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Controlled Radical (Co)polymerization of Fluoromonomers

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ABSTRACT: Controlled radical polymerizations (CRP) were pioneered in the late 1970s. Since then, tremendous investigations have been developed, especially from mid-1990s which generated much enthusiasm on CRP. However, the extraordinary scientific development of CRP contrasts with the limited number of commercially available products derived from these technologies. But, for fluoropolymers, the situation is different since iodine transfer polymerization of fluoroalkenes led to commercially available thermoplastic elastomers as soon as 1984. A browse or CRP of fluorinated monomers is presented and is classified into three families: (i) the CRP of fluorine-containing styrenic monomers mainly occur from nitroxide-mediated polymerization (NMP) or by atom radical transfer polymerization (ATRP); (ii) that of fluorinated (meth)acrylic monomers from NMP, ATRP, and in the presence of iniferters; and finally (iii) fluoroalkenes (which is a real challenge since these monomers are gaseous) can be (co)polymerized by iodine transfer polymerization or by processes that required either borinates or xanthates (MADIX). A peculiar interest lies in the CR copolymerization of fluoroalkenes with other comonomers (such as vinylidene fluoride, chlorotrifluoroethylene, 3,3,3-trifluoropropene, hexafluoropropylene, perfluoromethyl vinyl ether, or α-trifluoromethacrylic acid) in the presence of either xanthates, borinates, or iodo compounds. These technologies enable one to generate copolymers that exhibit well-defined architectures, such as telechelic, block, and graft copolymers. Merits and limitations of CRP of F-monomers are also reported. Finally, this Perspective is illustrated by several properties and applications of these fluorinated copolymers (such as surfactants, thermoplastic elastomers, fuel cell and ultrafiltration membranes, dielectrical polymers, optical storage devices, or polycondensates, the fluorinated segments of which bring softness and thermal stability). Hence, CRP can be regarded as a revolutionary method to produce precisely controlled, next-generation specialty fluorinated (co)polymers.

Introduction

Fluorinated polymers and copolymers[1−5] are attractive specialty polymers because of (i) their versatility (their morphology can be either thermoplastic, elastomeric, plastomeric, or even thermoplastelastomeric, and they can be semicrystalline or totally amorphous) and (ii) their unique combination of remarkable properties (mainly linked to the low polarizability and the strong electronegativity and small van der Waals radius (1.32 Å) of the fluorine atom and to the strong C−F bond (the energy dissociation of which is 485 kJ mol^{-1})). Hence, fluoroplastics containing a high fluorine content exhibit high thermal, chemical, aging, and weather resistance, excellent inertness to solvents, to hydrocarbons, to acids, and to alkalis, low surface energy (oil and water repellency), low dielectric constants, low flammability, low refractive index, and moisture absorption. Furthermore, the presence of a strong C−F bond has a crucial impact on the high resistances to oxidation and to hydrolytic decomposition.

Hence, these niche macromolecules[1−5] have been involved in many applications: building industries (paints and coatings resistant to UV and to graffiti), petrochemical (pipes and coatings as liners), and automotive industries (fluids for transmission[5]), aerospace and aeronautics (use of elastomers as seals, gaskets, O-rings for use in extreme temperatures for tanks of liquid hydrogen or hydrazine in boosters of space shuttles[5]), chemical engineering (high-performance membranes), optics (core and cladding of optical fibers), textile treatment, stone (especially coatings of old monuments for the cultural heritage), and microelectronics. In spite of 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 “high-tech” and modern technologies.

However, fluoroplastics have various drawbacks: the homopolymers are often crystalline, which hence induces a poor solubility in common organic solvents (that turns into an advantage regarding its chemical inertness) and are not easily cured or cross-linked.[6] This is why the generation of fluorinated copolymers[4,5,7,8] has extensively grown without possessing the disadvantages of homopolymers mentioned above. Indeed, these copolymers (composed of a mixture of comonomers) insert (bulky) side groups which produce disorder in the macromolecule, and hence they reduce or vanish the high crystallinity of the homopolymer.

Except for a few monomers (e.g., fluorinated oxetanes,[9] oxazolines,[10] and vinyl ethers that bear a fluorinated side group[11] that currently homopolymerize cationically, or hexafluoropropylene oxide[12] and α-trifluoromethacrylic acid[13] that polymerize under anionic conditions), most fluoropolymers are synthesized from conventional *radical* methods of polymerization.[1−6] Radical polymerization’s competitiveness with other methods (mainly ionic ones) of conducting polymerization is attributable to the simplicity of the mechanism and good reproducibility. Actually, the extensive use of free radical polymerization in practice is well-understood when considering (i) the ease of the process, (ii) the soft processable conditions of vacuum and temperature, (iii) the fact that reactants do not need to be highly pure as in the cases of cationic or anioninc polymerizations, and (iv) the absence of residual catalyst in the final products. Thus, it can be easily

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understood that more than 50% of all plastics have been produced industrially via radical polymerization and more than 95% of fluoropolymers are prepared this way.

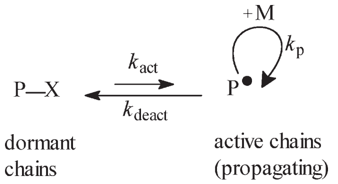
Because of the extraordinary development of modern techniques of controlled radical polymerization (CRP) of monomers, it was of interest first to briefly recall these methodologies. Actually, CRP has attracted growing attention as a useful tool to precisely control polymer structures. This may be due to the nature of the radical, which is an intermediate with a very short lifetime and a very high nonselective reactivity. That does not favor a well-controlled architecture as in the case of living carbanions that appear in anionic polymerization. However, the recent development of new methods to control the reactivity of radicals and to give a living character to the growing macroradicals offers new fascinating possibilities.

The interest is not only on the academic side but also for the industry since well-defined polymers produced by CRP find applications as high-performance elastomers, dispersants, lubricants, adhesives, etc., and can also open the way to novel electrical,[14] optical,[15] and biomedical materials.[16] Over 12 000 papers have been published on CRP in the past 15 years, and the industrial interest is based on an anticipated $20 billion/year market for products made by CRP.[17] However, in the past few years, it turned out to be not so obvious to develop CRP at industrial scale,[18] though those obtained from fluorinated monomers have been produced from early 1980s. Nowadays, fluorinated thermoplastic elastomers, still involved in electronics, aerospace, automotive industries, and medical applications, are currently produced at the industrial scale.

This Perspective points out various nonexhaustive methods to achieve the CRP of fluoromonomers. First, the different strategies of CRP are recalled, then a summary of surveys on CRP of fluorinated (meth)acrylates, styrenic, and alkenes will be briefly mentioned, followed by various nonexhaustive syntheses of well-architectured fluorocopolymers (telechelic, block, graft, alternated), and finally applications of such well-designed (co)polymers will be supplied.

Strategies of Controlled Radical (Co)polymerization

Since the 1990s, the international research activity in the field of controlled (or pseudoliving) radical polymerization (LRP) has grown to a considerable extent.[18,20] The general principle of the methods reported so far relies on a reversible activation−deactivation process between dormant chains (or capped chains) and active chains (or propagating radicals), as follows:



One of the oldest techniques is the iniferter method[21−23] (where iniferter stands for *ini*tiation−trans*fer*−*ter*mination), nitroxide-mediated radical polymerization (NMP),[24,25] atom transfer radical polymerization (ATRP),[26−28] iodine transfer polymerization (ITP),[19,29,30] reversed iodine transfer polymerization,[30] reversible addition−fragmentation chain transfer (RAFT)[31−34] including macromolecular design via interchange of xanthates (MADIX),[18,33,34] organo-heteroatom radical polymerization,[35,36] and CRP controlled by boron derivatives,[37] whose respective specific mechanisms are briefly summarized in Scheme 1.

Degenerative transfer also encompasses (R)ITP, RAFT, and MADIX processes.

From its birth to November 2008, more than 7000 ATRP articles have been referenced.[28]

In 2006, Matyjaszewski and co-workers reported an ATRP variation called ARGET (activators regenerated by electron transfer), in which the catalyst is continuously regenerated by nontoxic reducing agents such as ascorbic acid.[38] They also reported another variation called ICAR (initiators for continuous activator regeneration), in which radical initiators are used for the same purpose.[39]

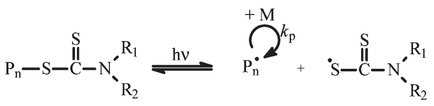
In Scheme 1e, for xanthates, authors sometimes refer to MADIX name, which stands for macromolecular design through interchange of xanthates, as claimed by the Rhodia Co. for this process.[18,33,34]

In addition to these strategies, organocobalt-mediated radical polymerization, OCRP, was rejuvenated in 2005 by Debuigne et al.,[40] who found that bis(acetylacetonato)cobalt(II) ($Co(acac)_2$) could mediate the polymerization of vinyl acetate (VAc) in a controlled manner. The same group published a comprehensive review about OCRP in 2009.[41]

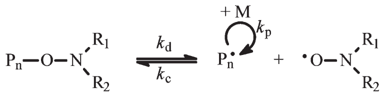
Furthermore, organostilbine compounds $R{-}SbR'R''$ are remarkable control agents[35,36] for CRP of nearly all monomers from methacrylates to VAc and *N*-vinylpyrrolidone (NVP),[35] such as $RTeR'$, $RSbR'2$ $RBiR'_2$ with $R = R' =$ Me, Ph, $(CH_3)_2C$-(COOEt), $(CH_3)_2CCN$, $(CH_3)CHPh$, and $PhCH_2$. However, no fluorinated monomers have yet been attempted.

The major benefit of such methods is the possibility of tailoring well-defined polymers (telechelic, block, graft, or star copolymers) by convenient radical polymerizations.

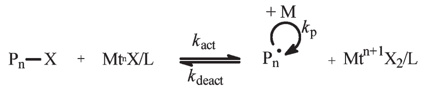
Scheme 1



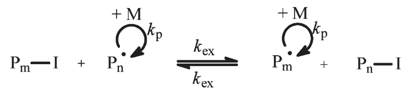
(a) Photo-Iniferter Method[21-23]



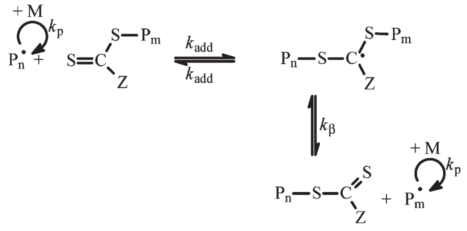
(b) Nitroxide-mediated radical polymerization (NMP)[24-25]



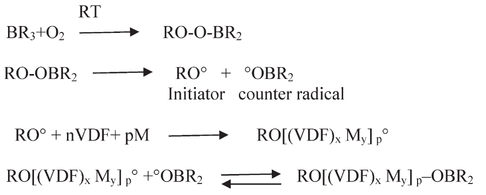
(c) Atom transfer radical polymerization (ATRP)[26-28]



(d) (Reversed) iodine transfer radical polymerization (ITP)[29-30]



(e) Reversible addition-fragmentation chain transfer process: RAFT (when Z represents an alkyl or aryl group) and MADIX (Z=Oalkyl)[18,31-34]



(f) Radical polymerization controlled by boron species[37]

Fluorinated organic compounds have sometimes been used in living radical polymerization[42] to take advantage of electronic or steric effects, to serve as labeling agents, or to impart specific properties to the resulting materials such as low surface energy, chemical resistance, and solubility in supercritical carbon dioxide, to name a few. Nonexhaustive examples are going to be given hereafter regarding various species involved in the schemes above.

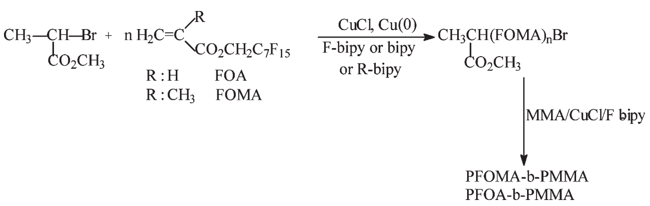
Though CRP tends to minimize termination reactions, few can occur, and as expected, classical recombination/disproportionation rates are noted for these monomers. Nevertheless, for fluoroalkenes, recombination is exclusively observed.[43]

Actually, the history of controlled radical copolymerization started in the late 1970s when Tatemoto pointed out the clever idea in the course of the Soviet−Japanese Conference[44] on the concept on the iodine transfer (co)polymerization of fluoroalkenes,[29] especially on vinylidene fluoride.

