (or traps) any macroradical by recombination and thus controls the polymerization via a fast equilibrium between the active species and the dormant ones (Scheme 33).

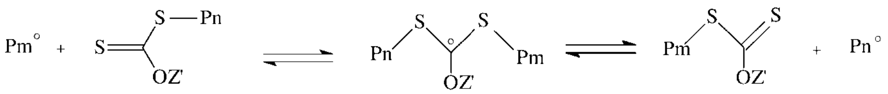
That technique enabled Chung's team to synthesize original poly(VDF-*co*-CTFE) copolymers and poly(VDF-*ter*-CTFE-*ter*-$F_2C{=}CF\text{-}R\text{-}Si(OR)_2CH_3$) terpolymers (Scheme 8) obtained in a controlled manner in solution or in bulk at ambient temperature, though the yields were lower than 65%.[125,128,139]

3.3.6. Poly(VDF-co-Comonomer) Copolymers Controlled via Xanthates

Besides ITP and radical copolymerizations controlled by borinates, the pseudoliving radical copolymerizations of VDF with other F-comonomers were successfully carried out in the presence of xanthate.

This strategy, also called "macromolecular design through interchange of xanthate" (MADIX), was pioneered by the Rhodia company[49] and could allow the controlled radical polymerization (CRP) of vinyl acetate (which is difficult to control from other techniques of CRP, except in rare examples of ITP[316]). However, to our knowledge, MADIX

Scheme 34. Xanthate-Mediated Controlled Radical Polymerization (the MADIX Process)[49]



copolymerization of fluoroalkenes is scarce: indeed, only radical copolymerizations of VDF with HFP,[317] VDF and PFSVE,[318] and VDF with TFP[319] were successful so far to lead to original poly(VDF-*co*-HFP)−xanthate, poly(VDF-*co*-PFSVE)−xanthate, and poly(VDF-*co*-TFP)−xanthate, respectively. These fluorinated copolymers bearing a xanthate end group were able to further yield original block copolymers (see section 4.1.2).

As for the mechanism (Scheme 34), after being created, $P_m^•$ macroradicals react onto the carbon atom of the C═S group. Then, the main reversible addition−fragmentation transfer (RAFT) occurs, thus inducing a fast equilibrium between the active and the dormant species. Afterward, the end group rearranges into P_m−S−C(S)OZ′ and then generates $P_n^•$ radical able to further propagate. Finally, $P_n^•$ subsequently undergoes a transfer to the xanthate.[49] Examples are supplied in section 4.1.2, which illustrates the synthesis of block copolymers.

3.3.7. Conclusion

Only three efficient methods dealing with controlled radical copolymerizations (CRcoP) of VDF have been achieved so far: ITP, MADIX, and copolymerization in the presence of boron-containing species. Though these methods have not been systematically applied on each VDF/M couple, various products have already been industrially implementated. Daiel and Tecnoflon copolymers, marketed by the Daikin and Solvay Solexis companies, are the first industrial products obtained by CRcoP (see section 4.1.2). In addition to well-established thermoplastic elastomers for O-rings, sealants, and gaskets, further promising applications can also be deduced from such a technology (fuel cell membranes or surfactants for which it is urgent to find alternatives regarding the cost, methanol crossover for the formers, and environment or health concerns such as the bioaccumulation for the latters).

4. Well-Defined Copolymers Based on Vinylidene Fluoride

As mentioned above, most fluorinated copolymers based on VDF are statistic. But, original well-architectured VDF-containing copolymers have already been synthesized such as block, graft, alternated, or telechelic fluorocopolymers, and a nonexhaustive list of examples are supplied below.

4.1. Fluorinated Block Copolymers Based on VDF

Macromolecular engineering has become a powerful tool to design controlled-architecture polymers:[4,47,320] telechelics, block, graft, or alternated copolymers, cycles, networks, dendrimers, and star-shaped polymers.[4] Among them, block copolymers have received much attention as "novel polymeric materials" with multicomponents since they are made of two or more different polymeric sequences linked together. The reason for their importance arises from their unique chemical structure that brings new physical and thermodynamic properties related to their solid-state and solution morphologies. Frequently, these copolymers exhibit phase separation producing a dispersed phase consisting of one block type in a continuous matrix of the second type. Their unusual colloidal and mechanical properties allow modification of solution viscosity, impact resistance, surface activity, and elasticity. Thus, several block[47,320] (and even graft) copolymers have produced a wide range of materials with tailorable properties depending on the nature and the length of the sequences (or of grafts[4,47]). They have found significant applications such as adhesives, sealants, surface modifiers for fillers and fibers, cross-linking agents for elastomers, additives for resin gelification and hardening, and compatibilizing agents or stable emulsion of homopolymer blends. Most important properties for these well-designed fluoropolymers deal with thermoplastic elastomers (for O-rings, shafts, diaphragms, sealants, gaskets), fuel cell membranes, surfactants, and various items (lenses, dental materials, etc.).

Scheme 35

$$CF_3(OC_2F_4)_m(OCF_2)_p Br + n\,VDF \xrightarrow{rad.} \text{poly(fluoroether)-b-PVDF}$$

Scheme 36

$$\text{PFPE—I} + n\,\text{VDF} + p\,\text{HFP} \xrightarrow{rad.} \text{PFPE-b-poly (VDF-co-HFP)}$$

In this section, two methods of synthesis are considered: traditional and controlled radical polymerizations.

4.1.1. Traditional (or Conventional) Radical Polymerization

By using an adequate chain transfer agent involving a C−Br bond cleavage, Moggi et al.[321] performed the radical telomerization of VDF with ω-bromoperfluorinated perfluoropolyethers (PFPEs) (Scheme 35) in a noncontrolled process.[4]

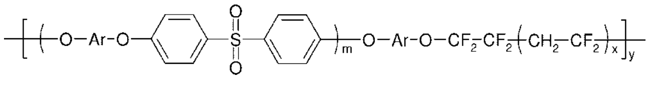
These PFPE-*b*-PVDF diblock copolymers exhibit a heterogeneous morphology with two amorphous zones assigned to the fluorinated blocks. The one attributed to the PFPE sequence had a T_g of −143 °C in all the cases, while that of the second block depended upon the chain length of oligo(VDF) blocks, varying from −82 to −52 °C for a number of VDF units ranging between 13 and 71.

In addition, the DuPont company, which develops Krytox products as PFPEs, also supplies an original series that possesses an iodo end group (PFPE-I). A similar investigation[322] as above but involving C−I cleavable bonds, was achieved and led to original PFPE-*b*-poly(VDF-*co*-HFP) diblock copolymers under telomerization conditions (Scheme 36).

According to the nature of the initiator and to the stoichiometry of the reaction, these obtained PFPE-*b*-poly(VDF-*co*-HFP) block copolymers exhibit molecular weights ranging between 1900 and 30 000 (starting from a PFPE-I having an average molecular weight, $\bar{M}_n = 1300$).

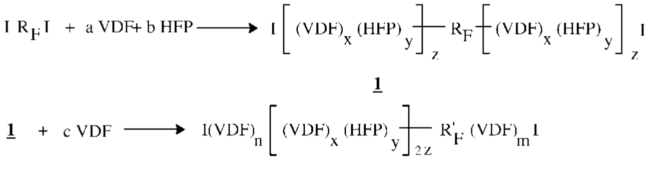
Another route to synthesize block copolymers containing PVDF was proposed by Holdcroft's group.[323] This Canadian team prepared poly(arylene ether sulfone)-*b*-PVDF block copolymers from the condensation of α,ω-bis(dihydroxy)-poly(arylene ether sulfone), PAES, of molecular weights 1800, 4900, and 9500 Da with a telechelic dibromooligo(VDF). The latter was achieved by well-known radical telomerization of vinylidene fluoride with 1,2-dibromo

Scheme 37[a]



[a] Ar can be bisphenol, bisphenol A, or bisphenol AF.

Scheme 38



tetrafluoroethane[324] (reaching molecular weights of ca. 1200 Da). The structure of the block copolymer is displayed in Scheme 37.

Surprisingly, the authors did not mention any expected dehydrofluorination of the oligo(VDF) since the above condensation occurs with the presence of a large excess of NaH. These Canadian authors noted that when observable, the T_g of PAES domains within the block copolymers occurred at a temperature lower than the corresponding PAES homopolymer due to the flexible nature of the surrounding oligo(VDF) regions. Block copolymers exhibited a similar thermal stability as that of the corresponding PAES homopolymer and a higher stability than that of the PVDF oligomer.

Sulfonation of bisphenol A polysulfone-*b*-PVDF block copolymer (M_n of PSU was 9500 Da) was successfully achieved[325] and led to proton exchange membranes. Their water uptake values varied from 14% to 77%, and their average number of water molecules to sulfonic acid group ratio, $[H_2O]/[SO_3H] = \lambda$, were 10−20, while their conductivity values ranged between 4 and 55 $mS \cdot cm^{-1}$, according to the sulfonic acid content.

4.1.2. Controlled Radical Copolymerization

Several examples of random copolymers achieved by controlled radical copolymerization have been reported in section 3.3, which also mentions the mechanisms. This subsection describes strategies to prepare fluorinated block copolymers by group transfer: for example, those prepared by degenerative transfer involving either macrotransfer agents that possess cleavable C−X bonds (X designates a halogen) or xanthates.

4.1.2.1. Block Copolymers via Halogen Transfer. Regarding the C−I cleavage, the pioneering work on ITP was realized by Tatemoto et al.[48,326] in the late 1970s, and these Japanese researchers synthesized poly(VDF-*co*-HFP)-*b*-PVDF block copolymers by controlled (or pseudoliving) iodine transfer polymerization[48,312] using an α,ω-diiodoperfluoroalkane (IR_FI such as IC_4F_8I or $IC_6F_{12}I$), which generated the first elastomeric block **1**. This was then able to initiate the polymerization of VDF (or of other comonomers) as illustrated in Scheme 38.

These special fluoropolymers, called thermoplastic elastomers (TPEs), marketed by the Daikin Company as early as 1984 under the Daiel trademark, are composed of soft segments (containing the poly(VDF-*co*-HFP) or poly(VDF-*ter*-HFP-*ter*-TFE) elastomeric blocks, Figure 16) and hard segments composed of various sequences (PVDF, PTFE, or poly(ethylene-*alt*-tetrafluoroethylene) thermoplastics).[327] Similar TPEs, based on poly(VDF-*co*-CTFE) central copolymeric block,[141] have also been mentioned in section 3.2.1. In the first step, iodine-terminated poly(TFE-*ter*-VDF-*ter*-HFP) terpolymers were synthesized by emulsion polymerization leading to α,ω-diiodopolymeric soft segments. In the second step, another emulsion polymerization of VDF (or TFE) to produce the hard segment took place in the presence of the iodine-terminated soft terpolymer to yield a hard−soft−hard triblock copolymer. Daikin Company commercializes several grades, for example, composed of one type that contains a poly(E-*ter*-TFE-*ter*-HFP) hard block (Dai-el T530) while the other one is based on PVDF blocks (Dai-el T-630).[327b] A similar strategy has also been proposed by Ausimont (nowadays Solvay-Solexis), which markets Tecnoflon block copolymers (Table 1), by a pseudoliving branching technology. Other fluorinated sequenced copolymers and TPEs using that process were reviewed a few years ago.[4,48]

Basic investigations have been proposed by Apostolo et al.[328] (also from Solvay Solexis) on the microemulsion copolymerization of VDF and HFP by degenerative transfer in the presence of $IC_6F_{12}I$, showing the linear dependence of the molar masses versus the monomer conversion. An interesting kinetic model was suggested to assess various rate constants. Moreover, the amount of iodinated chain end decreased with higher monomer conversion and showed a loss of the controlled behavior of that copolymerization. This was assigned to a high transfer to the polymer, called the "Pseudoliving Branching Technology".

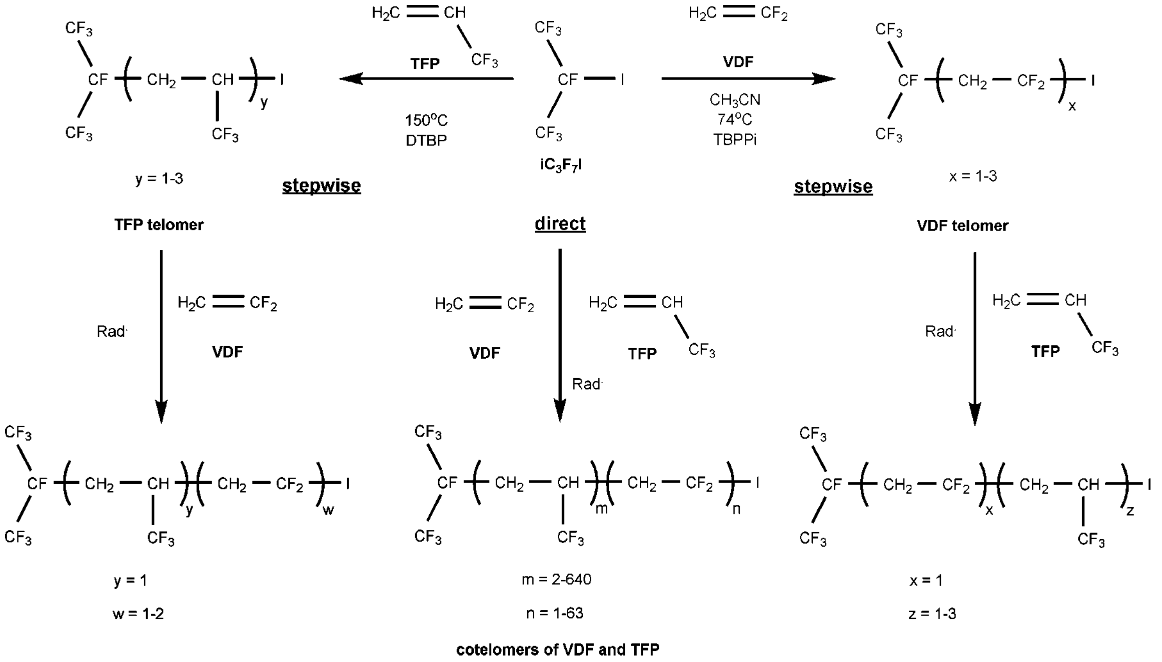
As a matter of fact, various models of multiblock copolymers containing VDF, trifluoroethylene, and HFP[221] or VDF and 3,3,3-trifluoropropene[223] (Scheme 39) were proposed from controlled stepwise (or sequential) cotelomerization of fluoroolefins.[221]

In addition, the synthesis of PVDF-*b*-polystyrene block copolymer[329] was achieved by sequential iodine transfer polymerization of VDF[48,312,330] followed by that of styrene in the presence of PVDF-I. The thermal stabilities of these block copolymers were intermediate between those of polystyrene and of PVDF obtained under similar conditions.

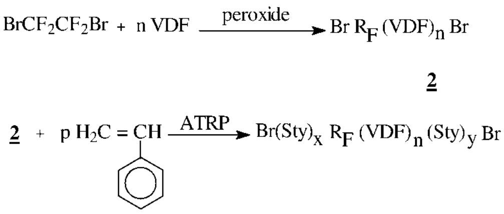
Jo et al.[331] could prepare PVDF-*b*-PMMA and PMMA-*b*-PVDF-*b*-PMMA block copolymers by ATRP of MMA with PVDF-I and I-PVDF-I (obtained by ITP of VDF with $C_6F_{13}I$ or $IC_6F_{12}I$). However, these Korean authors showed a low efficiency of the reactivation of $I-CF_2-PVDF$ in ATRP. On the other hand, various block copolymers have also been prepared from a pathway involving the cleavage of the C−Br bond (regarded stronger than the C−I one), and that process has been used to prepare di- or triblock copolymers. Indeed, ATRP of styrene (Sty) proceeded via the bromine transfer[332] from α,ω-dibrominated intermediates **2**, regarded as "macroinitiators". Surprisingly, the authors claimed narrow polydispersities of 1.1, while previous similar investigations[324] evidenced the presence of PVDF oligomers as side products obtained by direct initiation from the radicals (generated from the initiator such as di-*tert*-butyl peroxide) onto VDF. Beside these unexpected nonfunctional VDF oligomers, the dihalogenated compounds **2** were prepared by telomerization of vinylidene fluoride with 1,2-dibromotetrafluoroethane[324] (Scheme 40).

Another example of synthesis[333] of diblock copolymers (**4**) arises from the chlorine transfer radical polymerization (via a CCl_3 end group) of various M monomers (styrene, MMA, methyl acrylate, and butyl acrylate) initiated by VDF telomers (**3**) with $\overline{DP}_n$ ranging between 5 and 16, summarized in Scheme 41.

Scheme 39. Various Strategies of Syntheses of Poly(VDF-*co*-TFP), Oligo(VDF)-*b*-oligo(TFP), and Oligo(TFP)-*b*-oligo(VDF) Copolymers by Direct or Sequential Copolymerization of Vinyldene Fluoride (VDF) and 3,3,3-Trifluoropropene (TFP)[223]



Scheme 40



Scheme 41

$$\mathrm{Cl_3C{-}H} + n\,\mathrm{VDF} \xrightarrow{\text{rad.}} \mathrm{Cl_3C{-}(VDF)_n{-}H}$$

$\underline{3}$

$$\underline{3} + p\,\mathrm{M} \xrightarrow{\text{CuCl, bipyrid.}} \text{PVDF-b-poly (M)}$$

$\underline{4}$

Interestingly, whatever the VDF telomer/M couple, the average molecular weights in number $\bar{M}_n$ of block copolymer **4** increased linearly with the monomer conversions and experimental $\bar{M}_n$ values were close to the theoretical ones. In addition, narrow polydispersities ($\bar{M}_w/\bar{M}_n < 1.2$) were obtained. These statements are clear evidence of a controlled radical polymerization. Similarly, Shi and Holcroft[334] could prepare poly(VDF-*co*-HFP)-*b*-PS block copolymers by a first cotelomerization of VDF and HFP with chloroform followed by a similar ATRP of styrene. The sulfonation of these block copolymers led to poly(VDF-*co*-HFP)-*b*-PSSA block copolymers,[335a] which were subsequently processed into membranes for fuel cells. The nanostructure of film cast from these diblock copolymers was shown by the same group,[335b] in addition to the correlation between such nanostructures and the transport properties of the membranes[335a] obtained from these diblock copolymers. These data were given from small-angle neutron scattering and transmission electron microscopy, which also enabled the authors to evidence that these membranes possess structures at two length scales: phase separation at length scale of ca. 40 nm arising from the immiscibility of both blocks and substructure within the sulfonated polystyrene domains due to segregation of the hydrated ionic groups and the hydrophobic polystyrene chains.

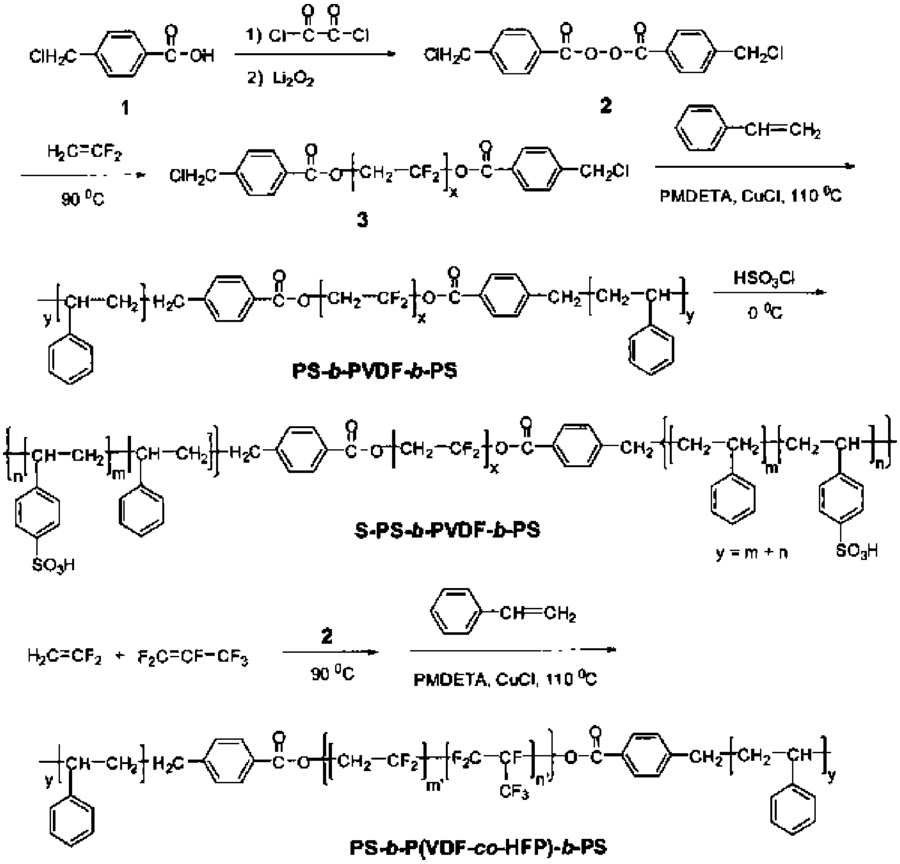
That ATRP strategy was even successfully applied for the preparation of PVDF-*b*-poly(pentafluorostyrene)[336] block copolymers by ATRP of pentafluorostyrene (PFS) in the presence of $\mathrm{CCl_3{-}PVDF}$. These original block copolymers are endowed with satisfactory thermostabilities. This survey completes a comprehensive review, which reports the ATRP of PFS by Jankova and Hvilsted[313] (section 4.1.2).

More recently, PSSA-*b*-PVDF-*b*-PSSA and PSSA-*b*-poly(VDF-*co*-HFP)-*b*-PSSA triblock copolymers with various degrees of sulfonation (DS) of polystyrene blocks have been synthesized by Xu et al.[337] via a different approach. These A−B−A triblock copolymers were claimed to be obtained from telechelic PVDF ($M_n = 56\,000\ \mathrm{g{\cdot}mol^{-1}}$) or poly(VDF-*co*-HFP) copolymers ($M_n = 32\,000\ \mathrm{g{\cdot}mol^{-1}}$) as the macroinitiators (see section 4.4), followed by ATRP of styrene, and finally sulfonation (Scheme 42). However, no evidence of the end-group functionalities in R−PVDF−R or R−poly(VDF-*co*-HFP)−R intermediates was given (they were claimed to be 2.00). Nevertheless, targeted molecular weights higher than 47 000 $\mathrm{g{\cdot}mol^{-1}}$ for PSSA-*b*-poly(VDF-*co*-HFP)-*b*-PSSA triblock copolymers were synthesized enabling them to ensure satisfactory mechanical properties for “durable and ductile films”.

These authors also noted that the T_g of the PS blocks in PS-*b*-PVDF-*b*-PS was 92 °C, while it reached 134 °C when the PS blocks were sulfonated, linked to the bulkiness of the sulfonate groups and the ionomer effect. Spectroscopic and thermal characterizations of the polymers were carried out such as tapping mode AFM and TEM, which revealed self-assembled microstructures with tunable ionic domains or a microphase separation and ionic aggregates that depend strongly on the DS value.[337]

The hydrophilic ionic clusters coalesced into larger channel structures when DS > 23%, coinciding with sharp increases of both water uptake and proton conductivity. As expected, different DS values ranging from 13% to 49% led to various

Scheme 42



ratios of average number of water molecules to sulfonic acid groups (λ = 4–68). The proton conductivity increased significantly when the ion-exchange capacity (IEC) increased from 0.5 to 1.5 mmol$\cdot$g^{-1} (Figure 30) and an optimal conductivity value of 0.091 S$\cdot$cm^{-1} was reached at 95% relative humidity (RH) and 30 °C for the membrane with a DS of 49% (Figure 31).[337] In addition, the copolymer membrane also showed a maximum proton conductivity between 60 and 70 °C (Figure 32) even higher than that of Nafion in that temperature range. Interestingly, the conductivities of the block copolymers were considerably higher than those of the random copolymers of polystyrene and sulfonated polystyrene that had similar IECs.[337]

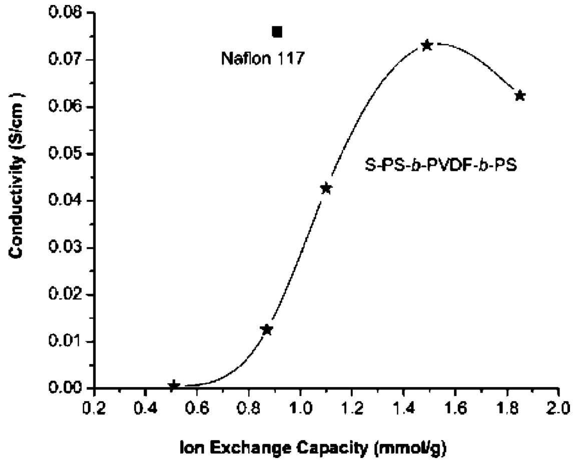


Figure 30. Conductivities of Nafion 117 and of membranes achieved from PSSA-*b*-PVDF-*b*-PSSA triblock copolymer as a function of the ion-exchange capacity. Reproduced with permission from ref 337. Copyright 2007 American Chemical Society.