1. Styrenic Monomers and (Meth)acrylates Bearing Fluorinated Groups

One review[42] and one book[4] published in 2002 and 2004, respectively, summarize the overall situation on the CRP of fluorinated styrenic and (meth)acrylates, and the reader will find all required information while a Danish group[15] more recently reviewed the CRP (mainly NMP, ATRP, and RAFT) of fluorinated acrylates, methacrylates, and styrene conomomers. However, in the following part, recent publications and patents are mentioned.

Scheme 2. ATRP of (Meth)acrylate Bearing a Fluorinated Side Group from Methyl Bromoisobutyrate and Obtaining F-Block Copolymers



Among the possible structures of nitroxide involved in CRP of fluorinated (meth)acrylates, BlocBuilder gave the best results.[45,46] It was commercialized in 2005 by Arkema Co. It allows the controlled polymerization of styrenic, acrylic, and some acrylamido monomers, in contrast to NMP of methacrylates which is not controlled.[46]

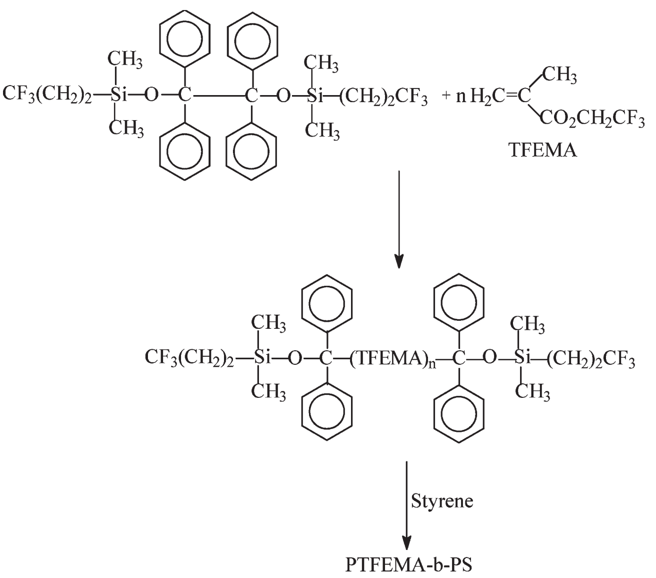
Further reactions were carried out in supercritical CO_2 to overcome the major issue linked to the insolubility of the resulting polymers from attempting the homopolymerization of F-methacrylate bearing a perfluorinated chain containing more than six carbon atoms. Hence, ATRP of (meth)acrylates, developed at the end of last century by Xia et al.[47] involved an activated organobromo initiator to achieve the synthesis of poly(1,1-dihydroperfluorooctyl acrylate), poly(FOA), and poly(1,1-dihydroperfluorooctyl methacrylate), PFOMA, macroinitiators in supercritical CO_2. They found that the more hydrophobic the bipyridine ligand, the higher the fluorinated (meth)acrylate conversion. Even these authors could synthesize F-diblock copolymers by sequential ATRP for methyl bromoisobutyrate (Scheme 2).

The other way to circumvent the issue of insolubility in common organic solvents was to shorten the fluorinated chain length of the acrylate. For example, Hansen et al.[48] carried out the ATRP of 2,2,2-trifluoroethyl methacrylate (TFEMA) from ethyl 2-bromoisobutyrate (2EBiB) to synthesize amphiphilic block copolymers of TFEMA with comonomers such as MMA, 2-methoxyethyl acrylate, and poly(ethylene oxide) methyl ether methacrylate. Thermal properties and surface activity have also been studied showing a significant contribution of the increase of the advancing water contact angle when the copolymer contained a high amount of TFEMA.

Within the same family as the monomers above that yet behave differently, α-fluoroacrylates have been polymerized by ATRP from 2-EBiB and 3-(trimethylsilyl)propyl 2-bromopropionate (2-SBP) as the initiators[49] and in the presence of CuCl (or CuBr) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the catalyst and the ligand, respectively. Indeed, in homo- or copolymerization, α-fluoroacrylates have a propagation rate much higher than that of an acrylate or a methacrylate. Interestingly, thanks to its $(CH_3)_3Si$ end group, 2-SBP initiator was used as a probe for ^1H NMR characterization to assess the true molecular weights (MWs) up to about 10 000. At $T >$ 90 °C, the radical polymerization was controlled as indicated by the MW versus monomer conversion linear relationship. In addition, analysis of the CFBr end groups by ^{19}F NMR further confirmed that the polymerization followed an ATRP mechanism. Furthermore, by calibration of size exclusion chromatography with polystyrene standards produced from 2-SBP initiator, the authors showed that the experimental MWs were close to the theoretical values and better than those assessed with PS or PMMA standards.[49]

Another strategy to polymerize TFEMA in a controlled way was achieved in the presence of fluorinated *tetraphenylethanes* which represent another class of iniferters (by thermal activation). These species were pioneered and then extensively investigated by Bledski and Braun.[50] However, to our knowledge, one investigation only dealing with fluorinated tetraphenylethane was reported. Actually, Roussel and Boutevin[51] synthesized a fluorinated

Scheme 3. Controlled Radical Polymerization of 2,2,2-Trifluoroethyl Methacrylate (TFEMA) in the Presence of Fluorinated Tetraphenylethanes Followed by the Insertion of a Polystyrene (PS) Sequence To Lead to PTFEMA-*b*-PS Block Copolymers



tetraphenylethane used in the thermal polymerization of TFEMA to yield telechelic (or α,ω-difunctional) oligomers (Scheme 3). These latter ones served as efficient macroinitiators to prepare PTFEMA-*b*-PS block copolymers,[51] besides the expected formation of homopolystyrene. The efficiency of the TFEMA oligomers as macroinitiators was 85%. Interestingly, in this special case, the fluorinated substituents were useful in the characterization of the polymeric chain ends by ^{19}F NMR.

Starting from TFEMA oligomers of M_n = 18 000, the molar masses of the diblock copolymers were ranging between 30 500 and 56 400.

Regarding fluorinated styrenes, Hvilsted's group[52] investigated the ATRP of 2,3,4,5,6-pentafluorostyrene (FS) at 110 °C using 1-phenylethyl bromide, PhEBr, and CuBr/2,2′-bipyridine as the initiator and the catalytic system, respectively.[52,53] The molar masses increased linearly with monomer conversions, with relative low polydispersities as clues of a CRP. 96% conversion of FS monomer was achieved in 100 min (leading to a molar mass of 16 000, with polydispersity index, PDI, $\overline{M}_w/\overline{M}_n \leq 1.2$ and T_g = 95 °C). This high rate assumingly reflects the electron-withdrawing character of the fluorine atoms on the phenyl ring. Hence, a wide range of molar masses were obtained, ranging between 4000 and 52 000 with PDIs of 1.08 and 1.50, while the glass transition temperatures were 77 and 101 °C, respectively. In this case, too, block copolymers were produced.

2. Iodine Transfer Polymerization of Fluoroalkenes

Iodine transfer polymerization (ITP) is an extension of the telomerization,[54] and a *quasi*-exhaustive review on the radical telomerization of fluoroalkenes covers a full chapter reported in a book.[4] Various fluorinated monomers (such as vinylidene fluoride, VDF, tetrafluoroethylene, TFE) have been successfully used in ITP. Basic similarities in these pseudoliving polymerization systems are found in the stepwise growth of polymer chains with each active species. The active living center, generally located in the end groups of the growing polymer, has the same reactivity at any time during polymerization even when the reaction is stopped.[29,30] In the case of ITP of fluoroalkenes, the terminal active bond is always the C−I bond originating from the initial iodine-containing chain transfer agent and monomer, as in Scheme 4.

Scheme 4. Iodine Transfer Polymerization of Vinylidene Fluoride in the Presence of 1-Iodoperfluoroalkane

$$C_nF_{2n+1}{-}I + (p+1)\,H_2C{=}CF_2 \xrightarrow{R^\bullet \text{ or } \Delta} C_nF_{2n+1}\,(C_2H_2F_2)_p{-}CH_2CF_2{-}I$$

Scheme 5. Radical Telomerization of Chlorotrifluoroethylene with 1-Iodo-1,2-dichlorotrifluoroethane

$$ClCF_2CFClI + F_2C{=}CFCl \longrightarrow Cl(CF_2CFCl)_n\,I$$

Various patents claim that molecular weights of these PVDFs were ranging between 30 000 and 10 000 000,[29] and yet polydispersities were narrow (1.2−1.3).[29,55] One clue may be due to the high transfer rate (c_{tr} was found to be ca. 7 at 74 °C[56]) as an efficient driving force which is faster than the termination rate since it is known that latter step of most fluoroalkenes proceeds exclusively through recombination.[43]

Tatemoto et al.[29,55,57] used peroxides as initiators of polymerization in solution involving usually perfluorinated or chlorofluorinated solvents. Improvement was also possible by using diiodo[29,55,57] and polyiodo compounds.[58]

Though most industrial works concern the controlled radical (co)polymerization of F-alkenes, quite a few concern the basic approach. Actually, Apostolo's group[59] reported an interesting kinetics of radical copolymerization of VDF and HFP while our group investigated ITP of VDF in solution and in the presence of various 1-iodofluoroalkyl chain transfer agents (CTA) and evidenced that the structure of the CTA has a drastic effect on the controlled behavior of the reaction.[60] Actually, when $C_6F_{13}I$ or $C_6F_{13}CH_2CF_2I$ was chosen, a pseudoliving behavior was noted while in the case of $HCF_2CF_2CH_2I$, no control of the ITP was observed.[56] The "livingness" is based on the labile $CF_2{-}I$ bond. As noted in the solution CRP of VDF, the weakness of the C−I bond is associated with a fast decomposition of the perfluorohexyl iodide,[56] thus contributing to initiation and to a significant increase in the initiation rate in the initial phase of the polymerization. In contrast, the stronger $CH_2{-}I$ bond does not allow a fast consumption of $HCF_2CF_2CH_2I$ CTA.[56,60b]

A similar strategy was achieved by Beuermann's team in supercritical CO_2 at 120 °C and 1500 bar, in homogeneous phase and in the presence of $C_6F_{13}I$[61] or $IC_6F_{12}I$,[62] and the SEC chromatogram indicated that the obtained polymers had low polydispersities ranging from 1.2 to 1.5 at the highest iodide concentration of 0.25 mol L^{-1}. Polymers with iodine end groups were subsequently functionalized with sodium azide and the generated ω-azido PVDF reacted onto symmetrical alkynes to yield PVDFs that bear triazole groups.[62]

Regarding other F-olefins, Haszeldine,[63] in 1955, already observed a kind of living character of the telomerization[4] of chlorotrifluoroethylene (CTFE) in the presence of $ClCF_2CFClI$ (achieved from the radical addition of iodine monochloride into CTFE), according to Scheme 5.

3. Radical Polymerization of Fluoroalkenes Controlled by Alkylboron Compounds

The other possible and more recent method to enable the homopolymerization and copolymerization of fluoroalkenes involves alkylboron compounds activated by oxygen. It was first pioneered by Natta et al.[64] in 1965 and later on was revisited and more deeply investigated by Chung's group.[37,65] BR_3 borane reacts with oxygen to generate $RO{-}OBR_2$ in which the oxygen−oxygen bond undergoes a homolytic cleavage to produce $RO^\bullet$ radical and $^\bullet OBR_2$ borinate (Scheme 1f). In fact, $RO^\bullet$ is an 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 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 counter radical 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 1f).

That strategy was nicely investigated for piezoelectrical polymers[65] after the selective reduction of chlorine atoms of chlorotrifluoroethylene (CTFE) units in poly(VDF-*co*-CTFE) copolymers to yield poly(VDF-*ter*-CTFE-*ter*-TrFE) or poly(VDF-*co*-TrFE) copolymers.