In conclusion, block copolymers obtained from the cleavage of C–X bond in chain transfer agents (CTAs) can be achieved. The decreasing order of the C–X bond dissociation energy (C–Cl > C–Br > C–I) shows that major industrial productions occur from iodine transfer polymerization of fluoroalkenes in the presence of $IC_nF_{2n}I$ as the CTAs. Exceptional thermoplastic elastomers have been produced from such a process. In addition, "hot" topics such as polymer electrolyte for fuel cells membranes have also been investigated as evidenced by the growing number of patents and publications. Further strategies to synthesize block

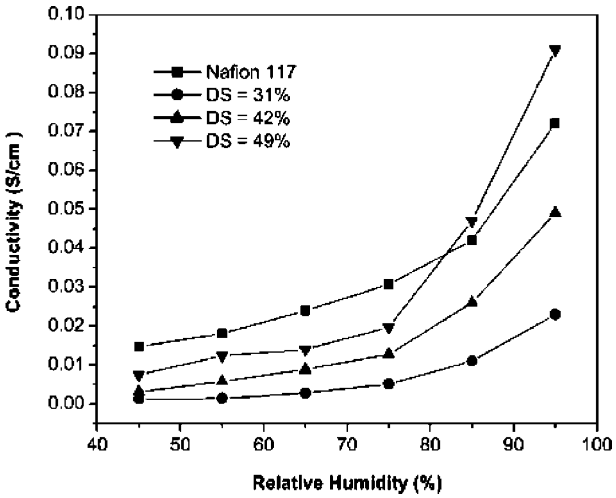


Figure 31. Proton conductivity versus the relative humidity of PSSA-*b*-PVDF-*b*-PSSA triblock copolymers and Nafion 117 membranes. DS stands for degree of sulfonation. Reproduced with permission from ref 337. Copyright 2007 American Chemical Society.

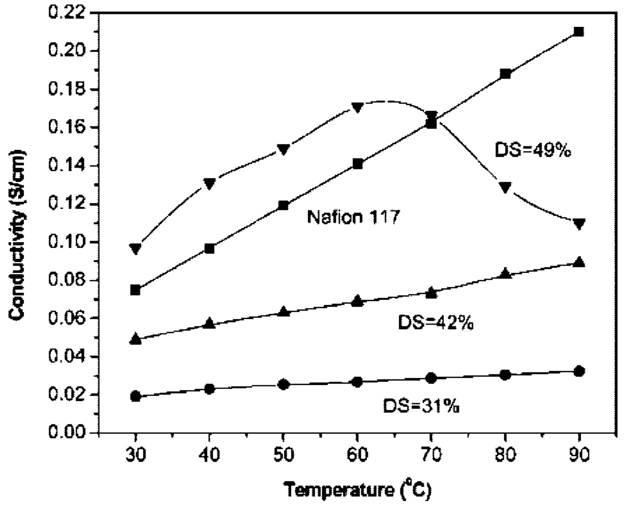


Figure 32. Variation of proton conductivity measured under 95% relative humidity versus temperature for PSSA-*b*-PVDF-*b*-PSSA triblock copolymers and Nafion117 membranes. Reproduced with permission from ref 337. Copyright 2007 American Chemical Society.

copolymers are presented below, involving xanthates as suitable CTAs.

4.1.2.2. Block Copolymers via Xanthate. As mentioned in section 3.3.6, MADIX technology has efficiently been used to control the radical (co)polymerization of vinyl acetate (VAc).[49] Regarding block copolymers, a first interesting example was reported by Severac[317] who realized the controlled radical copolymerization of VDF with HFP in the presence of $CH_3OCOCH(CH_3)SC(S)OEt$ xanthate (Scheme 43). Then, the intermediate poly(VDF-*co*-HFP) copolymer bearing a xanthate end group was able to reinitiate further poly(VDF-*co*-HFP) or poly(VAc) oligomeric chains via the cleavage of the C−S bond.

Molar masses and polydispersity indices for the intermediate copolymer were 6500 g·mol^{-1} (equivalent PMMA standards) and 1.47, respectively, while those of poly(VDF-*co*-HFP)-*b*-poly(VDF-*co*-HFP) and poly(VDF-*co*-HFP)-*b*-PVAc block copolymers were 10 600 g·mol^{-1} and 1.48 and 9400 g·mol^{-1} and 1.59, respectively. These results indicate a correct control of that copolymerization with an increase of the molar masses, while keeping satisfactorily narrow polydispersities.[317]

More recently, an original fluorinated xanthate was also synthesized[318] in two steps (Scheme 44).

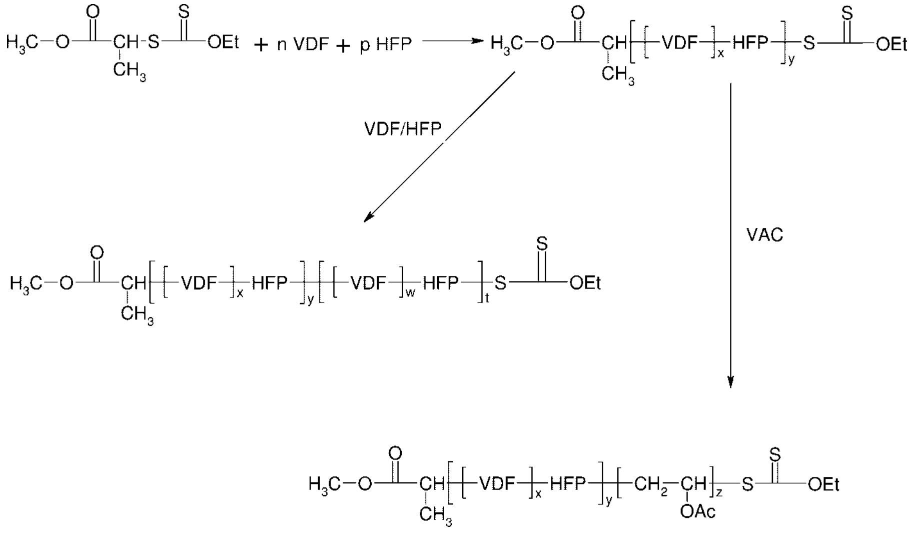
First, a radical copolymerization of VDF and HFP controlled by a fluorinated xanthate was carried out and led to poly(VDF-*co*-HFP)SC(S)OEt of molar masses up to 13 000 g·mol^{-1} and PDI = 1.45. Then, the resulting poly(VDF-*co*-HFP)−xanthate was involved in two reactions: (i) first, the radical polymerization of VDF (reaction REMX2-1) to allow the synthesis of poly(VDF-*co*-HFP)-*b*-PVDF block copolymers, the SEC chromatogram of which showed a shift toward lower elution time (Figure 33, that is, higher MW of ca. 20 000 g·mol^{-1}, assessed by ^{19}F NMR spectroscopy); (ii) the second reaction, REMX22, reported the radical copolymerization of HFP and VDF in 70/30 mol %/mol % feed ratio of VDF/HFP to lead to poly(VDF-*co*-HFP)-*b*-poly(VDF-*co*-HFP) block copolymers. This block copolymer also has a SEC response that indicates higher molar masses (Figure 33).

A similar strategy was also successfully applied for the synthesis of poly(VDF-*ter*-HFP-*ter*-PFSVE)-*b*-poly(VDF-*co*-HFP) block copolymers from poly(VDF-*ter*-HFP-*ter*-PFSVE) sequence (Scheme 45).[318] The searched application for these copolymers was to supply original fuel cell membranes.

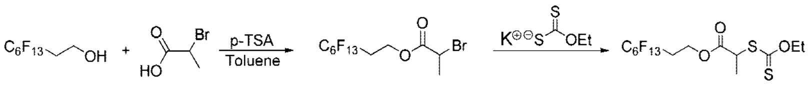
Another application from block copolymers achieved by that technique deals with fluorosurfactants. More recently, original poly(VDF-*co*-TFP)-*b*-oligo(vinyl acetate) diblock copolymers have been synthesized[319] by the control of fluorinated xanthates via the MADIX process (Scheme 46).

The acidic hydrolysis of the oligo(VAc) block led to a hydrophilic sequence making the resulting poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol) diblock copolymers amphiphilic and able to be used as novel surfactants.[319] Interestingly, low

Scheme 43



Scheme 44



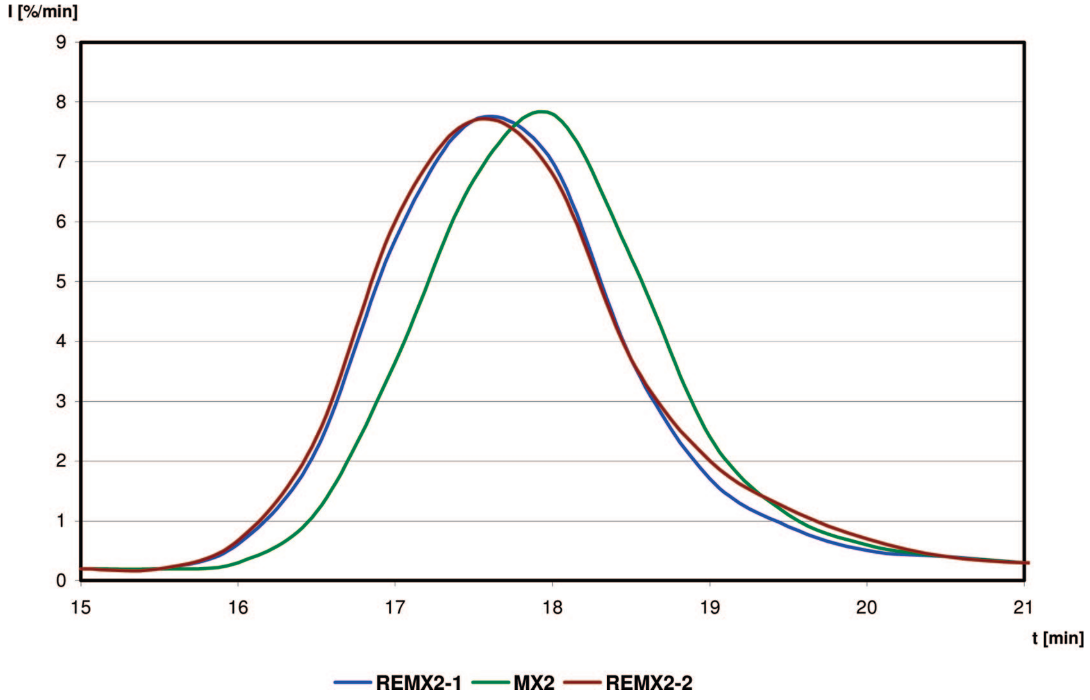
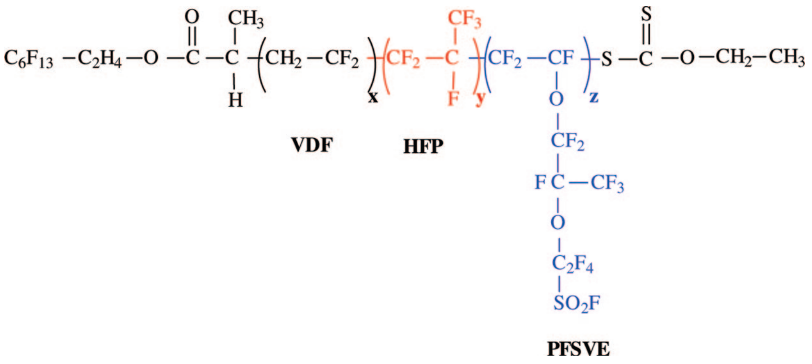
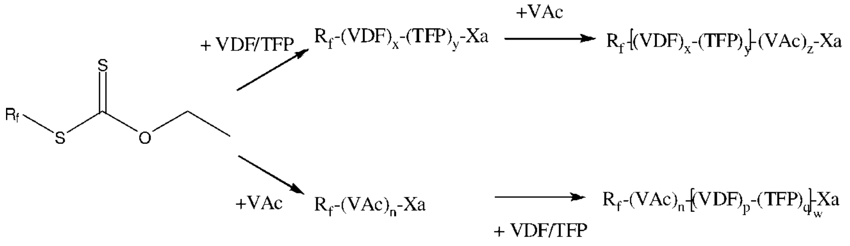


Figure 33. Superposition of SEC chromatograms of poly(VDF-*co*-HFP) copolymer (70/30 in feed) in the presence of MX2 fluorinated xanthate, reaction time $t = 7$ h: VDF (REMX2-1) and VDF/HFP (70/30 in feed) (REMX2-2); MX2 stands for $C_6F_{13}C_2H_4C(O)CH(CH_3)-$poly[(VDF)-*co*-(HFP)]$-SC(S)OCH_2CH_3$.[318]

Scheme 45



Scheme 46. Synthesis of Poly(VDF-*co*-TFP)-*b*-poly(vinyl acetate) Diblock Oligomer[a]



[a] Xa, VDF, TFP, and VAc represent S$-$C(S)OEt, vinylidene fluoride, 3,3,3-trifluoropropene, and vinyl acetate, respectively[319].

critical micellar concentrations (cmc's) and surface tensions (29 mN·m^{-1} for 4 g · L^{-1} copolymer concentration) were obtained (Figure 34),[338] almost as low as those of commercially available perfluorooctanoic acid (PFOA) or perfluorooctane sulfonic acid (PFOS) surfactants (which are regarded as persistant, toxic, bioaccumulable (their half-lives are 100 days and 5.4 years for rats and human beings,[339] respectively), and suspected mutagens).

According to the initial [monomer]/[xanthate] molar ratios, a wide range of surfactants[319] with molar masses ranging from 600 to 5000 g·mol^{-1} were prepared. Although the bioaccumulation has not been investigated yet, it can be advantageously assumed that the hydrophobic poly(VDF-*co*-TFP) block should undergo metabolic or enzymatic decomposition arising from the methylene or methyne "weak" points of VDF or TFP (Scheme 47), in contrast to commercially available fluorsurfactants, which possess too stable and inert C_7F_{15} or C_8F_{17} groups. Hence, these block cooligomers are potential nonbioaccumulable surfactant alternatives to PFOA or PFOS.[338]

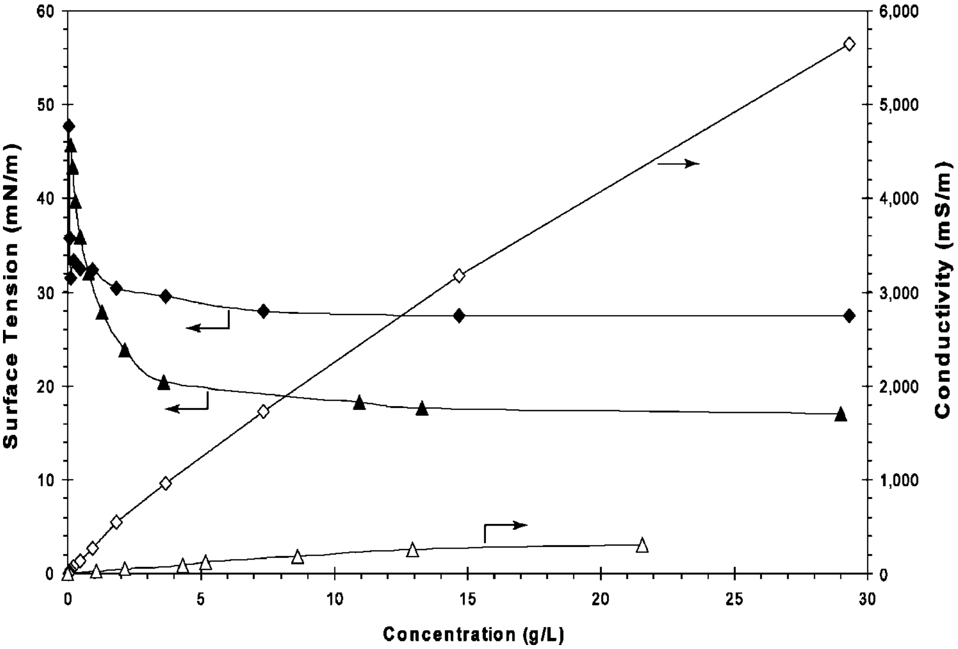
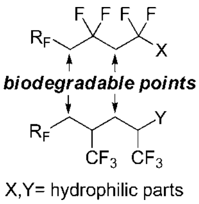


Figure 34. Surface tension and conductimetry curves of poly(VDF-*co*-TFP)-*b*-poly(VA) block cooligomers (diamonds) compared with those of ammonium perfluorooctanoate (triangles). VDF, TFP, and VA stand for vinylidene fluoride, 3,3,3-trifluoropropene, and vinyl alcohol, respectively.

Scheme 47



4.1.3. Conclusion

There are several pathways to prepare block copolymers based on PVDF (or poly(VDF-*co*-M) copolymer) sequences. The first series concerns conventional radical polymerization including various alternatives from the radical telomerization to the condensation of phenate onto Br−PVDF−Br species. However, more opportunities can be offered by controlled sequential radical copolymerizations of VDF with other fluorinated comonomers or with various M monomers (especially styrene) that have already led to interesting PVDF-*b*-poly(M) or poly(M)-*b*-PVDF-*b*-poly(M) block copolymers. Three main techniques offer such well-controlled architectures of VDF-containing copolymers: ITP, the use of borane, and MADIX for which the (co)polymerization involving xanthates. Suitable cleavable C−X bonds can also be used in group or atom transfer. Indeed, three main industrial products have been already produced (Daiel, Tecnoflon, and Viton marketed by Daikin, Solvay Solexis, and DuPont Performance Elastomers, respectively) for original thermoplastic elastomers, offering various products for many applications (gaskets, O-rings, shafts, sealants, or medical items). From these above methods, a wide range of other sulfonic acid-containing block copolymers are recently potential candidates for fuel cell membranes. In addition, nonbioaccumulable fluorinated surfactants have already been achieved. Nevertheless, the trends nowadays show that there is an increasing interest in the controlled radical copolymerization of VDF with fluoroalkenes for high-performance materials. Graft copolymers also are interesting candidates for high-tech areas and are discussed in the next section.

4.2. Fluorinated Graft Copolymers

4.2.1. Introduction

Five main synthetic methods for fluorinated graft copolymers are possible. They can be generated (i) from the direct (co)polymerization of *macromonomers*, (ii) from *transfer to the polymer*, (iii) from *grafting of various polymers* onto a polymeric backbone, (iv) from the *telomerization* of monomer(s) in the presence of *macrotelogen*, and finally (v) from a macroinitiator or a macroradical (generated from an activated polymer) via the “grafting from” procedure (Scheme 48) for which most examples are displayed hereafter.

4.2.2. Conventional Radical Copolymerization

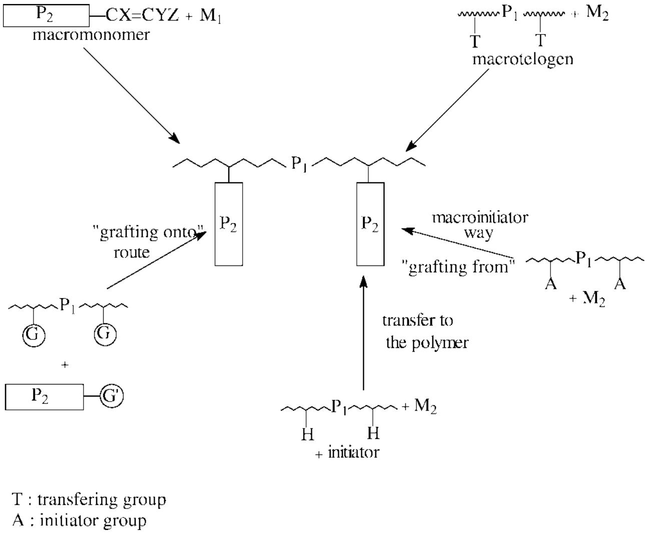
The last pathway has already led to various investigations regarding the grafting (produced by the polymerization of various monomers such as acrylates or styrenics) onto activated fluoropolymers, as illustrated by Scheme 49. For example, activation of PVDF can be realized by ozonization,[340−342] high-energy technologies such as γ rays,[343] swift heavy ions,[344] electron beam (EB),[345−347] or plasma.[348]

Recently, an extensive review on the synthesis of fluorinated graft copolymers from radiografting of F-polymers has been reported.[349]

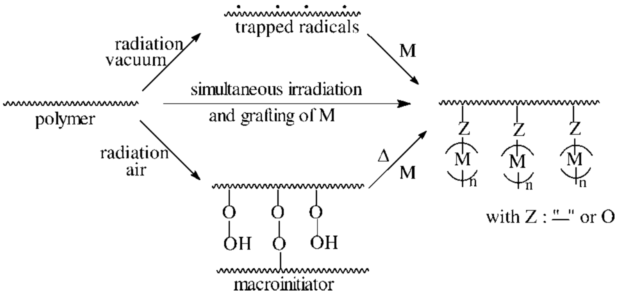
Hence, the activation of the polymer (in various states such as powders or films) leads either to trapped radicals or to macroinitiators, or in certain cases, it is accompained by a simultaneous activation/grafting of the monomer (Scheme 49).

Ozonization, which has been extensively summarized,[342] is an original means for activating polymers, though it has encountered slight difficulties when applied to PVDF. However under hard conditions, a little degradation was noted.[341] Nevertheless, the ozone pre-activated PVDF backbone led to macroinitiators containing mainly peroxides (90%) (titrated by diphenyl picryl hydrazyl or by iodometry,[341] and hydroperoxides (10%).[350] The content of hydroperoxides was noted to decrease as the ozonization temper-

Scheme 48. Various Strategies To Synthesize Graft Copolymers



Scheme 49. Various Ways To Synthesize Graft Copolymers from Radiografting Films or Powders



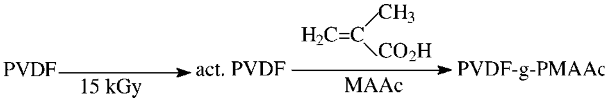
ature was increased, while the latter species were evidenced according to the method of Zeppenfeld.[351]

The second step concerns the grafting, carried out in bulk, which leads to a higher degree of grafting, or in solution of an oligomer or polymer based on MMA, styrene, glycidyl methacrylate (GMA), or acrylic acid (AAc). Kang's team[352] also used that concept to prepare PVDF-*g*-PAAc graft copolymers (even achieving 100% AAc grafting!)[352b] for original microfiltration membranes with well-controlled pore sizes, uniform surface composition, and pH sensitive properties.

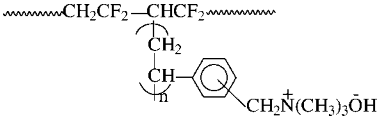
Nevertheless, in all cases, adapted experimental recipies were proposed to remove the corresponding homopolymers (which were obtained in ca. 40% yield).[353]

These produced PVDF-*g*-poly(M) graft copolymers were tested in various applications. First, the mechanical behavior of the PVDF/PS blend was greatly improved by adding PVDF-*g*-PS copolymer, leading to a 2.5-fold increase in the break-stress for a 50/50 wt % blend.[353] Second, the adhesion of PVDF to a glassy-epoxy composite was achieved by using PVDF-*g*-PAAc and PVDF-*g*-PGMA graft copolymers. In both cases, a great increase of the peeling strength was noted. Third, the introduction of hydrophilic groups (brought by acrylic acid, MMA, or GMA) enabled PVDF to be less hydrophobic.[353] Indeed, to improve the surface hydrophilicity of PVDF, many investigations have been devoted to the surface modification of fluoropolymers by chemical,[354] plasma,[355] irradiation,[356] corona discharge,[357] flame,[358] and vacuum ultraviolet radiation.[359] For example, the synthesis of PVDF-*g*-PMAAc (where MAAc stands for methacrylic acid) was reported in 1998 by Mascia and Hashim[360] according to a two-step procedure (Scheme 50).

Scheme 50



Scheme 51



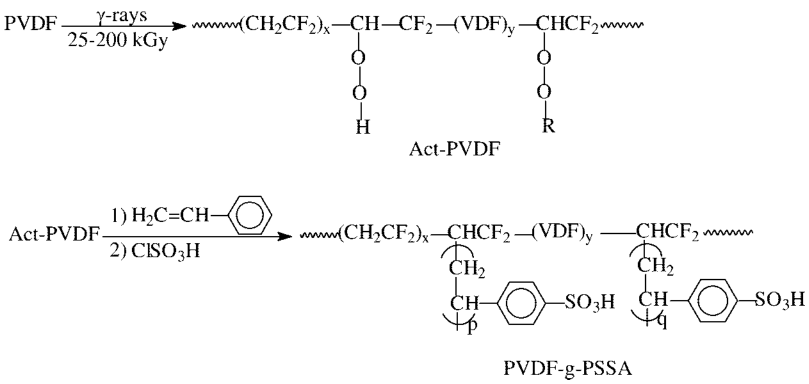
Furthermore, Liu et al.[361] also used that strategy to synthesize PVDF-*g*-PEOMA graft copolymer, where PEOMA stands for poly(ethylene glycol methacrylate). By a phase inversion method, this group obtained nanoporous membranes endowed with interesting electrochemical properties for potential applications for lithium ion rechargeable batteries: high liquid electrolyte uptake capacity, high conductivity (1.6×10^{-3} S·cm^{-1} at 30 °C), a satisfactory transference number (0.15), and an electrochemical stability.

More recently, Danks et al.[362] synthesized PVDF-*g*-PVBC graft copolymers from the activation of two grades of PVDF by γ-rays (^{60}Co) followed by the grafting of vinyl benzyl chloride (VBC or chloromethylstyrene). According to the grade, the degree of grafting was either 38% or 54%, while the average thickness was 54 μm. Then, the chloromethyl end groups of the grafts underwent an amination reaction into benzyl trimethylammonium (BTMA) hydroxide[362] or BTMA chloride (BTMAc)[363] (Scheme 51) for anion exchange membrane applications.