In conclusion, though controlled radical polymerization of fluorinated monomers lies on a couple of strategies, they must be well-adapted to the nature of used F-monomers: ATRP of pentafluorostyrene,[15] fluoroacrylates controlled by nitroxides or by ATRP, or the use of borinate,[51] the macromolecular design by interchange of xanthate[4,33,34] (MADIX), or the iodine transfer polymerization.[4,29,30] However, ATRP requires heavy metals which are sometimes hard to get rid of, RAFT or MADIX processes lead to pink and stinky products, and the procedure with boron species may be dangerous to handle. Hence, it can be understood why ITP, pioneered in the late 1970s,[29,44] has already yielded commercially available polymers.

In addition to these surveys on homopolymerization, many investigations were developed on the radical copolymerization, briefly summarized below.

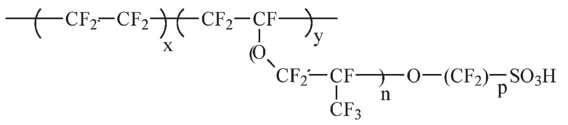
4. Controlled Radical Copolymerization

4.1. Introduction. Copolymerization offers the opportunity to design "specific polymers" and according to the reactivity of both comonomers,[8] thermoplastics,[4] or elastomers[5] can be produced. It is the most general and powerful method to perform effective systematic changes in polymer properties and is widely used in the production of commercially available polymers and in basic investigations of structure−properties 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. Concerning a theoretical point of view, the kinetics of radical copolymerizations of various fluoroalkene couples have also been studied[66] or extensively reviewed in the case of the copolymerizations of VDF with commercially available or synthesized comonomers bearing various substituents.[8]

4.2. Random Copolymers Synthesized by Controlled Radical Polymerization. Bokar and Sen[67] investigated the ATR copolymerization of 1*H*,1*H*,2*H*-perfluorooct-1-ene with methyl acrylate and showed a pseudoliving behavior of such a copolymerization. The challenge was to make possible the copolymerization of $C_6F_{13}CH{=}CH_2$ regarded as a nonpolymerizable monomer in radical polymerization.

4.2.1. Poly(VDF-co-HFP) Copolymers. Basic emulsion iodine transfer copolymerization of VDF and hexafluoropropylene (HFP) initiated by ammonium persulfate (APS) and controlled by IC_4F_8I was pioneered by Tatemoto in the early 1980s.[19] According to APS and IC_4F_8I concentrations, molecular weights of the produced rubbery copolymers were ranging between 900 and 10 000 $g \cdot mol^{-1}$ while PDI values were in the 1.17−1.30 window. A further step claimed the cross-linking of these diiodopolymers with peroxides and triallyl isocyanurate (as a classical method to cross-link elastomers[5,6]).

Scheme 6. Chemical Structure of Poly(TFE-*co*-PFSVE) Copolymers[a]



[a] PFSVE stands for perfluoro-4-methyl-3,6-dioxaoct-7-ene sulfonyl fluoride, and x ranges from 5 to 14 for $y = 1$; n can be 0, 1, or 2 and $p = 2-4$.

Twenty years later, the kinetics of microemulsion ITP of VDF and HFP in the presence of $IC_6F_{12}I$ was extensively investigated by Apostolo et al.[58] (from the Solvay Solexis Co.), who assessed the different rate constants and proposed various models. These authors also showed the linear dependence of the molar masses versus the monomer conversion. 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 "pseudo-branching and living technology".[68]

Other studies in solution were published by various groups.[69,70] As a matter of fact, telechelic diiodoelastomers of MW < 10 000 g mol^{-1} and narrow polydispersities (claimed PDI were in the 1.01−1.23 range[69]) were obtained. They were bearing VDF−I end groups only, and as in the case of the polymerization of VDF, the molecular weights of the resulting poly(VDF-*co*-HFP) copolymers had a drastic influence on the percentages of both CH_2CF_2I and CF_2CH_2I end groups. More recently, our group revisited that strategy to prepare telechelic di(meth)acrylate poly(VDF-*co*-PMVE) copolymers for (semi)interpenetrated polymer networks for fuel cell membranes.[71]

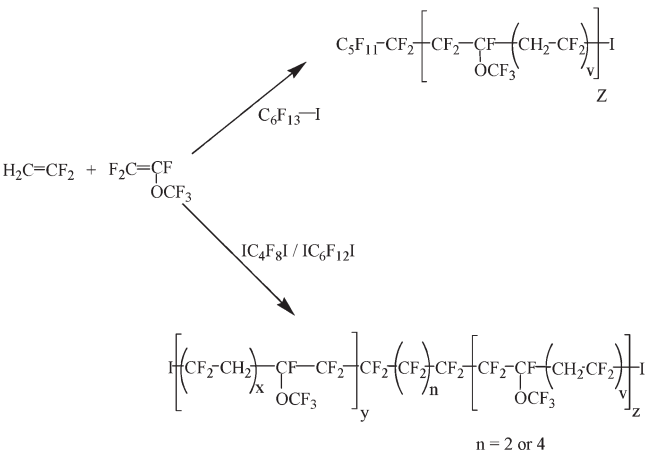
4.2.2. Copolymers Based on VDF and (Functional) Perfluoroalkyl Vinyl Ethers. Although perfluoroalkyl vinyl ether are expensive monomers, the goal to use them in radical copolymerization with either TFE or VDF dealt with the decrease in the crystallinity rate of PTFE and PVDF and even to obtain elastomers. The challenge is still to reach T_gs lower that −40 °C for low-temperature resistance applications.[72] Further, though an abundant literature reports that, under radical conditions, functional perfluoroalkyl vinyl ethers (PAVEs) or perfluoroalkoxy alkyl vinyl ethers (PAAVEs) copolymerize with TFE to lead to proton exchange membrane for fuel cell, PEMFC[73] (Scheme 6), to our knowledge the CR copolymerization of TFE with perfluoro-4-methyl-3,6-dioxaoct-7-ene sulfonyl fluoride (PFSVE) has never been reported.

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 percentage VDF is lower than 85%, although little development has been achieved.[5] Indeed, the ether linkage(s) brought by the PAVE (or PAAVE) comonomer enables the resulting macromolecules to exhibit a low glass transition temperature, and in certain cases, elastomers resistant to low temperature endowed with good thermal stability have been obtained.

Though various articles[74,75] and patents[76−79] report successful conventional radical copolymerization of VDF and PAVE, only one publication mentions the CR coP of VDF with perfluoromethyl vinyl ether (PMVE) via the ITP process in the presence of $C_6F_{13}I$ or α,ω-diiodoperfluoroalkane as the chain transfer agents[80] (Scheme 7). This led to various features in term of pseudoliving behavior, end groups, and molar masses (Figure 1) even in the absence of fluorosurfactant.

This radical copolymerization is regarded as controlled (or pseudoliving). The careful NMR characterization enabled us to assess the MW and to well identify the end groups (exclusively composed of VDF−I, and % $-CH_2CF_2I$ > 95%

Scheme 7. Iodine Transfer Copolymerization of Vinylidene Fluoride with Perfluoromethyl Vinyl Ether in the Presence of Monoiodo or Diiodo Perfluorinated Chain Transfer Agents



when M_n < 2600 g mol^{-1}). The resulting poly(VDF-*co*-PMVE) copolymers had T_g values of ca. −60 °C for satisfactory thermal stability.[80b]

The nature of the CTA ($C_6F_{13}I$ or $IC_nF_{2n}I$) did not affect (i) the yield of the copolymerization versus the PMVE feed mol % and (ii) the reactivity ratios, r_i, of both comonomers: $r_{VDF} = 2.53$ and $r_{PMVE} = 0$ at 80 °C[80b] or $r_{PMVE} = 0.11$ and $r_{VDF} = 1.06$ at 80 °C[81] in emulsion copolymerization or $r_{PMVE} = 0$ and $r_{VDF} = 3.4$ at 74 °C[75] in solution.

These fluorinated diiodides were chemically modified into original telechelic bis(hydroxyl), diazido,[82] diacrylates,[83] bis(triethoxysilanes),[84] bis(methyldiethoxysilanes),[84] and poly(VDF-*co*-PMVE) copolymers, as precursors of novel cross-linked elastomers.[85]

4.2.3. Controlled Poly(HFP-co-TFE) Copolymers in the Presence of Perfluoroalkylsulfonyl Chloride. Feiring et al.[86] attempted the radical copolymerization of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) in the presence of perfluoroalkylsulfonyl chloride. The exact nature of the initiation process remained unclear by the authors, since several metals were potentially present in the polymerization. Various metallic species (including Cu(I), Ni(II), and Fe(II)) were separately shown to act as the catalysts. Actually, the fluoroolefin copolymerization was believed to proceed by a standard free radical mechanism because termination of polymerization by formation of a perfluoroalkyl chloride end group would most probably be irreversible under these conditions.

4.2.4. Iodine Transfer Copolymerization of α-Trifluoromethacrylates and Fluoroalkene(s). As mentioned above, α-fluoroacrylate was successfully polymerized under ATRP conditions, but examples of controlled radical copolymerization of fluoroalkenes with F-acrylates are scarce since acrylates or methacrylates are more reactive than fluoroalkenes. To the best of our knowledge, the only example deals with the iodine transfer copolymerization of VDF with α-trifluoromethacrylic acid (TFMA) achieved in emulsion,[87] 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* (Scheme 8).

Probably, the carboxylic acid enabled the self-emulsion of the process. The molecular weights of the resulting copolymers could be targeted from $([VDF]_0 + [TFMA]_0)/[(I)R_FI]_0$ initial molar ratios. They reached values up to 220 000 g mol^{-1} in the absence of chain transfer agent. In addition, the copolymers obtained exhibit small sizes of particles (ca. 100 nm).[87]

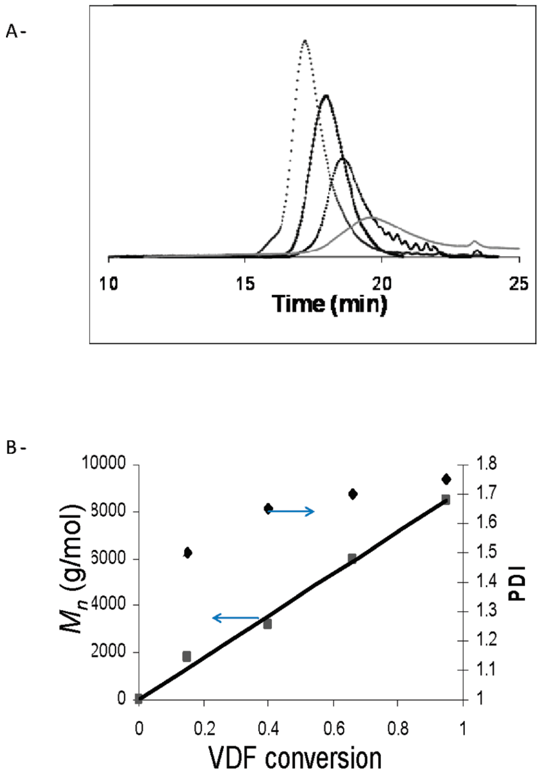
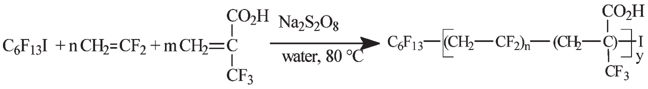


Figure 1. (A) Evolution of SEC traces for different conversions (right to left: 18%, 38%, 63%, and 95% of VDF conversion) for the iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE) using $IC_6F_{12}I$ as the chain transfer agent (54/46 in molar feed ratio in VDF/PMVE, composition of copolymer 65/35 mol % of VDF/PMVE). (B) Evolution of molar masses, (■) M_n, and (◆) polydispersity indices, PDI, versus VDF conversion. The straight line corresponds to the theoretical curve. Reproduced from ref 80b.