The originality of the work lies on the ability of these quaternary ammonium side groups to conduct hydroxide ions to use this graft copolymer as novel membranes for alkaline fuel cells for portable applications. Unfortunately, this last step led to too brittle PVDF-*g*-PBTMAc graft copolymers because of degradation of the polymer backbone by the expected dehydrofluorination. Hence, the resulting materials, which possessed lowered ion exchange capacity (IEC = 0.31 and 0.71 mequiv·g^{-1}), were unsuitable for use as membranes for fuel cells or electrochemical devices. Hence, these British authors decided to apply the same strategy from a perfluorinated copolymer, such as FEP, which is not base-sensitive, and they could obtain a membrane endowed with an IEC of 1.0 mequiv·g.$^{-1}$.

Softer strategies were utilized in our laboratory to graft phosphonated (meth)acrylates onto ozonized PVDF.[364] Interestingly, phosphorus-containing (co)polymers[365] are endowed with interesting properties such as fire proofing,[366] complexation, anticorrosion, and adhesion (especially from phosphonic acid functions[364]). Adhesion was advantageously taken into account for realizing a graft copolymer able to be applied onto galvanized steel.[364] Indeed, these experiments show a neat improvement of the adhesive behavior of the PVDF coating compared with a similar copolymer containing carboxylic acid functions. Another property brought by the phosphonic acid function is the protonic conductivity, and the resulting copolymers can be used in proton exchange membranes, well-summarized in the excellent review of Lafitte and Jannasch.[365] Such a growing interest application has also attracted many scientists who have designed original graft copolymers for PEMFCs.[367] Indeed, various attempts of grafted PVDFs have also been investigated in that area to substitute perfluorosulfonic polymeric ones to compete with Nafion. Among them, PVDF-*g*-PSSA graft copolymers

Scheme 52



has the advantages to be cheaper and less permeable to methanol than Nafion, hence providing better chances for a direct methanol fuel cell (DMFC) as shown by Saarinen et al.[368]

The same group[346] carried out the activation of PVDF (with doses of 25, 50, 100, and 200 kGy). The membranes were immersed into neat styrene, and they were kept for 0.5, 1, 2, and 4 h at room temperature under nitrogen.[346] As expected, it was observed that the higher the dose rate and the longer the grafting time, the higher the degree of grafting (d.o.g.). Interestingly, the authors claimed that no homopolystyrene was formed. The sulfonation of PVDF-*g*-PS membranes (in chlorosulfonic acid) led to degrees of sulfonation of 11−71%.[346] In these conditions, the authors did not observe any trace of chlorine atom in the poly(vinylidene fluoride)-graft-poly(styrene sulfonic acid) (PVDF-*g*-PSSA) membrane. This procedure is summarized by Scheme 52.

Further, Shen et al.[369] used Al_2O_3 to produce a PVDF-*g*-PSSA composite with satisfactory conductivities, while Horsfall's[370] group preferred PVDF-*g*-PSSA graft copolymers for direct methanol fuel cells.

PVDF and poly(VDF-*co*-HFP) copolymers (which are hydrophobic) have been structurally modified by radiation grafting with styrene comonomers, which enables them to link sulfonic groups. Copolymers were obtained by Soresi et al.[371] who optimized the conditions of process, the energy of the radiation field (electrons, γ-rays), the absorbed dose, and the physicochemical properties of the starting polymer (e.g., degree of crystallinity, porosity, etc.). These Italian researchers[371] have reported the synthesis and the thermal, morpholological, and electrochemical characterizations of proton-conducting polymers. Membranes obtained from poly(VDF-*co*-HFP) copolymers (containing 5 mol % HFP) and from common porous and dense PVDF homopolymer films were compared. High grafting degrees and water uptakes were reached depending on the nature of the polymer matrix. Room-temperature conductivities exceeding 60 $mS\cdot cm^{-1}$ at 90% RH were observed in the case of the sulfonated membrane made from the PVDF-based copolymer.

A similar process was achieved by Nasef et al.[372] who prepared two classes of composite polymer electrolyte membranes, one conducting lithium ions (Li^+) and the other conducting protons (H^+). Porous PVDF films were impregnated with styrene and subjected to electron beam (EB) irradiation to obtain PS-filled PVDF precursor films that were subsequently treated with either chlorosulfonic acid to obtain H^+-conducting composite membranes or $LiPH_6$/EC/DEC liquid electrolyte to obtain Li^+-conducting composite membranes. Properties of the obtained membranes were found to achieve grafting contents up to 46% with superior Li^+ and H^+ conductivities of 1.91×10^{-3} $S\cdot cm^{-1}$ and 5.95×10^{-2} $S\cdot cm^{-1}$, respectively.

Chen et al.[373] synthesized and compared several electrolytes from a radiografting process of different fluoropolymers: PTFE, ETFE, poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymers (FEP), poly(vinyl fluoride) (PVF), and PVDF. First, they noted that PTFE and PVF were not suitable for the preparation of PEMFCs. In addition, membranes prepared from PVDF could not reach the same success as FEP or ETFE could, since the resulting hydrogenated membranes were not chemically stable. Indeed, authors supplied the following decreasing order of the radiation degradation caused in the films: PTFE > FEP > PFA > cross-linked PTFE > ETFE > PVDF > PVF. Furthermore, PVDF had the best grafting ability among other fluoropolymers, for which the decreasing order was: PVDF > PVF > ETFE > FEP > cross-linked PTFE > PFA > PTFE.

These authors also showed that irradiated PVDF swelled more easily in the monomer solution. PVDF-*g*-PSSA copolymers were achieved by grafting styrene onto a preirradiated PVDF membrane with a degree of grafting up to 87%, followed by immersion into a chlorosulfonic acid solution, leading to a tough and flexible electrolyte. Maximum IEC value was 2.65 $mmol\cdot g^{-1}$, while the proton conductivity of the membrane was 0.085 $S\cdot cm^{-1}$, lower than those achieved from FEP ($\sigma = 0.117$ $S\cdot cm^{-1}$) or PFA ($\sigma = 0.095$ $S\cdot cm^{-1}$). Interestingly, comparing both conductivities from PVDF and ETFE isomers, the authors noted that the membrane made of PVDF had a higher conductivity value than that achieved from ETFE over the entire ion exchange capacity range. This may be attributed to the higher crystallinity of PVDF that arises from a higher sulfonic acid density in the amorphous region.

Though many surveys focusing on the synthesis of graft copolymers that contain PVDF from the above high-energy beam method have been investigated, the presence of homopolymer and the control of the degree of grafting are still severe issues to overcome.[374−376]

Another alternative synthesis of fluorinated graft copolymers (**5**) concerns the direct radical terpolymerization of VDF, HFP, and allylamido perfluoropolyethers (PFPE)[377] (Scheme 53).

An interesting VDF-containing graft copolymer regarded as a thermoplastic elastomer was discovered by the Central Glass Company[142] and is named Cefral Soft. Its synthesis first involves the radical terpolymerization of VDF and CTFE with an olefinic peroxycarbonate (see section 3.2.1, Scheme 11), further leading to poly(VDF-*co*-CTFE)-*g*-PVDF graft copolymers via a "grafting from" procedure. Interestingly,

Scheme 53

$$n\,\mathrm{VDF} + p\,\mathrm{HFP} + q\,\mathrm{H_2C{=}CHCH_2NHCO{-}PFPE} \longrightarrow \mathrm{poly(VDF\text{-}co\text{-}HFP\text{-}g\text{-}PFPE)}$$

5

Katoh et al.[378] characterized these commercially available Cefral Soft original graft copolymers by ^{19}F NMR spectroscopy.

4.2.3. Controlled Radical Polymerization

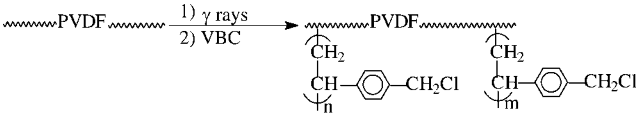
Few fluorinated graft copolymers synthesized by controlled radical copolymerization have been reported in the literature, especially by the "grafting from" approach. To the best of our knowledge, nitroxide-mediated living free radical polymerization (NMP), reversible addition−fragmentation chain transfer (RAFT) polymerization, and ATRP are key strategies to prepare them.

The first one was successfully used by Holmberg et al.[379] who prepared original PVDF membranes first irradiated by EB and then the free radicals formed were immediately quenched with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). In the second step, the produced TEMPO-capped macroinitiator sites were utilized in the controlled graft copolymerization of styrene via NMP. After sulfonation of the PS grafts, the resulting PVDF-*g*-PSSA membranes were compared with those obtained from the conventional preirradiation grafting method. Noteworthy is the fact that the membranes using the controlled grafting technique are grafted through the membrane already at a degree of grafting of 14%, whereas the penetration limit for the membranes prepared by conventional radiation-induced grafting is ca. 30%. Preliminary H_2/O_2 fuel cell tests showed promising results from PVDF membranes grafted by means of NMP in contrast to those obtained by conventional preirradiation grafting. Indeed, the former could be used in a fuel cell for 930 h at 70 °C without any drop in current density, while the latter failed within 150−200 h under similar conditions.

Another "controlled" strategy was claimed by Chen et al.[380] for the synthesis of original PVDF-*g*-PMMA and PVDF-*g*-PPEGMA graft copolymers (where PEGMA stands for poly(ethylene glycol) monomethacrylate) from the RAFT polymerization of MMA and PEGMA at the PVDF surfaces. First, PVDF surfaces were exposed to aqueous LiOH, followed by successive reduction with $NaBH_4$ and DIBAL-H to obtain hydroxyl functionality. Azo functionalities, as surface initiators for grafting, were further immobilized on the PVDF surfaces by esterification of 4,4′-azobis(4-cyanopentanoic acid) and the surface hydroxyl groups. The chemical composition and surface topography of these graft copolymers were characterized by XPS, FTIR spectroscopy, and AFM. The authors noted a linear increase in the graft concentration of PMMA and PPEGMA with time, indicating that the chain growth from the surface was consistent with a "controlled" process.

Kang's team[381] also used that strategy from ozone-pretreated PVDF, which further could react with 1-phenylethyl dithiobenzoate enabling them to get PVDF bearing various pending dithioester side groups. These allowed controlled radical polymerization of PEGMA[381a] and acrylic acid[381b] (AAc) to obtain PVDF-*g*-PEGMA and PVDF-*g*-PAAc (claiming "living PAAc graft chains on the surface") for the preparation of microfiltration membranes. Furthermore, the PVDF-*g*-PAA membrane was functionalized in a subsequent surface-initiated block copolymerization with *N*-isopropylacrylamide (NIPAAM) and the resulting PVDF-*g*-PAA-*b*-PNIPAAM membranes exhibited both pH- and temperature-dependent permeability for aqueous solutions.

Scheme 54



PVDF-g-PVBC

The "grafting from" method based on ATRP technique has also been widely used as an efficient polymerization for preparing well-defined graft copolymers.[382−390] Several non-exhaustive examples of F-graft copolymers designed from the specific cleavage of C−X bonds (where X represents a halogen) via ATRP are given below. Indeed, various investigations dealing with ATRP to introduce PS, further sulfonated into PSSA, have been successfully achieved and various authors have been inspired to prepare PVDF-*g*-PSSA graft copolymers from that strategy.

4.2.3.1. C−Cl Cleavage. As mentioned above, Sundholm's group[382] performed the synthesis of PVDF-*g*-PVBC graft copolymers where VBC stands for vinyl benzyl chloride according to the same strategy (Scheme 54).

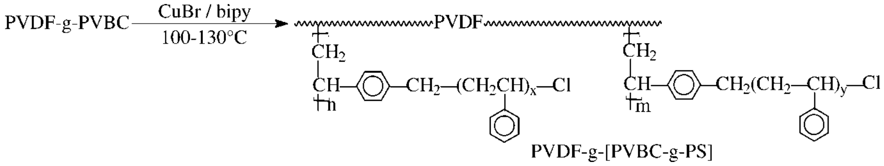
These PVDF-*g*-PVBC graft copolymers acted as suitable macroinitiators via their chloromethyl side groups for the ATRP of styrene involving copper bromide/bipyridine as the catalytic system leading to controlled PVDF-*g*-[PVBC-*g*-PS] graft copolymers (Scheme 55).

The degree of (styrene) grafting increased linearly versus time and thus indicates first-order kinetics, regardless of the polymerization temperature. It reached 400% after 3 h at 120 °C.[382] As a matter of fact, such a high degree of grafting (d.o.g.) could not be possible with conventional uncontrolled radiation-induced grafting methods because of termination reactions. The polystyrene grafts were sulfonated hence leading to well-architectured PVDF-*g*-[PVBC-*g*-PSSA] graft copolymers for the design of proton-exchange membranes for fuel cells applications with the highest conductivity reaching 70 mS·cm^{-1}.