Scheme 8. Iodine Transfer Copolymerization of Vinylidene Fluoride with α-Trifluoromethacrylic Acid



$$C_6F_{13}I + n\,CH_2{=}CF_2 + m\,CH_2{=}C(CO_2H)(CF_3) \xrightarrow[\text{water, 80 °C}]{Na_2S_2O_8} C_6F_{13}-[(CH_2-CF_2)_n-(CH_2-C(CO_2H)(CF_3))]_y-I$$

Such a strategy has also been efficient to obtain original poly(VDF-*ter*-TFMA-*ter*-HFP) terpolymers by radical terpolymerization of TFMA with VDF and HFP controlled by $IC_6F_{12}I$ (Scheme 9). The fluorocopolymers were involved with nanosilica to lead to original nanocomposites[88] endowed with exceptional thermal properties.

Additionally, these terpolymers were further blended with a poly(styrene)-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) triblock terpolymer to lead to micellar structures[89] containing a core formed of poly(VDF-*co*-HFP) segments and TFMA/P2VP hydrogen-bonded complexes and a corona of PS and PEO chains. Average radii of the micelles were assessed for different PS−POE/poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymers (ranging between 13 and 31 nm, Figure 2). Depending on the content of VDF in the used poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymers, microphase-separated fluorinated nanodomains could be observed inside the core. For the copolymer containing the higher amount of PVDF segments, multicompartmentalized cores have been visualized in agreement with the formation of poly(VDF-*co*-HFP) nanodomains in the micellar core. Furthermore, those micellar structures exhibit a reversible thermoresponsive behavior since they disassembled upon heating above 50 °C and reassemble upon cooling.

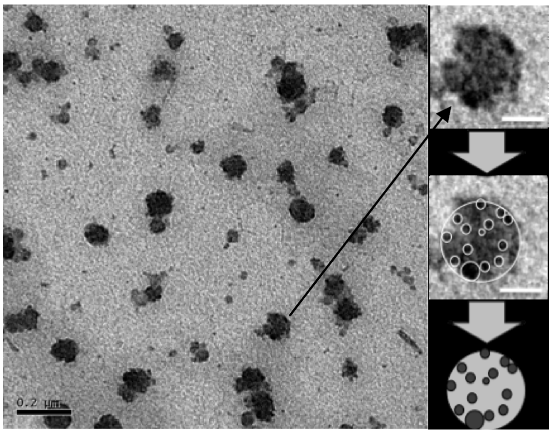
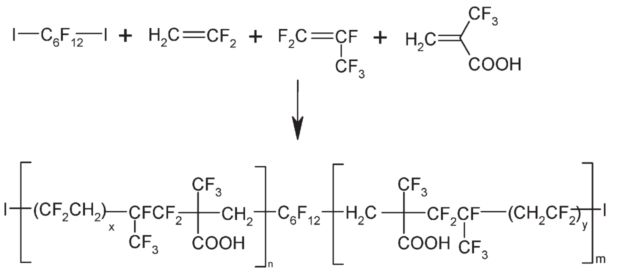


Figure 2. TEM image (left) of micelles formed by the poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymers/poly(S-*b*-2VP-*b*-EO) blend (the scale bar represents 200 nm). Focus on a multicompartmentalized core (right, scale bar is 40 nm). Fluorinated domains are represented in dark gray.[89]

Scheme 9. Iodine Transfer Terpolymerization of Vinylidene Fluoride with α-Trifluoromethacrylic Acid and Hexafluoropropylene in the Presence of 1,6-Diiodoperfluorohexane



4.2.5. 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 in the presence of $C_6F_{13}I$ as the CTA and initiated by *tert*-butyl peroxypivalate (TBPPI)[90] (Scheme 10).

Original terpolymers were produced, and as expected, the CTA concentration influences both the molar mass values and the thermal properties of the resulting terpolymers (they had narrow polydispersity indices[90]). The control of that reaction was evidenced by the linear dependence of the average molar masses versus the monomer conversion.[90]

4.2.6. Fluorinated Copolymers Controlled by Borinates. A more recent technique, developed at the Penn State University[37,65,91,92] which 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 vinylsilanes[92] or fluoroalkenes such as HFP[91] or CTFE.[92] Interestingly, that system is able to control the polymerization of VDF via the $^{\bullet}OBR_2$, a stable radical that acts as a counter radical (as reported in Scheme 1f).

That technique enabled Chung's team to synthesize original poly(VDF-*co*-CTFE) copolymers and poly(VDF-*ter*-CTFE-*ter*-F_2C = CF−R−$Si(CH_3)_2OR$) terpolymers obtained in a controlled manner in solution or in bulk at ambient temperature, in fair yields (< 65%)[37,92] (Scheme 11), where X can be H or $C_2H_4Si(OEt)_3$.

4.2.7. Poly(VDF-co-comonomer) Copolymers Controlled via Xanthates. Besides ITP and radical copolymerizations controlled by borinates, the pseudoliving radical copolymerizations of F-alkenes were successfully carried out in the presence of xanthate.

A first investigation concerns the radical copolymerization of F-monomers with methyl acrylate and vinylidene chloride in the presence of a xanthate that led to gradient copolymers for hydrophobic coatings. This property could be achieved thanks to the fluorinated segments that moved up to the surface.[93]

This strategy, also called "macromolecular design through interchange of xanthate" (MADIX), was pioneered by the Rhodia Co.[33,34] and favors the controlled radical polymerization (CRP) of vinyl acetate (VAc) regarded as the best technique for such a polymerization of VAc. However, to our knowledge, MADIX copolymerization of fluoroalkenes is scarce: indeed, only radical copolymerizations of VDF with HFP,[94] VDF and perfluoro-3,6-dioxo-4-methyl-7-ene sulfonyl fluoride (PFSVE),[95] and VDF with 3,3,3-trifluoropropene (TFP)[96] were successful so far to lead to original poly(VDF-*co*-HFP)-xanthate, poly(VDF-*co*-FFSVE)-xanthate, and poly(VDF-*co*-TFP)-xanthate, respectively. These fluorinated copolymers that bear a xanthate end group were able to further yield original block copolymers (see section 5.1.2).

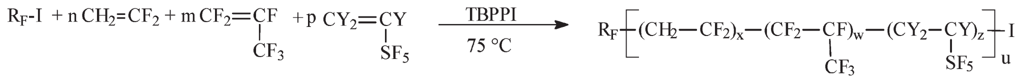
4.2.8. Conclusion. In conclusion of this section, only three efficient methods that deal with the controlled radical (co)polymerizations (CRcoP) of fluoroalkenes have been achieved so far: ITP, MADIX, and the copolymerization in the presence of boron-containing species. Though these methods have not been systematically applied to all (M_1, M_2) couples, various products have already been industrially implemented. Daiel and Tecnoflon copolymers, marketed by the Daikin and Solvay Solexis companies, are the first industrial products obtained by CRcoP (section 5.1.1). 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 out alternatives regarding the cost, methanol crossover for the formers, and environment or health concerns such as the bioaccumulation and persistency for the latters.

5. Well-Defined Fluorocopolymers

Original well-architectured fluorinatd macromolecules have already been synthesized such as block, graft, alternated, or telechelic fluorocopolymers, and a nonexhaustive list of examples is supplied below.

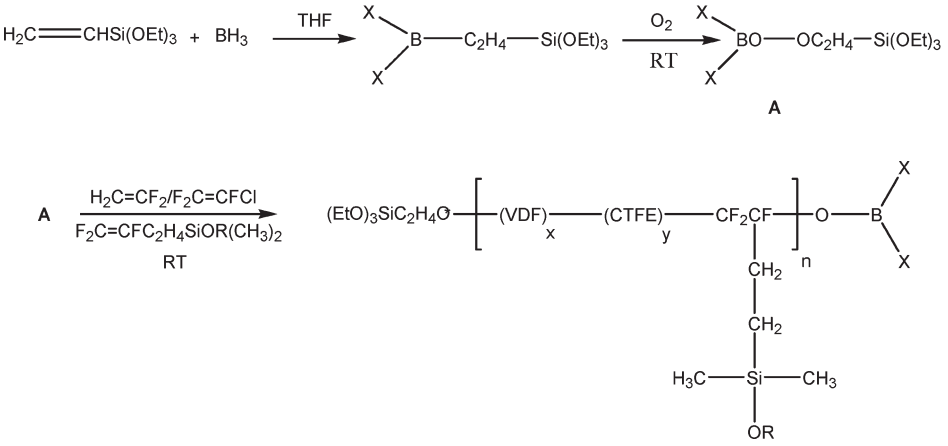
5.1. Fluorinated Block Copolymers. Methods to obtain block copolymers by radical processes have been developed rather lately about other processes and especially ionic methods. Among telechelics, block, graft, or alternated copolymers, cycles, networks, dendrimers, and star-shaped polymers,[4] block copolymers have received much attention as "novel polymeric materials" with multicomponents since they are made of two or more different polymeric sequences linked together.[97,98] Frequently, block 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 modifications of solution viscosity, impact resistance, surface activity, and elasticity. Thus, several block[4,20,98] (and also 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

Scheme 10. Iodine Transfer Terpolymerizartion of Vinylidene Fluoride, Hexafluoropropylene, and 1,1,2-Trifluoro-2-pentafluorosulfanylethylene[90]



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

Scheme 11. Radical Terpolymerization of Vinylidene Fluoride with Chlorotrifluoroethylene and 4-Alkoxydimethylsilyl-1,1,2-trifluorobutene Controlled by an ω-Triethoxysilane Borinate



(for O-rings, shafts, diaphragms, sealants, gaskets in automotive and aerospace industries), fuel cell membranes, surfactants, and various other items (lenses, dental materials, etc.). Various strategies to synthesize F-block copolymers have been chosen, and Table 1 sums up the different routes ranging from radical to anionic, cationic, metathesis, GTP, and condensation processes.

In addition, NMP of methacrylates bearing a fluorinated chain is not controlled by using the Blocbuilder alkoxyamine (Scheme 12) while ill-defined methacrylate-based block copolymers can be synthesized by initiating methyl methacrylate (MMA) polymerization with a SG1-capped polyacrylate.[46]

5.1.1. Block Copolymers via Halogen Transfer. This subsection describes strategies to prepare fluorinated block copolymers by group transfer: for example, those prepared by degenerative transfer involving either macrotransfer agents which possess cleavable C−X bond (X designates a halogen) or xanthates.

The synthesis of block copolymers from the C−I cleavage (Tables 2 and 3) on ITP was pioneered by Tatemoto et al.[19,29,44,106] in the early 1980s, and these Japanese researchers synthesized poly(VDF-*co*-HFP)-*b*-PVDF block copolymers by controlled (or pseudoliving) iodine transfer polymerization[29,30] using an α,ω-diiodoperfluoroalkane (IR_FI such as IC_4F_8I or $IC_6F_{12}I$) which generated a first elastomeric block **1**. This latter was then able to initiate the polymerization of fluorinated comonomers, including VDF, as illustrated in Scheme 13.

These thermoplastic elastomers (TPEs), marketed by the Daikin Co. as soon 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, e.g., Figure 3) and hard blocks composed of various crystalline sequences (PVDF to get (Dai-el T-630),[19,29d,131] PTFE, or poly(ethylene-*alt*-tetrafluoroethylene) or poly(E-*ter*-TFE-*ter*-HFP) hard block (Dai-el T530) thermoplastics).[19] Similar TPEs, based on poly(VDF-*co*-CTFE) central copolymeric block,[106] have been prepared, involving in a second step, the ITcoP of ethylene (E) and CTFE or E and TFE. Other hard segments can be composed of a combination of VDF (in high amounts) with HFP or CTFE, or of copolymers of TFE with PMVE, VDF, or HFP, or terpolymers based on TFE and E and containing propylene, isobutylene, HFP, 1*H*-pentafluoropropene, PMVE, 3,3,3-trifluoropropene, or hexafluoroisobutylene.

Daikin is not the only producer of TPEs since DuPont Polymers (formerly DuPont Dow Elastomers and then DuPont Performance Elastomers) and Ausimont (now Solvay Solexis) are also quite active in that area. Hence, that last company markets Tecnoflon block copolymers (Table 3) under a "pseudoliving and branching technology".[68] Other fluorinated sequenced copolymers and TPEs using that process were reviewed a few years ago.[4,29,68]

In addition, the use of α,ω-diiodofluoroalkanes favors the control of the (co)polymerization. Table 2 lists various transfer agents used in the ITP of fluoroalkenes.[29,68,80,132] Although not all the reactions have been carried out in the same experimental conditions, the polydispersities of the final TPE as low as 1.73 were achieved, and when a fluorinated nonconjugated diene[108,109] was involved in terpolymerization of fluoroalkenes, the PDI is even lower (1.4). This improved control of ITP, called "pseudoliving and branching technology",[68,108,109] was extensively studied at Ausimont (now Solvay-Solexis S.A.) and enabled production of competitive thermoplastic elastomers. For example, this is the case of Tecnoflon FTPE XPL. Table 3 summarizes various TPEs made from α,ω-diiodofluoroalkanes containing soft sequences (I−soft−I) able to reinitiate other thermoplastic chains in the second step to yield a hard−soft−hard triblock copolymer (Scheme 14).

Table 3 also lists the T_g and T_m values of these fluorinated thermoplastic elastomers. Even when PMVE was added in the soft block, the T_g could not be significantly lowered when that block contained TFE units.[107−109] However, VDF and PMVE led to the optimum softness[80] (i.e., the lowest T_g values) Further, the introduction of a small amount of nonconjugated diene slightly lowered the T_g and increased the T_m by a few degrees.[108,109]

Most of these TPEs could be used from −30 to 250 °C and can be utilized in continuous service at 200 °C (in contrast to conventional elastomers that usually decompose at this temperature).

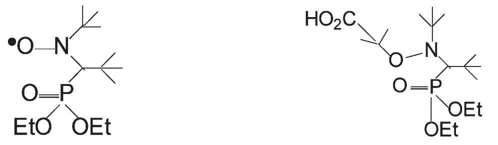
Interestingly, the TPEs can be cross-linked by the peroxide/triallyl (iso)cyanurate system,[133] or by gamma (^{60}Co)

Table 1. Overview of the Synthesis of Fluorinated Diblock Copolymers Achieved from Various Methods[a]

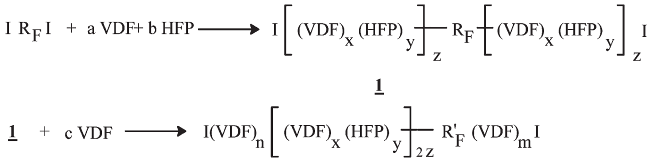
method	initiator, catalyst, or chain transfer	structure of F-diblock	reference
radical iniferter	thiuram	PBuMA-*b*-PTFEMA	99
		PS-*b*-PFOA	100
		PDMAEMA-*b*-PFOA	101
		PDMAEMA-*b*-PFA	102
	tetraphenylethane	PTFEMA-*b*-PMMA	51
NMP	TEMPO	PS-*b*-PFA	103
	polymer1 BlocBuilder	polymer1-*b*-polymer2 BlocBuilder	45, 46
RAFT	dithioester	R_F-PS, R_F-PMMA,	104
		R_F-PEA, R_F-PBut	104
	xanthate	R_F-PVAc; poly(VDF-*co*-TFP)-*b*-PVAc	105, 96
ITP	R_FI	poly(fluoroalkene)-*b*-poly(fluoroalkene)	29, 106−109
		PVDF-*b*-PS	110
		PVDF-*b*-poly(cyano monomer)	111
ATRP	PTFMS	PTFMS-*b*-PS; PTFMS-*b*-PFS	15, 53
	CCl_3−PVDF telomers	PVDF-*b*-PS, PVDF-*b*-PMMA	112
		PVDF-*b*-PEA	112
	CCl_3−PVDF telomers	PVDF-*b*-PPFS, PVDF-*b*-PSSE	113
	CCl_3−poly(VDF-*co*-HFP) cotelomers	poly(VDF-*co*-HFP)-*b*-PPFS	114
cationic	CF_3SO_3H	PHVE-*b*-PFVE	115
	$ZnCl_2$	PHVE-*b*-PFVE	11d, 116
	X/scCO_2	PFVE-*b*-PHVE	11c, 116
	HO-PTFE telomers	PTFE-*b*-PCL	117
	HO-PFPE−OH telomers	PCL-*b*-PFPE-*b*-PCL	118
anionic	*sec*-BuLi/1,1-diphenylethylene	PHEMA-*b*-PFBMA	119
		PMMA-*b*-PFMA	120
	BuLi/LiCl	PMMA-*b*-PFMA	121
	1,1-diphenyl-3-methyl pentyllithium/LiCl	P(tBuMA)-*b*-P(2-FBSMA)	122
		PS-*b*-P(But-R_F), PS-*b*-P(I_p-R_F)	123−125
metathesis	C_8F_{17}	oligo(TFE)-*b*-PE	126
GTP	MMTP	PMMA-*b*-PFMA	127
		PTHPMA-*b*-PFMA	128
condensation	none	PEO-*b*-R_F	129
		PDMAA-*b*-R_F	130

[a] But, EA, FA, FMA, FOA, FBSMA, FVE, HFP, HVE, I_p, MMTP, PE, PFPE, PFS, THPMA, TFEMA, TFMS, TFP, and VAc stand for 1,3-butadiene, ethyl acrylate, F-acrylate, 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl methacrylate, 1,1-dihydroperfluorooctyl acrylate, 2-(*N*-methyl perfluorobutane sulfonamido) ethyl methacrylate, F-vinyl ether, hexafluoropropylene, hydrogenated vinyl ether, isoprene, 1-methoxy-2-methyl-1-trimethylsilyloxy-1-propene, polyethylene, perfluoropolyether, 2,3,4,5,6-pentafluorostyrene, tetrahydropyranyl methacrylate, 2,2,2-trifluoroethyl methacrylate, 4-methoxy-2,3,5,6-tetrafluorostyrene, 3,3,3-trifluoropropene, and vinyl acetate, respectively.

Scheme 12. Chemical Structures of SG1 Nitroxide (left) and Blocbuilder Alkoxyamine (right)



Scheme 13. Sequential Iodine Transfer Copolymerization of Various Fluoroalkenes To Achieve Block Thermoplastic Elastomers



or beta rays,[109] or by Huisgen 2 + 2 cyclopolar addition (or "click chemistry"[85,134]) which confers improved thermal stability, a high resistance to vapor, UV, chemical agents, ozone, and hydrocarbons, and better mechanical properties (tensile modulus, compression set) than those of non-cross-linked fluoroelastomers.

Numerous applications in high-tech areas such as aerospace, aeronautics,[107−109] and engineering or in optics[106] arising from their outstanding properties are listed in Table 4. These TPEs are useful as O-rings,[133] hot melts,[135] pressure-sensitive adhesives, tough transparent films[136] (Figure 4), sealants that exhibit good chemical and aging resistances, protection (as coatings) of metals,[136] or even in specific applications such as dental plates[135] (since Dai-el T530 is claimed to show neither erythrocyte hemolysis nor cytotoxicity and does not generate any harmful substances).

As a matter of fact, various models of multiblock copolymers containing VDF, trifluoroethylene and HFP,[137] or VDF and 3,3,3-trifluoropropene[138] were proposed from controlled sequential (or stepwise) cotelomerization of fluoroolefins (Scheme 15).

Jo et al.[139] claim to synthesize 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 noted 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 C−Br bond (regarded stronger than C−I bond). Indeed, ATRP of styrene (Sty) via the bromine transfer[140] from α,*ω*-dibrominated intermediates **2** regarded as "macroinitiators" led to di- or triblock copolymers. Surprisingly, the authors claimed narrow polydispersity indices of 1.1 while previous similar investigations[141,142] 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 VDF with 1,2-dibromotetrafluoroethane.[141]

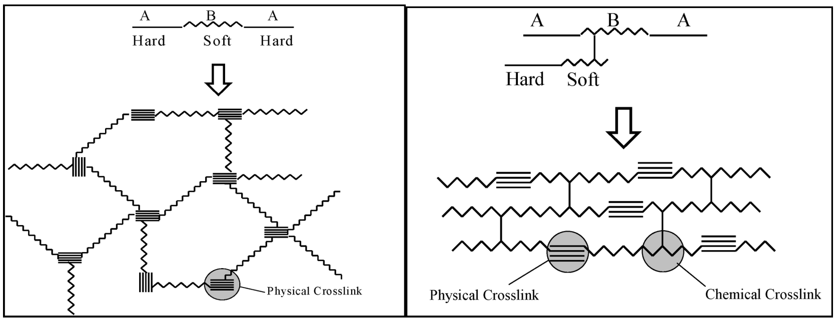


Figure 3. Schematic representations of the cross-linked structures obtained after molding of a fluorinated thermoplastic elastomers block copolymer produced by pseudoliving technology[68] (left) and involving a nonconjugated diene that induces chemical cross-links (right).

Table 2. Effect of the Nature of the Transfer Agent on the Molar Masses (M_n) and Control of the Iodine Transfer Copolymerization of Fluoroalkenes[a]

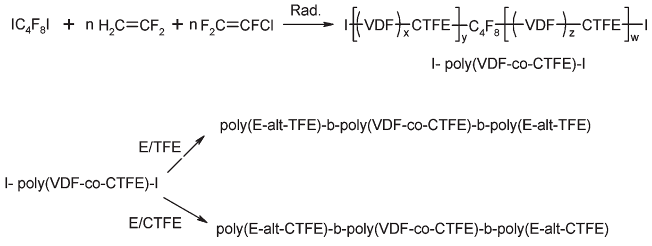
transfer agent	fluoroalkenes	M_n	PDI	reference
none	VDF/HFP		5	68
i-C_5H_{12} or i-$C_{10}H_{22}$	VDF/HFP		5	29a, 29c
EtOAc	VDF/HFP		2.9	68
i-C_3F_7I	VDF/HFP	140 000	2.7	29a, 29c
IC_4F_8I	VDF/HFP	120 000	2.3	68
IC_4F_8I	VDF/HFP	143 000	1.7	29a, 29c
IC_4F_8I	VDF/HFP		1.5	29c
IC_4F_8I	VDF/PMVE	1000−10 000	1.2	80
$IC_6F_{12}I$	VDF/HFP		1.7	68
$H_2C{=}CHC_6F_{12}CH{=}CH_2/IC_4F_8I$	VDF/HFP		1.3	68
triazine triiodide	VDF/HFP/TFE	116 000	1.9	132

[a] VDF, HFP, PMVE and PDI stand for vinylidene fluoride, hexafluoropropylene, perfluoromethyl vinyl ether, and polydispersity index, respectively.

Table 3. Iodine Transfer Polymerization of Fluoroalkenes for the Synthesis of Fluorinated Hard-*b*-Soft-*b*-Hard Triblock Copolymers (n.g. Stands for Not Given)

soft block	% comonomers in soft block	hard block	soft/hard ratio (wt %)	T_g (°C)	T_m (°C)	reference
I[(VDF)$_x$HFP]$_y$I	n.g.	PVDF	n.g.	n.g.	160	29c
I[(VDF)$_x$HFP]$_y$I	n.g.	poly(E-*alt*-TFE)	n.g.	n.g.	220	29c
I[(CTFE)$_x$(VDF)$_y$]$_z$I	45/55	poly(E-*co*-CTFE)	85/15	−6	247	106
I[(CTFE)$_x$(VDF)$_y$]$_z$I	45/55	poly(E-*co*-TFE)	90/10	−8	252	106
I[(VDF)$_x$(FVA)$_y$]$_z$I	n.g.	PVDF	n.g.	n.g.	n.g.	29b
I[(TFE)$_x$P]$_y$I	55/45	poly(E-*co*-TFE)	80/20	−1	267	107
I[(VDF)$_x$HFP(TFE)$_y$]$_z$I	56/19/25	PVDF	80/20	−12 to −15	165	108
I[(VDF)$_x$HFP(TFE)$_y$]$_z$I	35/40/25 (wt)	poly(E-*alt*-TFE)	n.g.	−8	222	29
I[(VDF)$_x$HFP(TFE)$_y$]$_z$I	50/30/20	poly(E-*co*-HFP-*co*-TFE)	85/15	n.g.	n.g.	131
I[(VDF)$_x$HFP(TFE)$_y$]$_z$I	54/21/25	poly(E-*alt*-TFE)	80/20	−13	266	108a
I[(VDF)$_x$PMVE(TFE)$_y$]$_z$I	62/19/19	PVDF	80/20	−30	160	108, 109
I[(VDF)$_x$PMVE(TFE)$_y$]$_z$I	73/17/10	poly(E-*co*-TFE)	72/28	−33	254	107
I[(VDF)$_x$PMVE(TFE)$_y$]$_z$I	n.g.	poly(E-*co*-TFE)	n.g.	−13 to −15	266	108, 109
I[(VDF)$_x$PMVE(TFE)$_y$]$_z$I	57/23/20	poly(E-*co*-TFE-*co*-PMVE)	75/25	n.g.	180	109
I[(TFE)$_x$P(VDF)$_y$]$_z$I	n.g.	poly(E-*co*-TFE)	85/15	−13	262	107
I[(TFE)$_x$E(PMVE)$_y$]$_z$I	45/19/36	poly(E-*co*-TFE)	71/29	−16	245	107

Scheme 14. Strategies of Synthesis of Fluorinated Thermoplastic Elastomers via a Two-Step Procedure[a]



[a] VDF, CTFE, E, and TFE stand for vinylidene fluoride, chlorotrifluoroethylene, ethylene, and tetrafluoroethylene, respectively.