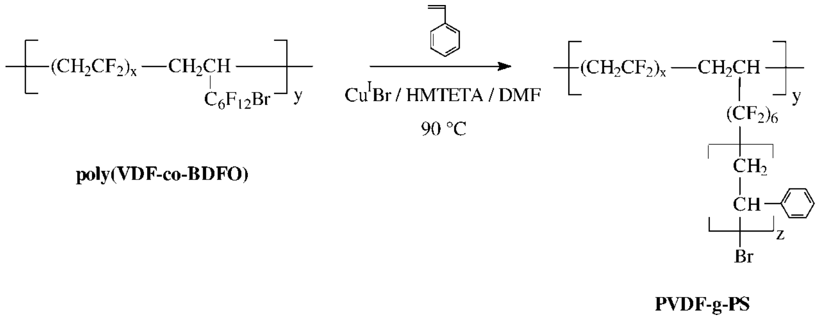
In another approach and surprisingly, Zhang and Russell[383] prepared PVDF-*g*-PS and PVDF-*g*-PBuA graft copolymers (where BuA means butyl acrylate) from ATRP of styrene (or BuA) when a poly(VDF-*co*-CTFE) random copolymer was used as the initiator. The authors claimed that the grafting was achieved from the cleavage of the C−Cl bond of CTFE, though regarded as quite stable! They could obtain poly(VDF-*co*-CTFE)-*g*-PS and poly(VDF-*co*-CTFE)-*g*-poly(*t*BuA) graft copolymers that had molecular weights up to 250 000 g·mol^{-1}. No spectroscopic evidence was supplied in that article.

This was also claimed by Kim's group,[384] who synthesized proton-conducting poly(VDF-*co*-CTFE)-*g*-PSSA graft copolymers by a similar "grafting from" method using an ATRP process. Unfortunately, the ^{1}H NMR spectra of poly(VDF-*co*-CTFE)-*g*-PSSNa graft copolymers were not convincing, and the publication lacks both the SEC chromatograms and ^{19}F NMR spectra. In addition, control of the polymerization was not evidenced. Nevertheless, these Korean authors characterized the microphase-separated structure of the polymer electrolyte membranes and showed that the ion exchange capacity, the water uptake, and the proton conductivity of the resulting membranes continuously increased with the increase of the PSSA content. These membranes were advantageously UV cross-linked after the

Scheme 55



Scheme 56. Synthesis of PVDF-*g*-PS Graft Copolymers by Atom Transfer Radical Polymerization of Styrene with a Poly(VDF-*co*-BDFE) Macroinitiator[a]



[a] BDFO, HMTETA, and DMF stand for 8-bromo-1*H*,1*H*,2*H*-perfluorooct-1-ene, 1,1,4,7,10,10-hexamethyltriethylenetetramine, and dimethylformamide, respectively.[385]

chlorine dangling atoms were converted into azido groups and hence exhibited a reduced water uptake from 300% to 83% and also better mechanical properties. However, the conductivity values slightly decreased from 0.074 to 0.068 $S \cdot cm^{-1}$ at room temperature under 95% RH.

In addition, Holdcroft's team[335] synthesized PVDF-*g*-PSSA and poly(VDF-*co*-HFP)-*b*-PSSA copolymers of different molecular and equivalent weights, and compared the morphologies (i.e., the nanoarchitectures) and the electrochemical properties of the resulting membranes prepared therefrom. TEM pictures revealed different morphologies between the structures playing a major role for the understanding of swelling, conductivities, and effective proton mobility through the membrane versus IEC. These authors noted that the graft membranes possess a significantly higher percolation threshold than the diblock membranes (ca. 1.0−1.2 and 0.6 $mmol \cdot g^{-1}$ for grafts and for diblocks, respectively), which correlates with water uptakes. Comparing the "in-plane" to "through-plane" proton conductivities (the latter is relevant to proton conduction in fuel cells) shows different results for the obtained membranes produced from these types of designed structures: the proton conductivity assessed from the first method for the diblock membrane was found to be ca. 2.4 times greater than "through-plane" conductivity indicating a mild degree of anisotropy; in contrast, the graft membranes had very similar "in-plane" and "through-plane" proton conductivity (anisotropy = 0.95). As a reference, these Canadian authors determined the conductive anisotropy of Nafion112 membrane of ca. 1.4.

4.2.3.2. C−Br Cleavage. To our knowledge, only one survey reports the synthesis of graft copolymers from an initiator that contains a C−Br cleavable bond. Actually, the chemical modification of poly(VDF-*co*-BDFO) copolymers,[385] synthesized by conventional radical copolymerization of VDF with 4-bromo-3,3,4,4-tetrafluorobut-1-ene (BDFO),[227] was successfully achieved by ATRP of styrene catalyzed by CuBr and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the ligand (Scheme 56).

Interestingly, the linear molar masses of the produced PVDF-*g*-PS graft copolymers versus the styrene conversion relationship (Figure 35) and narrow polydispersity indices (starting from 1.8 for poly(VDF-*co*-BDFO) random copolymers) evidence a controlled behavior of that graft copolymerization.[385]

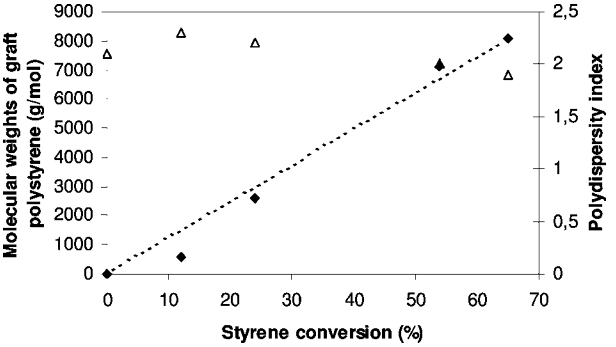
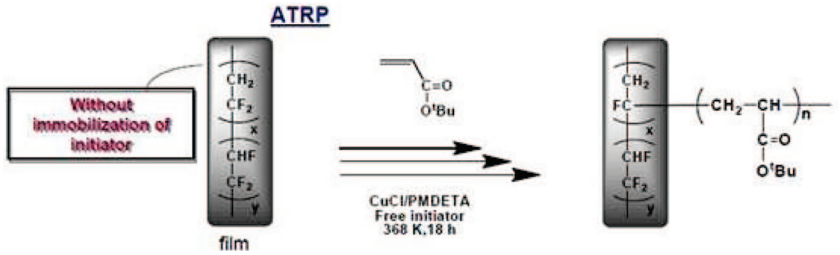


Figure 35. Dependence of molecular weight (◆) and polydispersity index (Δ) of PVDF-*g*-PS copolymer versus styrene conversion for the ATRP of styrene using poly(VDF-*co*-BDFO) copolymers as the macroinitiator. $[DMF]_0/[styrene]_0/[macroinitiator]_0/[HMTETA]_0/[Cu^IBr]_0 = 500:100:10:0.5:0.5$; $T = 90$ °C. BDFO, HMTETA, and DMF stand for 8-bromo-1*H*,1*H*,2*H*-perfluorooct-1-ene, 1,1,4,7,10,10-hexamethyltriethylenetetramine, and dimethylformamide, respectively. Reproduced with permission from ref 385. Copyright 2006 American Chemical Society.

4.2.3.3. C−F Cleavage. Surprisingly, ATRP of methacrylates was reported to be successful from the cleavage of the C−F bond in PVDF to produce PVDF-*g*-poly(methacrylates)[386] graft copolymers, though no significant spectroscopic evidence was revealed by the authors. Indeed, if that grafting occurs, it can be anticipated that it arises from the cleavage of the less stable C−H in methylene and not in the more stable difluoromethylene site of VDF as claimed by these authors. Indeed, it is well-known that the chemical resistance of PVDF is not as broad as that exhibited by perfluoropolymers because the somewhat acidic hydrogen atoms along the chain are reactive in strongly basic media, leading to the formation of fluoride salt byproducts.

The same group[387] also claimed the synthesis PVDF-*g*-PPEOMA graft copolymers by ATRP of poly(ethylene oxide) monomethacrylate from PVDF, according to a similar strategy. Although this synthesis is quite surprising for the

Scheme 57. ATRP of Butyl Acrylate from Poly(VDF-*co*-TrFE) Copolymer [a])



[a] Reproduced with permission from Prof Takahara, "Fluoropolymers 2008" Conference, Charleston, SC, 2008.[390a]

same reasons, the authors mentioned that these comb polymers were used for water filtration in which the hydrophilic domains could provide a pathway for water transport.

Nevertheless, this above strategy was also used by a Korean group,[388] who synthesized PVDF-*g*-PSSA and PVDF-*g*-PSPMA graft copolymers (where PSPMA stands for poly(sulfopropylmethacrylate)) after 48 h at 120 °C with maximum successful degrees of grafting of 25 wt % and 35 wt %, respectively. The ionic exchange capacity values, water uptakes, and proton conductivities were 0.45 and 0.63 mequiv$\cdot$g^{-1}, 33.4 and 46.8 wt %, and 0.007 and 0.015 mS$\cdot$cm^{-1}, respectively. However, neither the ^{19}F NMR spectra nor the SEC chromatograms were provided. Moreover, the ^{1}H NMR spectra were not convincing especially because of the intense signals assigned to the high amount of solvent and because an unexpected broad signal was observed instead of the characteristic quintet centered at 2.9 ppm, assigned to methylenes of VDF.

Nandi's group[389] also used ATRP of *N*,*N*-dimethyl aminoethyl methacrylate (DMAEMA) in the presence of PVDF as the initiator to synthesize PVDF-*g*-PDMAEMA graft copolymers with increasing graft density for increasing polymerization times (though the graft lengths were similar).

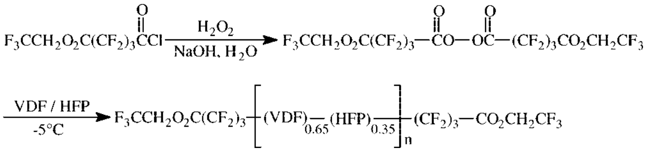
Nevertheless, this above strategy was also recently used by Takahara's group[390] who synthesized poly(VDF-*co*-TrFE)-*g*-poly(acrylic acid sodium salt)[390a] and PVDF-*g*-poly(butyl acrylate)[390b] graft copolymers (Scheme 57).

In contrast to all strategies above that report "grafting from" a fluorinated backbone, scarce opportunities to produce poly(M)-*g*-PVDF have already been depicted in the literature. However, an example has been proposed by the Montell Technology Company,[391] which claimed an "uncontrolled" synthesis of polypropylene-*g*-PVDF graft copolymers by a simple radical grafting of VDF from polypropylene (PP). According to the natures of the solvents and the initiators, this company could incorporate various VDF percentages, ranging from 3.4 mol % only when water was used as the solvent, to 10.1 and 17.5 mol % in the presences of *t*-butyl cyclohexyl peroxydicarbonate or *t*-butyl peroxypivalate, respectively, in fluorinated solvents.

4.3. Fluorinated Alternating Copolymers

Although VDF does not copolymerize with vinyl ethers as CTFE, 1,1-dichlorodifluorethylene, perfluoroacrylonitrile or TFE do, it is able to produce alternating copolymers with hexafluoroisobutylene,[296,297] hexafluoroacetone,[192] methyl trifluoroacrylate[275,276] or α-trifluoromethacrylic acid.[191,315] The first one was produced by the Allied Company under the CM1 trade name, nowadays marketed by Honeywell International Ltd..