In addition, the synthesis of PVDF-*b*-polystyrene block copolymer[110] was achieved by sequential iodine transfer polymerization of VDF[56,60b] 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.[110]

Another example of synthesis[112] of diblock copolymers (**4**) arises from the combination of a telomerization followed by the chlorine transfer radical polymerization (via a CCl_3 end group) of various M monomers (such as styrene, MMA, methyl acrylate, and butyl acrylate) initiated by VDF telomers (**3**)[142b] (Scheme 16).

Interestingly, whatever the (VDF telomer; M) couple, the average molecular weights in number ($\overline{M}_n$) of block copolymer **4** increased linearly with the monomer conversions, and experimental ($\overline{M}_n$) values were close to the theoretical ones. In addition, narrow polydispersity indices ($\overline{M}_w/\overline{M}_n < 1.2$) were obtained. Similarly, that ATRP strategy was successfully applied for the preparation of PVDF-*b*-poly(pentafluorostyrene[113a] or PVDF-*b*-poly(styrene sulfonate ethyl ester[113b]) block copolymers by ATRP of pentafluorostyrene or of styrene sulfonate ethyl ester in the presence of CCl_3−PVDF.

Table 4. Examples of Items Made from Fluorinated Thermoplastic Elastomers, Properties, and Fields of Applications[29a,c,106−109,131−133,135,136]

	molding	weather and chemical resistance	transparency	elasticity	safety	vulcanizability	mechanical properties	applications
medical, biochemical	X	X	X	X	X			tubing, rubber stoppers, medical materials
physical and chemical equipment	X	X	X	X		X		tubing, seals, pipets
semiconductor industry	X	X	X	X	X			tubing, seals
chemical industry		X		X		X		anticorrosion paints, diaphrams, hoses, linings
food industry	X	X	X	X	X			hoses, sealing materials
electronics industry	X	X		X			X	wiring, sealing material
civil engineering	X	X		X			X	sealing materials, films, nonflammable materials
textile industry				X			X	coatings, filaments, fibres, water-repellant treatments
optics			X		X			lenses
other fields			X	X			X	adhesives (hot melts)

Figure 4. Various items based on Daiel thermoplastic elastomers (courtesy of Daikin).

These original block copolymers are endowed with satisfactory thermostabilities. This survey completes a comprehensive review which reports ATRP of PFS.[15] In the same way, poly(VDF-*co*-HFP)-*b*-PS block copolymers were achieved by a first cotelomerization of VDF and HFP with chloroform followed by a similar ATRP of styrene.[114] The sulfonation of these resulting block copolymers led to poly(VDF-*co*-HFP)-*b*-PSSA block copolymers[143] (where PSSA stands for poly(styrenesulfonic acid)) which were subsequently processed into protonic membranes for fuel cell. The nanostructure of film cast from these diblock copolymers was shown by the same group[144] in addition to the correlation between such nanostructures and the transport properties of the membranes[143] obtained from these diblock copolymers.

To conclude, two main strategies of synthesis of block copolymers obtained from the cleavage of C−X bond in chain transfer agents (CTAs) are suggested. The decreasing order of the C−X bond dissociation energy (C−Cl > C−Br > C−I) shows that major industrial productions occur from the sequential iodine transfer (co)polymerization of fluoroalkenes in the presence of $IC_nF_{2n}I$ as the CTAs. The second route concerns the ATRP of various monomers in the presence of fluorinated telomers that bear a Cl_3C end group. Exceptional thermoplastic elastomers leading to numerous applications (O-rings, shafts, dental resins, etc.) have been produced from such a process. In addition, "hot" topics such as polymer electrolyte for fuel cells membranes have also been investigated from the second route when the PS block was sulfonated into a PSSA sequence, as evidenced by the growing number of patents and publications. Further strategies to synthesize block copolymers have also been explored involving xanthates as suitable CTAs and are briefly summarized below.

5.1.2. Block Copolymers via Xanthates. The last strategy for block copolymer synthesis deals with a few examples reported by the MADIX process, involving a thiocarbonyl thio transfer agent, according to a reversible addition−fragmentation chain transfer mechanism (Scheme 17).

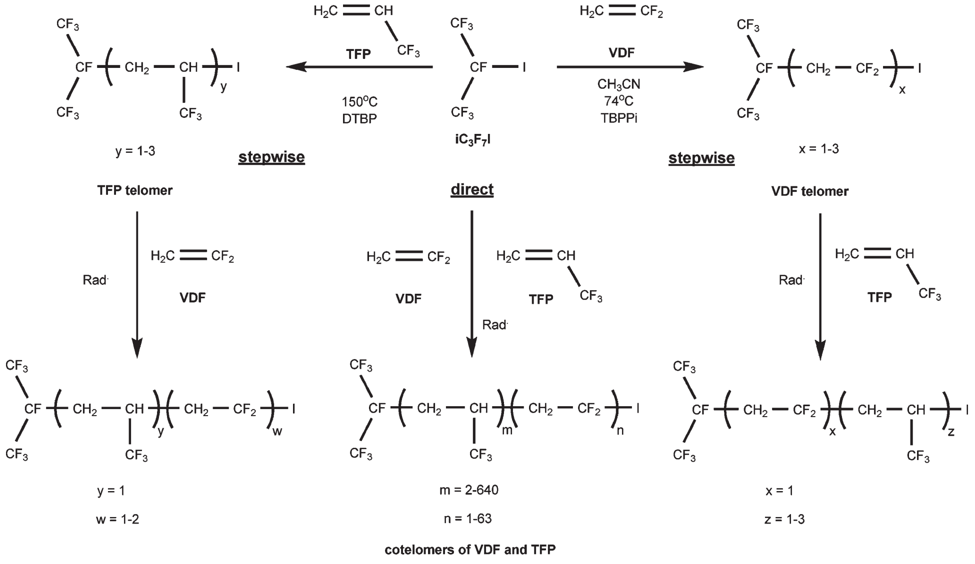
A first interesting example was reported by Severac,[94] who achieved the controlled radical copolymerization of VDF with HFP in the presence of $CH_3OCOCH(CH_3)SC(S)OEt$ xanthate (Scheme 18).

The intermediate poly(VDF-*co*-HFP) copolymer bearing a xanthate end group was able to further reinitiate poly(VDF-*co*-HFP) or poly(VAc) oligomeric chains via the cleavage of the C−S bond adjacent to the C=S group, and it is noted a satisfactory control of the copolymerization. A significant increase of the molar masses (from 6500 g mol^{-1} for the intermediate copolymer to 10 600 or 9400 g mol^{-1} with steady polydispersity indices PDIs (from 1.47 to 1.48 and 1.59) for poly(VDF-*co*-HFP)-*b*-poly(VDF-*co*-HFP) and poly(VDF-*co*-HFP)-*b*-PVAc block copolymers, respectively.[94]

Few fluorinated xanthates (that bear a short fluorinated group) have been prepared.[105d,e] More recently, an original fluorinated xanthate was also synthesized[95,96] into two steps (Scheme 19).

First, a radical copolymerization of VDF and HFP controlled by such a fluorinated xanthate led to a poly(VDF-*co*-HFP)−SC(S)OEt intermediate of molar masses up to 13 000 g mol^{-1} and PDI = 1.45. Then, the resulting macromolecular xanthate containing VDF and HFP was involved into two reactions: (i) First, the radical polymerization of VDF to allow the synthesis of poly(VDF-*co*-HFP)-*b*-PVDF block copolymers, with a molecular weight of ca. 20 000 g mol^{-1} and PDI = 1.62, as an original TPE. Interestingly, the ^{19}F NMR spectrum shows the signal centered at −71 ppm assigned to $CH_2CF_2SC(S)OEt$. (ii) The second reaction

Scheme 15. Direct or Sequential Cotelomerization of Vinylidene Fluoride (VDF) or 3,3,3-Trifluoropropene (TFP) in the Presence of 2-Iodoperfluoroisopropane[138]

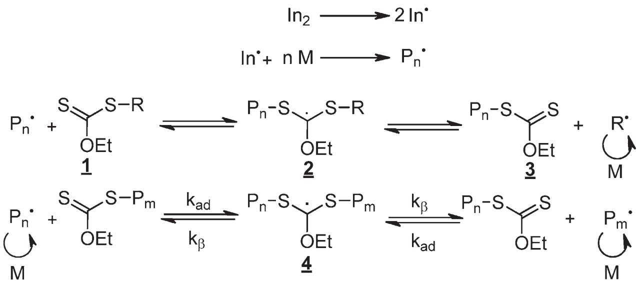


Scheme 16. ATRP of Various Monomers (Styrene, MMA, Methyl Acrylate, and Butyl Acrylate) from PVDF−CCl$_3$[112] **Obtained by Radical Telomerization of VDF with Chloroform**[142]

$$Cl_3C{-}H + n\,VDF \xrightarrow{\text{rad.}} Cl_3C{-}(VDF)_n{-}H \quad \underline{3}$$

$$\underline{3} + p\,M \xrightarrow{\text{CuCl, bipyrid.}} \text{PVDF-b-poly (M)} \quad \underline{4}$$

Scheme 17. Mechanism of Reversible Addition−Fragmentation Chain Transfer (RAFT)/Macromolecular Design through Interchange of Xanthate (MADIX)[a]



[a] In, M, Pn, and Pm represent the initiator, the monomer, and the polymers, respectively.

concerns 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.[95]

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[95] (Scheme 20).

The searched application for these copolymers was to supply original fuel cell membranes, after hydrolysis of SO_2F into SO_3X ($X = K$ or Na) and then into sulfonic acid. In this case, too, the nature of the end group and the contents of the different fluorinated units have also been assessed by NMR spectroscopy.

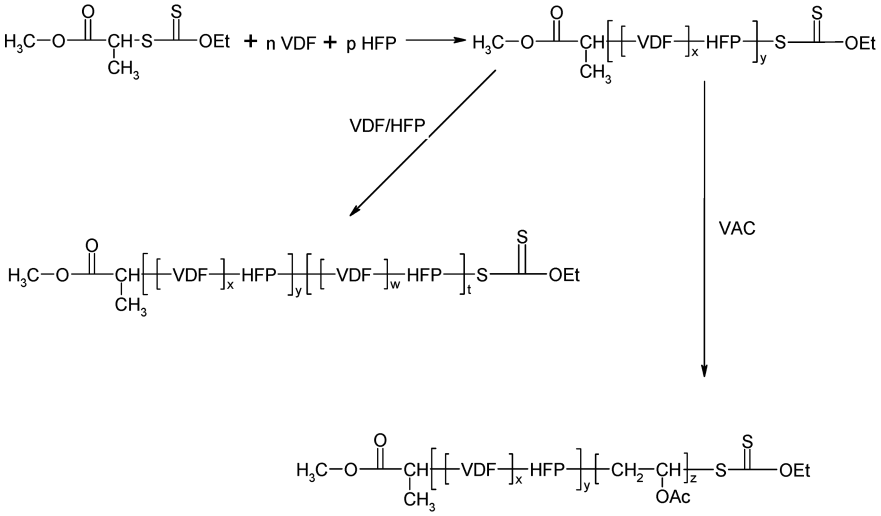
Another relevant application from block copolymers achieved by MADIX process deals with fluorosurfactants. Original poly(VDF-*co*-TFP)-*b*-oligo(vinyl acetate) or oligo(VAc)-*b*-poly(VDF-*co*-TFP) diblock copolymers (where TFP stands for 3,3,3-trifluoropropene) were synthesized[96] by the control of fluorinated xanthates (Scheme 21).

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, as novel surfactants.[96] Interestingly, low critical micellar concentrations and surface tensions (17 mN m^{-1} for 0.5% of copolymer) were achieved (Figure 5)[96b] almost as low as those of commercially available perfluorooctanoic acid (PFOA) or perfluorooctanesulfonic acid (PFOS) surfactants. Because they possess too stable C_7F_{15} or C_8F_{17} groups, both these latter species are regarded as persistent, toxic, bioaccumulable[145,146]—their half-lives are 5.4[147a] or 3.26[147b] years for human beings[147]—and even suspect to be mutagenic.

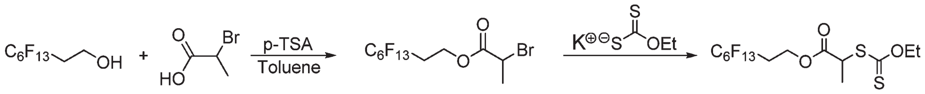
According to the [monomers]$_0$/[xanthate]$_0$ initial molar ratios, a wide range of surfactants[96] were obtained, the molar masses of which ranged from 600 to 5000 g mol^{-1}. Although the bioaccumulation has not been investigated yet, it can be advantageously assumed that the hydrophobic poly(VDF-*co*-TFP) block should be able to undergo metabolic or enzymatic decomposition arising from the methylene or methyne "weak" points of VDF or TFP (Scheme 22), and thus these original diblock co-oligomers are regarded as potential non-bioaccumulable surfactant alternatives to commercially available PFOA or PFOS.[145]

5.1.3. Conclusion. Several pathways to prepare fluorinated block copolymers are possible by sequential controlled radical copolymerizations such as (i) ATR copolymerization of (meth)acrylates or styrenes bearing fluorinated side chains or pentafluorostyrene while (ii) other strategies are possible for fluorinated alkenes or with various M monomers (especially styrene) that have already led to interesting fluoroblock-*b*-poly(M) or poly(M)-*b*-fluoroblock-*b*-poly(M) block copolymers. Three main techniques offer such well architectured copolymers based on F-alkenes: ITP, the use of borane, and Madix process for which the (co)polymerization requires xanthates; (iii) suitable cleavable C−X bonds can also be used in group or atom transfer.

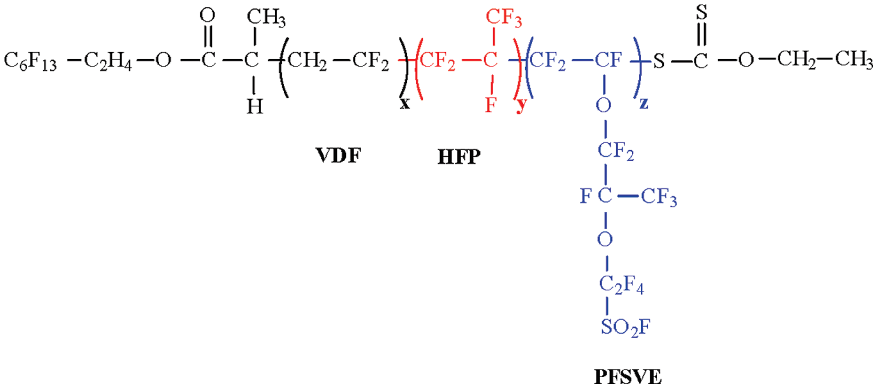
Scheme 18. Stepwise Copolymerization of Vinylidene Fluoride (VDF) and Hexafluoropropylene (HFP) and Vinyl Acetate (VAc) Controlled with a Xanthate



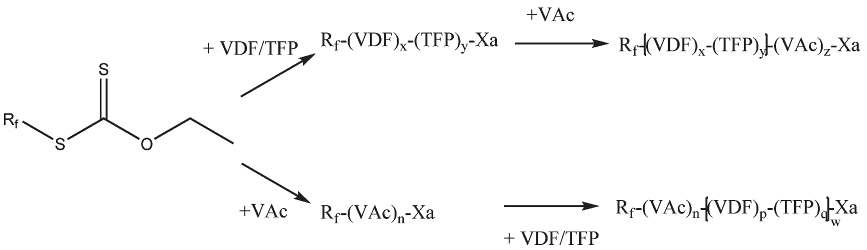
Scheme 19. Synthesis of Original Xanthate Containing a C_6F_{13} End Group



Scheme 20. Chemical Structure or Terpolymers Achieved from the Radical-Controlled Terpolymereization of Vinylidene Fluoride (VDF) with Hexafluoropropylene (HFP) and Perfluoro-4-methyl-3,6-dioxaoct-7-ene sulfonyl fluoride (PFSVE) Sulfonyl Fluoride in the Presence of a Fluorinated Xanthate



Scheme 21. Synthesis of Poly(VDF-*co*-TFP)-*b*-oligo(VAc) and Oligo(VAc)-*b*-poly(VDF-*co*-TFP) Diblock Oligomers[a]



[a] Xa, VDF, TFP, and VAc represent S−C(S)OEt, vinylidene fluoride, 3,3,3-trifluoropropene, and vinyl acetate, respectively.[96]

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, sulfonic acid-containing block copolymers are recently relevant candidates for fuel cell membranes. In addition, potential non-bioaccumulable fluorinated surfactants have already been achieved. Nevertheless, the nowadays trends show that there is an increasing interest in the controlled radical copolymerization of fluoroalkenes for high-performance materials. In addition, graft copolymers can also lead to interesting materials involved in high-tech areas and are summarized below.

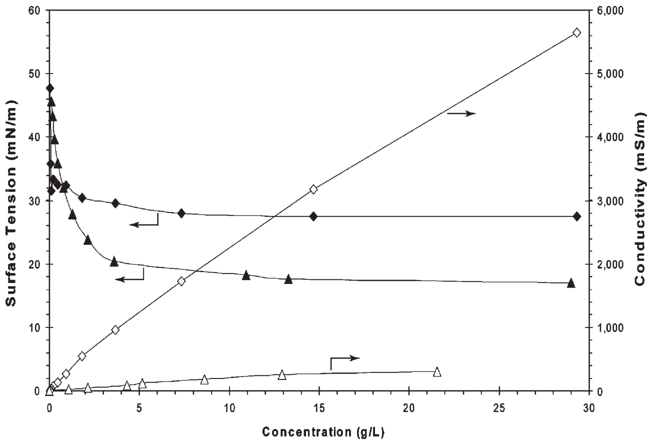
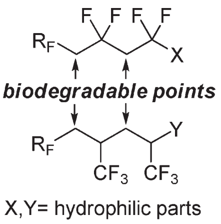


Figure 5. Surface tension and conductimetry curves of poly(VDF-*co*-TFP)-*b*-poly(VA) block co-oligomers (diamonds) compared to those of ammonium perfluorooctanoate (triangles). VDF, TFP, and VA stand for vinylidene fluoride, 3,3,3-trifluoropropene, and vinyl alcohol, respectively.

Scheme 22. Structures of Original Fluorosurfactants Based on Vinylidene or 3,3,3-Trifluoropropene Units That Contain Possible Degradable Points



5.2. Fluorinated Graft Copolymers. *5.2.1. Introduction.* Among various synthetic ways of fluorinated graft copolymers, the main strategies lie on (i) the direct (co)polymerization of macromonomers, (ii) the transfer to the polymer, (iii) from the 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 that seems the most appropriate pathway for such well-defined F-polymers.[4] Various investigations regarding the radiografting (produced by the polymerization of various monomers such as acrylates or styrenic monomers) onto activated fluoropolymers (PTFE, PCTFE, and PVDF) or copolymers (ETFE, FEP, PFA, poly(VDF-*co*-HFP), poly(VDF-*co*-TFE), and poly(VDF-*co*-TrFE) copolymers) have been achieved by many authors. These activations can be carried out by ozonization,[148] by high-energy technologies such as γ rays,[149] swift heavy ions,[150] electron beam (EB),[151] or plasma.[152]

The key methods of CRP have successfully been used for exploring new routes of fluorinated graft copolymers, and the driving force was to insert "controlling" groups as pendant groups or reversibly cleavable C$-$X bond in the polymeric backbone. To the best of our knowledge, nitroxide-mediated pseudoliving free radical polymerization (NMP),[153] reversible addition$-$fragmentation chain transfer (RAFT)[154] polymerization, and ATRP have been the most pertinent strategies to prepare them (Table 5).[153−168]

Another radical but noncontrolled route deals with the synthesis of a fluorinated copolymer bearing initiator (such as a peroxycarbonate) and of molecular weight of ca. 56 000 g mol^{-1} that is able to initiate the polymerization of fluoromonomers leading to side polymeric grafts.[169] This strategy is currently industrialized by Central Glass Co. which produces Cefral graft thermoplastic elastomers and well-characterized by NMR.[169b] Even blends made of such a copolymer with PVDF were attempted. Many other nonexhaustive methods of preparation of F-graft copolymers (Table 5) also exist such as the chemical modification of hydrocarbon polymers (polybutadiene, polyisoprene, PMMA, PDMS, polyphosphazene, polysulfone, poly(vinyl alcohol), etc.) by perfluoroalkyl groups or the radiografting of fluorinated (co)polymers. They have extensively been reported in a chapter of a book[170] and thus are not mentioned in this Perspective.

5.2.2. Fluoropolymers Bearing Tempo Side Groups for Nitroxide-Mediated Living Free Radical Polymerization (NMP). The first strategy deals with the synthesis of 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).[153] 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 obtained PVDF-*g*-PSSA copolymers were processed into membranes and were compared to those obtained from the conventional preirradiation grafting method. Interestingly, these membranes arising from the controlled grafting technique were 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 was ca. 30% and showed promising results in preliminary H_2/O_2 fuel cell tests. Indeed, the former one could be used in a fuel cell for 930 h at 70 °C without any drop in current density while the latter ones failed within 150$-$200 h under similar conditions.

5.2.3. Graft F-Copolymer from F-Backbone Bearing Dithioester Side Groups. Kang's team[154] also used that strategy from ozone-irradiated PVDF that could further react with 1-phenylethyl dithiobenzoate. These original PVDFs bearing various dithioester dangling groups enabled the controlled radical polymerization of poly(ethylene oxide) monomethacrylate, PEOMA,[154a] and acrylic acid, AAc,[154b] to obtain PVDF-*g*-PPEOMA and PVDF-*g*-PAAc (claiming "living PAAc graft chains on the surface") for the preparation of microfiltration membranes. Furthermore, the PVDF-*g*-PAAc membranes were 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.

5.2.4. Graft F-Copolymer from F-Backbone Bearing Azo Side Groups. Another process was investigated by Chen et al.,[155] who synthesized PVDF-*g*-PMMA and PVDF-*g*-PPEOMA graft copolymers from the polymerization of MMA and PEOMA at the PVDF surfaces claimed "controlled" by the authors since they noted a linear increase in the graft concentration of PMMA and PPEOMA with time. This is a bit controversial since the linear increase of the molar masses versus the monomer conversion was not reported. Nevertheless, the difficulty rose in the preparation of the macro-azoinitiator, from PVDF surfaces exposed first 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) with the surface hydroxyl groups.