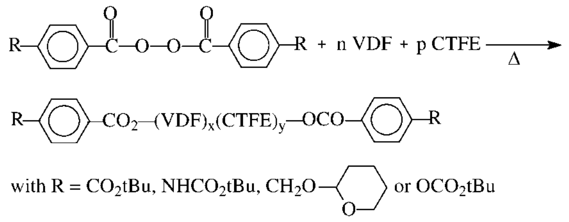
Scheme 58



$$F_3CCH_2O_2C(CF_2)_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow[NaOH,\ H_2O]{H_2O_2} F_3CCH_2O_2C(CF_2)_3-\overset{O}{\overset{\|}{C}}O-O\overset{O}{\overset{\|}{C}}-(CF_2)_3CO_2CH_2CF_3$$

$$\xrightarrow[-5°C]{VDF / HFP} F_3CCH_2O_2C(CF_2)_3\left[(VDF)_{0.65}-(HFP)_{0.35}\right]_n(CF_2)_3-CO_2CH_2CF_3$$

Scheme 59



4.4. Telechelics Containing VDF Base Units

4.4.1. Telechelics from Functional Initiators

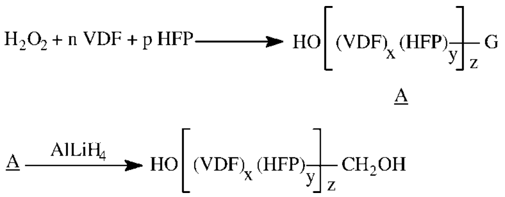
About 40 years ago, fluorinated telechelic peresters,[392−394] synthesized by the oxidation of fluorinated acid chlorides or by the direct addition of acid fluorides to hydrogen peroxide, were successfully used by Rice and Sandberg for initiating the copolymerization of VDF and HFP under dead end copolymerization (DEP) leading to original fluoroelastomers[394] (Scheme 58). The average molecular weight determined by vapor pressure osmometry was ca. 4000 g$\cdot$mol^{-1}. While propagation of monomers occurs in a classical way, the termination step proceeds by recombination, only.[52]

More recently, in a similar DEP strategy, original telechelic poly(VDF-*co*-CTFE) copolymers were synthesized by the radical copolymerization of VDF and CTFE initiated by various aroyl peroxides[395] (Scheme 59). Molecular weights were 48 000 or 56 000 g$\cdot$mol^{-1} and PDI = 1.5−1.6. However, no evidence of a functionality of 2.00 was reported by the authors. Nevertheless, the application was quite interesting: hybrid materials from these telechelic copolymers[395] and oleic acid-capped titanium oxide (TiO_2) nanoparticules were prepared into uniform films, which showed a good thermal stability (withstanding 200 °C for 14 h without any significant changes).

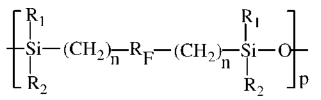
Hydrogen peroxide was also used to prepare novel α,ω-dihydroxylated poly(VDF-*co*-HFP) cooligomers of low molecular weights (800−3000 g$\cdot$mol^{-1}) under DEP conditions in a two-step procedure[396] (Scheme 60, where G designates CH_2OH or CO_2H).

A similar strategy was used for the preparation of telechelic oligoVDFs from the photoinduced dead end polymerization of VDF in the presence of hydrogen peroxide.[397]

Scheme 60



Scheme 61



where R_1, R_2 : CH_3, $C_2H_4CF_3$ and R_F : $(CF_2)_x$ x = 1

n = 2 or $C_2F_4OC_2F_4$

4.4.2. Telechelics from Fluorinated Telomers Based on VDF

Obviously, the use of a chain transfer agent enables one to obtain lower molecular weights and, according to the nature of this reactant, functional compounds can be produced or a better control of the copolymerization can be achieved. Depending on the amount and on the transfer efficiency of such a reagent, conditions of telomerization[4] can be achieved. Such a reaction represents a very interesting model of (co)polymerization since it leads to low molecular weight polymers with well-defined end groups. A quasi-exhaustive list of chain transfer agents used in the telomerization of main fluoroalkenes has previously been reported.[4] α,*ω*-Diiodopoly(VDF-*co*-PMVE) copolymers,[241] $I(TFE)_x(VDF)_y(HFP)_zI$ telomers, were synthesized and then functionalized into telechelic nonconjugated dienes.[398] These were hydrosilylated with fluorohydrogenosilanes to produce fluorinated dichlorosilanes, hydrolyzed into disilanols. The condensation of these disilanols or their copolycondensation with the dichlorosilanes led to hybrid fluorosilicones endowed with improved thermostability, and exhibit the structures[399−401] shown in Scheme 61, where R_F can also designate poly(VDF-*ter*-TFE-*ter*-HFP) cotelomers.

A first series was achieved by researchers at the Dow Corning Corp.,[399] from TFE telomers, while later, our laboratory supplied novel hybrid fluorosilicones based on fluorinated telomers containing VDF, TFE, and HFP base units.[400−402] The fluoropolymers are rather stable in a wide range of temperatures; interesting low T_g's were reached ($T_g \approx -40$ °C) along with satisfactory thermal stability ($T_{dec} =$ 400 °C) under air. Their structures are similar to that above with $n = 2$ or 3; R_1, R_2 = CH_3, $C_2H_4CF_3$, or $C_2H_4C_4F_9$, and $R_F = (VDF)_a(TFE)_b(HFP)_c$ with $a = 0$ or 1, $b = 2$ or 3; and $c = 0$ or 1. More information on these hybrid F-silicones has been reviewed.[403,404]

4.5. Chemical Modification of PVDF and VDF-Containing Copolymers

Although mentioned in section 4.2, the chemical modification of PVDF or of VDF-containing copolymers has already led to numerous grafted copolymers bearing long chain grafts via the "grafting from" route. This section considers only slight chemical modifications with short chain length groups.

Another survey related to fuel cell membranes was suggested by Chung et al.[138] The strategy to obtain poly(VDF-*co*-CTFE) copolymers was mentioned in section 3.2.1 (Scheme 8) from the radical terpolymerization of VDF with $F_2C{=}CF{-}R{-}Si(CH_3)_2OR$ (R being an alkyl group) and CTFE in the presence of borinate. Then, the grafting of an aryl trialkoxysilane containing a sulfonyl chloride occurred via the hydrolysis/condensation between the trialkoxysilane of the poly(VDF-*co*-CTFE) copolymer and the aryl sulfonyl chloride reactant (Scheme 9).

Another investigation involving the chemical modification of VDF-containing copolymers (produced from the radical terpolymerization of VDF with HFP and α-trifluoromethacrylic acid (MAF)[191,405] yielded original materials bearing *para*-benzene sulfonic acid side groups as potential materials for fuel cell membranes (the conductivities of which were ca. 0.020 $S \cdot cm^{-1}$),[406] as depicted in Scheme 62. Prior to chemical modification, it was noted that the higher the MAF contents in the poly(VDF-*ter*-HFP-*ter*-MAF) terpolymers (ranging from 1 to 44 mol %),[406] the worse the thermal stability was due to the decarboxylation of CO_2H functions.

More attractive membranes have been obtained from route 2 in the presence of paraphenol sulfonic acid to avoid the presence of the ester group as a weak point.

In addition, another original procedure to prepare fuel cell membranes consists of grafting an amino sulfonated synthon (prepared by radical addition of a mercaptoethylamine hydrochloride onto styrene sodium sulfonate in water)[407] onto commercially available poly(VDF-*co*-HFP) copolymers. Such a strategy shows the classic mechanism of grafting of amines onto the VDF−HFP diad[10] in three steps (Scheme 63) and confirmed model reactions.[408] Molar percentages of grafted telomer were assessed by both ^1H NMR spectroscopy and elemental analysis, which led to the ionic exchange capacity. Though the conductivities were lower than that of Nafion117, they increased with the IEC. In addition, the produced membranes started to decompose from 170 °C under severe oxidative conditions.[407]

Another alternative to modify poly(VDF-*co*-HFP) copolymers lies in the grafting of parasulfonic phenolate leading to original modified copolymers bearing a sulfonic acid group, also showing some protonic conductivity.[409]

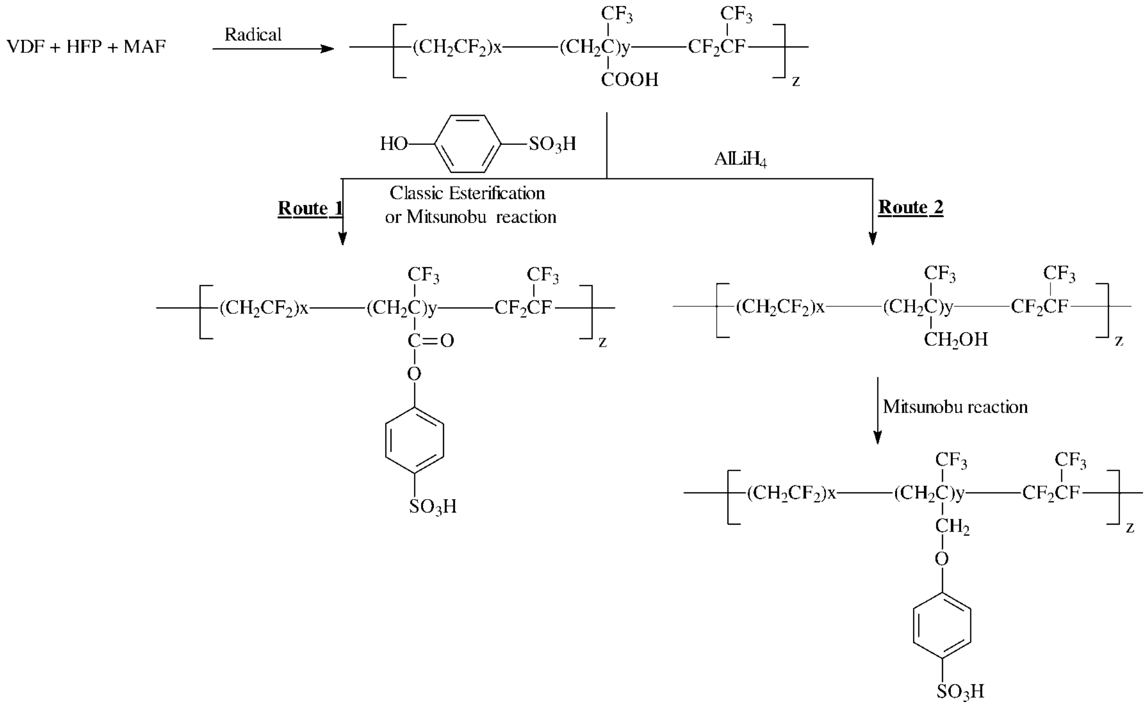
The Arkema company[410] has recently claimed the grafting of ca. 2 wt % maleic anhydride onto a poly(VDF-*co*-HFP) copolymer (containing 16 wt % HFP), leading to an original copolymer with the following characteristics: a crystallization temperature of 103 °C, a threshold strength of 18 MPa, and a viscosity in the molten state of 900 Pa·s. Though the content of maleic anhydride is still low, such modified fluoropolymers, marketed under the KynarADX trade name,[295] exhibit improved adhesion to thermoplastics, elastomers, or inorganic materials in multilayer systems.

4.6. Conclusion

There are many strategies to synthesize well-designed fluoropolymers containing PVDF or poly(VDF-*co*-M) random, block, or graft copolymers, either by conventional or by controlled radical polymerization. Though VDF copolymers have not found potential applications in optics (because of the presence of hydrogen atoms in VDF units) such well-architectured copolymers containing VDF can be used in many other fields. To compare applications, six main types can be distinguished:

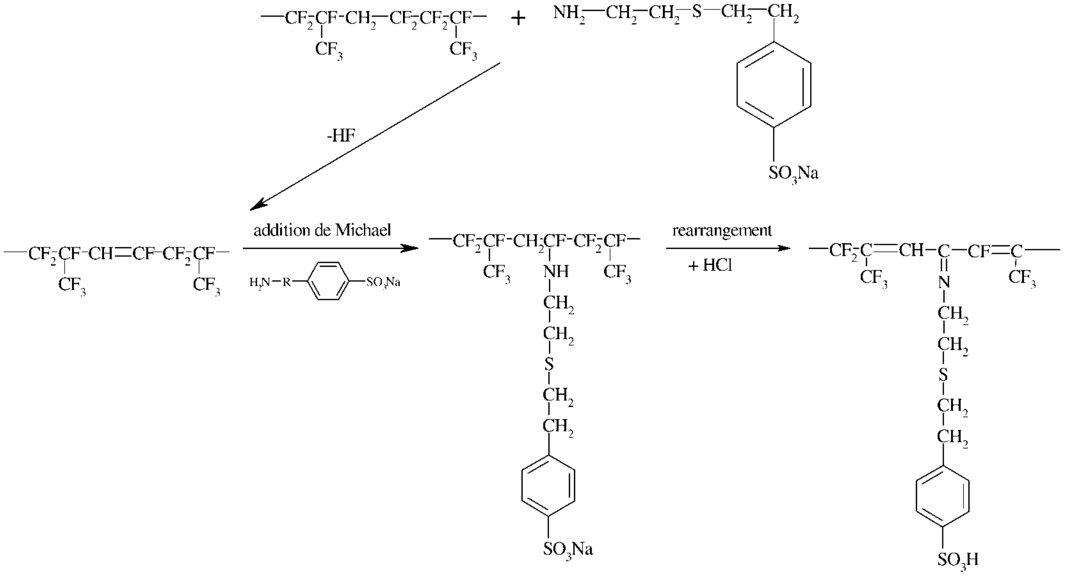
(i)*Thermoplastic elastomers* involved in seals, gaskets, and O-rings applications. Cefral and Dai-el (just like Tecnoflon) are three commercially available products marketed by

Scheme 62. Obtaining of Original Fuel Cell Membranes from poly(VDF-*ter*-HFP-*ter*-MAF) Terpolymers[406]



[a] MAF stands for α-trifluoromethacrylic acid.

Scheme 63. Chemical Modification of Poly(VDF-*co*-HFP) Copolymers by Amino Sulfonate for Fuel Cell Membranes[407]



Central Glass and Daikin (and Solvay Solexis), exhibiting graft and block structures, respectively.

(ii)*Surfactant* applications. Though a few designed molecules have already been obtained, it is expected that more and more compounds can be synthesized since the methylene groups of VDF units in the oligo(VDF) groups or microblock can be either metabolized or enzymatically degraded or cleaved, which leads to potentially nonbioaccumulable products as interesting alternatives to PFOA and PFOS surfactants.[338]

(iii)The field of *membranes*. Various approaches have led to different types of membranes (mainly for microfiltration[380,381] or for fuel cells) from block or graft copolymers. First, Xu et al.[337] noted that the conductivities of the block copolymers are considerably higher than those of the random copolymers of sulfonated polystyrene possessing similar IECs. In addition, the membranes obtained from preirradiated PVDF or poly(VDF-*co*-HFP) copolymers followed by grafting PS (further sulfonated into PSSA) were not chemically stable. However, under NMP of styrene from irradiated PVDF membranes quenched with TEMPO, better electrochemical properties[379] and thermal stabilities were noted. Holdcroft's team[335] compared the potential of PVDF-*g*-PSSA and poly(VDF-*co*-HFP)-*b*-PSSA copolymers and the electrochemical properties of the resulting membranes. These authors noted that the graft membranes possess a significantly higher percolation threshold than the diblock membranes, and this statement correlates with water uptake values. This is in good agreement with specific micro- or nanostructures such as lamellae or, better, in giroids as reported by Liebler.[411]

(iv)*Rechargeable lithium ion batteries*. Quite a few works have been proposed, besides Liu et al.[361] who prepared nanoporous membranes endowed with satisfactory electro-

chemical properties from PVDF-*g*-PEOMA graft copolymers.
(v)*Coatings*. To our knowledge, neither block nor graft copolymers containing VDF have yet been achieved, but random and PVDF/PMMA blends are well-established products, Kynar being a valuable example;
(vi)*Telechelics* containing VDF for possible thermostable polymers. Except a few hybrid fluorosilicones, neither polycondensates (polyesters, polyamides, and polyimides) nor polymers resulting from polyaddition have ever been synthesized.

5. Applications and Future Trends of Fluoropolymers Based on Vinylidene Fluoride

The above sections have already mentioned that PVDF and poly(VDF-*co*-M) copolymers have shown an extensive use in a wide range of products. PVDF homopolymers can find many applications that are well-documented in various reviews.[5,9] Among them, the following can be found:
(1) Paints and coatings, for example, binders for long lasting weather-resistant finishes for metals, decorative films for lamination to surfaces, automotive trim applications, aircraft interior surface in-mold lining processing, resistance to weather and chemicals (chlorine and bromine for example[412]), primer coatings, and corrosion-resistant coatings for tank liners.
(2) Chemical processing equipment, for example, flexible tubings for deep sea oil transport, packing for distillation towers, high purity water systems, piping for chemicals, pumps and instrument parts, and fuel handling systems including underground storage tank systems and automotive fuel lines.
(3) Electrical and electronic devices, for example, jacketing of cables for plenum areas including signaling, communication, and power lines, insulating compounds for jacketing wires and cable assemblies, cathodic protection, industrial power control systems, high-temperature wiring, and wire and cable sheathing.
(4) Specialty applications, for example, microporous membranes (PVDF is regarded as one of the most attractive polymers in microporous membranes industry), toners (PVDF is an essential ingredient at low levels in almost all commercially available toners for photocopy machines and many laser printers), fishing lines and nets, musical strings, processing aids for polyolefins, monofilament and fabrics used in filtering wood pulp during bleaching, lithium ion batteries, electrode binders, piezo- and pyroelectric transducers for motion sensors, hydrophones, microphones, audio devices, high-frequency speakers, ultrasound scanners, pressure switches, supercapacitors, electrolytic capacitors, aircraft interior sound control, jet engine fan blades, and biomedical applications such as actuators or suture wires.

Thermoplastic poly(VDF-*co*-M) copolymers have found applications in coatings and membranes, while fluoroelastomers are developed for use as fuel tank hatch and joint sealants, fuel vapor seals, and O-rings for hydraulic systems in aircraft and aerospace applications. Fluoroelastomers are now widely used in the industry as O-rings, V-rings, gaskets, and other types of static and dynamic seals, such as diaphragms, valve seals, hoses, coated cloth, shaft seals,[5−8,11] expansion joints, etc. They are also used in cars as O-rings for fuel and shaft seals and other components of fuel and transmission systems[5−8,11] since they even do not swell in oil.

Commercial applications of fluoroelastomers reflect their rather special combination of properties: excellent resistance to heat, fluids, and oxidizing media combined with good physical properties.

Other industries such as energy-consuming industries, military aircraft, and petrochemical industries require fluoropolymers for sealants, gaskets, O-rings, and linings resistant to corrosive materials.

Aerospace propellant systems often utilize very aggresive fuels and oxidizers, which are incompatible with all currently available elastomers, including fluoroelastomers. FFKM is often used in these systems due to their oxidative stability and compatibility with both oxidizers and hydrazine-type fuels.

Fire-resistant lubricants containing phosphate esters and lubrication oils containing amines are both interesting applications where the use of FFKM (which does not swell in these media) greatly extends seal life.

FFKM is the most suitable material available for use in semiconductor processing equipment. In these applications, the elastomer comes in direct contact with dry process chemicals and reactive plasmas. The elastomer is typically exposed to aggressive wet chemical environments such as sulfuric acid/hydrogen peroxide or ammonium hydroxide/hydrogen peroxide/ultrapure deionized water mixtures.

Although discovered more than 40 years ago, perfluoroelastomers represent a production of several tons a year. However, they are growing at a fast pace in terms of applications and introduction of new composition to meet industrial needs. Perfluoroelastomers represent less than 1% of the total fluoroelastomers field, dominated by VDF-base copolymers.

It is expected that new fluoropolymeric materials and new curing chemistry will be developed in the future, due to continued escalation at severe service conditions and improvements in broad temperature damping characteristics and low-temperature resilience. Blends of fluoropolymers with other polymers and recyclability features will also contribute to their continuing success in many engineering and aggressive service environments.

6. Conclusion

Vinylidene fluoride is a versatile, nontoxic, environmentally friendly gaseous monomer that can be easily homopolymerized (its propagation rate to the square root of termination rate is $0.14\ L^{0.5}\cdot mol^{-0.5}\cdot s^{-0.5}$ at 74 °C in solution and $1.3-2.23\ L^{0.5}\cdot mol^{-0.5}\cdot s^{-0.5}$ at 120 °C in supercritical CO_2) and can also copolymerize in the presence of radicals leading to thermoplastics, elastomers, or thermoplastic elastomers. PVDF and poly(VDF-*co*-M) copolymers can find many applications in a wide range of areas such as energy (fuel cell membranes, lithium ion batteries, dye sensitized solar cells, actuators), aerospace, aeronautics, and automotive industries (e.g., elastomeric sealants, O-rings, gaskets that are resistant to low and high temperature and in aggressive media), microfiltration and ultrafiltration membranes, blends, and composites (even with nanofillers). Hence, a wide variety of advanced materials can be prepared from copolymers being random for most of them (except for VDF/hexafluoroisobutylene, VDF/methyl trifluoroacrylate, and VDF/α-trifluoromethacrylic acid, which are alternating). Conventional radical copolymerization has traditionally led to a wide variety of poly(VDF-*co*-M) copolymers, while published academic investigations have reported the kinetics of copolymerization of VDF with M monomers. More recently, iodine transfer copolymerization or other controlled radical copolymerizations of VDF with M monomers (in the presence of fluoroiodide or xanthate chain transfer agents) have been attractive and can explain the possible limitation of defects of chainings. Moreover, certain VDF-containing polymers can be regarded as well-architectured polymers. Among them and besides the above alternating copolymers, three categories can be proposed: (i) *Block copolymers* are prepared under conventional or more recent controlled radical polymerization methods. In these last cases, PVDF−X acts as original initiator especially in halogen transfer radical polymerization (X stands for chlorine, bromine, or iodine atom). (ii) *Graft copolymers* can be achieved from direct copolymerization (or terpolymerization) or from the polymerization of monomers in the presence of macroinitiators produced from the activation of fluoropolymers (e.g., from ozone, electron-beam, swift heavy ions, or γ rays). (iii) *Telechelics* are obtained either from the radical polymerization of fluoroalkenes (including VDF) in the presence of functional initiators (telechelic peresters or hydrogen peroxide) or from telomerization of fluoroalkenes with adequate chain transfer agents.

In addition, thermoplastic elastomers are easily made and are versatile materials containing both soft and hard segments. Interestingly, various combinations of synthetic block microstructures are possible based on the comonomers involved in the different blocks to achieve both thermoplastic or elastomeric segments and hence to reach suitable T_g's and T_m's. Various strategies applied by different companies have led to commercially available block copolymers, regarded as the first ones produced on an industrial scale. However, lowering their T_g's is still a challenge, which is inherent to the T_g of the elastomeric block, which is always higher than −33 °C (although the 3M company recently produced an original statistic cross-linkable terpolymer endowed with a T_g of −40 °C[413]). Nevertheless, many applications of these TPEs have been found in civil and engineering domains such as hot melts, gaskets, O-rings, diaphragms of pumps, pressure-sensitive additives, medical contact lenses, electronic chemical items, coatings for food industries, and other devices involved in high-tech industries. According to the investigations achieved in the last five years, the growing interest in new materials based on PVDF or poly(VDF-*co*-M) copolymers used for emerging applications devoted to energy is worth noting. More recently, block and graft copolymers based on VDF have been designed as membranes for fuel cells.

However, limitations still exist. Appopriate cure site comonomers for the copolymerization of VDF are still sought and should be expected to enable one to go to another generation of cross-linked thermoplastic or fluoroelastomers. In addition, VDF-containing polymers stable to bases or alkalies are scarce and claimed in few patents. This offers additional chances for a technology that already forms the basis of the commercial production of classes of chemicals that are among the most advanced and successful products in fluorine chemistry.

Hence, further challenges deserve to be explored and should attract the interest of industrial or academic researchers.

7. List of Symbols and Abbreviations

AIBN	α,α′-azobisisobutyronitrile
ATRP	atom transfer radical polymerization
BPO	dibenzoyl peroxide
C_{ex}	exchange constant
CTA	chain transfer agent
CRP	controlled radical polymerization
CSM	cured site monomer
CTFE	chlorotrifluoroethylene
DMF	dimethyl formamide
DMFC	direct methanol fuel cell
DP_n	number average degree of polymerization
DS	degree of sulfonation
DSC	differential scanning calorimetry
DSSC	dye sensitive solar cell
DT	degenerative transfer
DTBP	di-*tert*-butyl peroxide
E	ethylene
EB	electron beam
GPC	gel permeation chromatography
HFIB	hexafluoroisobutylene
HFP	hexafluoropropylene
IR_FI	α,ω-diiodoperfluoroalkane
ITP	iodine transfer polymerization
CRP	controlled radical polymerization
M	monomer (or comonomer)
MADIX	macromolecular design through interchange of xanthates
MAF	α-trifluoromethacrylic acid
MEA	membrane electrode assembly
M_n	number-average molecular weight
M_w	weight-average molecular weight
LCB	long chain branching
NMP	nitroxide-mediated polymerization
NMR	nuclear magnetic resonance
P	propylene
PAAVE	perfluoroalkoxyalkyl vinyl ether
PAVE	perfluoroalkyl vinyl ether
PDI	polydispersity index
PEMFC	proton exchange membrane fuel cell
PEO	poly(ethylene oxide)
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFP	pentafluoropropylene
PMMA	poly(methyl methacrylate)
PMVE	perfluoromethyl vinyl ether
PSSA	poly(styrene sulfonic acid)
PTFE	poly(tetrafluoroethylene)
PVDF	poly(vinylidene fluoride)
R	alkyl group
RH	relative humidity
RAFT	reversible addition−fragmentation chain transfer polymerization
R_F	perfluorinated group
R_FI	perfluoroalkyl iodide
SEC	size exclusion chromatography
SEM	scanning electron microscopy
semi-IPN	semi-interpenetrated polymer network
S	styrene
TEM	transmission electron microscopy
TFE	tetrafluoroethylene
TFP	3,3,3-trifluoropropene
T_g	glass transition temperature
TPE	thermoplastic elastomer
TrFE	trifluoroethylene
VAc	vinyl acetate
VDF	vinylidene fluoride (or 1,1-difluoroethylene)
Δ	heating

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