5.2.5. ATRP Involving C$-$X Cleavage Born by the Fluorinated Backbone

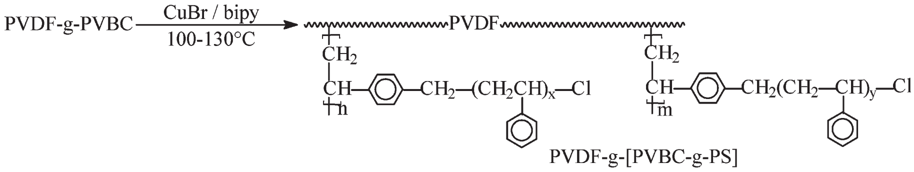
5.2.5.1. Introduction. The "grafting from" method based on the ATRP technique has also been widely used as an

Table 5. Overview of the Synthesis of Fluorinated Graft Copolymers Achieved from Radical Methods[a]

method	initiator, catalyst or chain transfer	structure of F-graft copolymers	reference
controlled			
NMP	PVDF bearing TEMPO side groups	PVDF-*g*-PSSA	153
RAFT			
	PVDF bearing dithioester groups	PVDF-*g*-PPEOMA	154a
		PVDF-*g*-PAAc	154b
-			
	PVDF bearing azo groups	PVDF-*g*-PPEOMA	155
		PVDF-*g*-PMMA	155
ATRP	PVDF	PVDF-*g*-PSSA	156, 157
	PVDF	PVDF-*g*-PDMAEMA	158, 159
	PVDF	PVDF-*g*-PSPMA	158
	PVDF-*g*-PVBC	PVDF-*g*-PVBC-*g*-PS	160
	poly(VDF-*co*-CTFE) copolymers	poly(VDF-*co*-CTFE)-*g*-PtBuA	161
	poly(VDF-*co*-CTFE) copolymers	poly(VDF-*co*-CTFE)-*g*-PS	161
	poly(VDF-*co*-CTFE) copolymers	poly(VDF-*co*-CTFE)-*g*-PSSA	162
	poly(VDF-*co*-CTFE) copolymers	poly(VDF-*co*-CTFE)-*g*-PSSA	144, 163
	poly(VDF-*co*-CTFE) copolymers	poly(VDF-*co*-CTFE)-*g*-PPEOMA	164
	poly(CTFE-*alt*-VE) copolymers	poly(CTFE-*alt*-VE)-*g*-PS ammonium	165
	poly(VDF-*co*-TrFE) copolymers	poly(VDF-*co*-TrFE)-*g*-P(*tert*-BuMA)	166
	poly(VDF-*co*-TrFE) copolymers	poly(VDF-*co*-TrFE)-*g*-PBuA	166
	poly(VDF-*co*-TrFE) copolymers	poly(VDF-*co*-TrFE)-*g*- PAAc salt	167
	poly(VDF-*co*-BDFO) copolymers	PVDF-*g*-PS	168
uncontrolled	poly(VDF-*co*-CTFE)-*g*-peroxycarbonate	poly(VDF-*co*-CTFE)-*g*-PVDF	169
	PVDF bearing azo groups	PVDF-*g*-PPEOMA	155
	PVDF bearing azo groups	PVDF-*g*-PMMA	155
radiografting	(FP)/irradiation	FP-*g*-PS; FP-*g*-PMMA	170

[a] BDFO, CTFE, DMAEMA, FP, PAAc, PAAc salt, PPEOMA, PSPMA, PSSA, PtBuA, PVBC, PVDF, S, TEMPO, TrFE, and VE stand for 8-bromo-1*H*,1*H*,2*H*-perfluorooct-1-ene, chlorotrifluoroethylene, (*N*,*N*-dimethylamino)ethyl methacrylate, fluoropolymer, poly(acylic acid), poly(acrylic acid) salt, poly(poly(ethylene oxide) methacrylate), poly(sulfopropyl methacrylate), poly(styrenesulfonic acid), poly(*tert*-butyl acrylate), poly(vinylbenzyl chloride) (or poly(chloromethylstyrene)), polyvinylidene fluoride, styrene, 2,2,6,6-tetramethylpiperidinyl-1-oxy, trifluoroethylene, and vinyl ether, respectively.

Scheme 23. ATRP of Styrene from PVDF-*g*-PVBC To Generate Controlled PVDF-*g*-[PVBC-*g*-PS] Graft Copolymers



efficient polymerization for preparing well-defined graft copolymers.[156−168] Several nonexhaustive examples of F-graft copolymers designed from the specific cleavage of C−X bond (where X represents a halogen) via ATRP are listed in Table 5. Indeed, various investigations dealing with ATRP to introduce polymeric grafts have been successfully achieved. These grafts are (i) PS (for further sulfonation into PSSA to process original polymer electrolyte membranes for fuel cells), (ii) poly(acrylic acid), (iii) poly(*tert*-butyl methacrylate) and poly(poly(ethylene oxide) methacrylate) (to make hydrophilic the fluoropolymer for various applications including ultrafiltration membranes), or (iv) poly(aryl) bearing ammonium functions (for membrane−electrode binders or solid alkaline fuel cells).

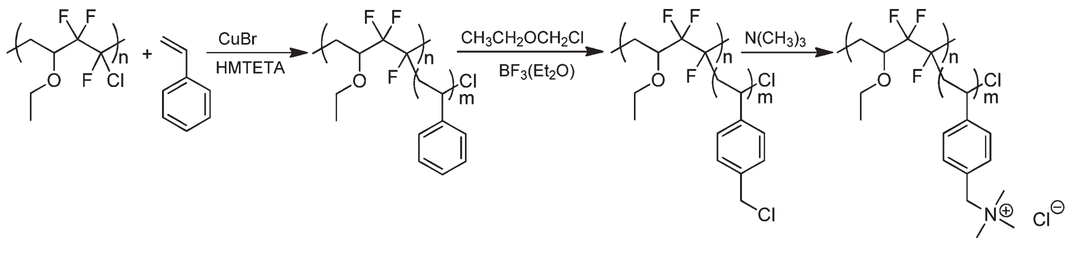
5.2.5.2. From C−Cl Cleavage by ATRP. Sundholm's group[160] performed the synthesis of PVDF-*g*-PVBC graft copolymers by irradiation of PVDF via electron beam followed by grafting vinyl benzyl chloride (VBC). In a subsequent step, these resulting PVDF-*g*-PVBC graft copolymers acted as suitable macroinitiators (via their chloromethyl side groups) in the ATRP of styrene involving copper bromide/bipyridine as the catalytic system leading to controlled PVDF-*g*-[PVBC-*g*-PS] graft copolymers (Scheme 23).

The degree of polystyrene grafting increased linearly versus time (which hence indicates a first-order kinetics) regardless of the polymerization temperature, leading to 400% after 3 h at 120 °C.[160] The driving force of this survey was the high degree of grafting obtained that could not be possible to achieve from conventional uncontrolled radiation-induced grafting methods because of the presence of termination reactions. The polystyrene grafts were further sulfonated, leading to PVDF-*g*-[PVBC-*g*-PSSA] graft copolymers for proton-exchange membranes for fuel cells (and the highest conductivity reached was 70 mS cm^{-1} at RT, 100% relative humidity).

In another approach, Zhang and Russell[161] prepared PVDF-*g*-PS and PVDF-*g*-PtBuA graft copolymers (where tBuA means *tert*-butyl acrylate) by ATRP of styrene or tBuA, respectively, from poly(VDF-*co*-CTFE) copolymers (Table 5). The resulting graft copolymers exhibit molecular weights up to 250 000 g mol^{-1}. Surprisingly, the authors claimed that the grafting was achieved from the cleavage of C−Cl bond of CTFE, though regarded as quite stable without any spectroscopic evidence.

Similarly, Koh et al.[164] synthesized poly(VDF-*co*-CTFE)-*g*-PPOEMA as an amphiphilic comb copolymer with hydrophobic poly(VDF-*co*-CTFE) backbone and hydrophilic PPOEMA side chains at 73:27 wt %. Microphase-separated poly(VDF-*co*-CTFE)-*g*-POEMA comb copolymer, evidenced by spectroscopic techniques and by TEM, led to nanocomposite films with *in situ* reduction of silver triflate precursor to silver nanoparticles under UV irradiation (with average size silver nanoparticles of 4−8 nm).

Scheme 24. Original Binders or Solid Alkaline Fuel Cell Membranes Processed from Graft Copolymers Achieved by ATRP of Styrene Initiated by Poly(chlorotrifluoroethylene-*alt*-vinyl ether) Alternated Copolymers[165] (after Cl$^-$/OH$^-$ anion exchange); HMTETA stands for 1,1,4,7,10,10-hexamethyltriethylene tetramine



Additionally, Kim's group[162] and then Holdcroft's[144,163] team synthesized proton conducting poly(VDF-*co*-CTFE)-*g*-PSSA graft copolymers in a similar "grafting from" method using an ATRP process. The first group characterized the microphase-separated structure of the polymer electrolyte membranes and showed that the ion exchange capacity (IEC), the water uptake, and the proton conductivity of the resulting membranes continuously increased with the increased of the PSSA content. However, the ^{1}H NMR spectra of poly(VDF-*co*-CTFE)-*g*-PSSNa graft copolymers were not convincing, the absence of both the SEC chromatograms and ^{19}F NMR spectra, and the noncontrolled evidence of the polymerization did not support the requirements of ATRP and satisfactory proofs of the resulting copolymers. After the chlorine dangling atoms were converted into azido group, these membranes were advantageously UV cross-linked which induced a reduced water uptake from 300% to 83% in addition to better mechanical properties. However, these advantages contrast a bit with conductivity values that slightly decreased from 0.074 to 0.068 S cm^{-1} at room temperature under 95% relative humidity.

In addition, Holdcroft's team[144,163] synthesized graft PVDF-*g*-PSSA and block poly(VDF-*co*-HFP)-*b*-PSSA copolymers of different molecular and equivalent weights and investigated the influence of both architectures onto the electrochemical properties of the resulting membranes. Different morphologies (well identified by TEM) between both structures play a major role for the understanding of swelling, conductivities, and effective proton mobility through the membrane versus IEC. These authors noted that the membranes made from the graft copolymer possessed a significant higher percolation threshold than those arising from the diblock copolymer (ca. 1.0−1.2 and 0.6 mmol g^{-1} for grafts and for diblocks, respectively). This statement also correlates with water uptakes. These authors noted that (i) the "in-plane" proton conductivity of the diblock membranes was ca. 2.4 times greater than "through-plane" conductivity which indicates a mild degree of anisotropy; (ii) in contrast, the graft membranes had very similar "in-plane" and "through-plane" proton conductivity (for an anisotropy of 0.95) compared to that of Nafion112 membrane of ca. 1.4.

The same group[163] confirmed the importance of polymer microstructure's role on the morphology of membranes, the size of ionic clusters and their ionic purity, water sorption, and the proton conductivity from a series of proton exchange membranes obtained from partially sulfonated poly(VDF-*co*-CTFE)-*g*-polystyrene (the degrees of polymerization were 35, 88, and 154 units per graft). A disordered phase-separated morphology comprised of small interconnected ionic clusters varying from 2 to 4 nm in size was obtained. For a given IEC, membranes prepared from the short graft chain series possessed larger ionic domains due to their relatively higher degree of sulfonation (DS), which facilitates ion clustering. For high IEC membranes (ca. 2.50 mmol/g), the short grafts remained water-insoluble, absorbed less water, and afforded higher conductivity than longer graft analogues.

More recently, original cationic fluorinated graft polymers were synthesized by ATRP of styrene from alternating poly(chlorotrifluoroethylene-*alt*-ethyl vinyl ether) copolymers as the macroinitiator[165] (Scheme 24). Then, produced PS grafts in the resulting poly(CTFE-*alt*-vinyl ether)-*g*-polystyrene copolymers were chloromethylated before an amination occurred to generate original potential membrane/electrodes binders or membranes for alkaline fuel cells[171] (after Cl$^-$/OH$^-$ exchange of the counteranion, the conductivities of the films reached 1 mS cm^{-1}).

5.2.5.3. From C−Br Cleavage by ATRP. To our knowledge, only one survey[168] reports the preparation of graft copolymers from an initiator that contains C−Br cleavable bonds. Actually, poly(VDF-*co*-BDFO) copolymers, synthesized by conventional radical copolymerization of VDF with 4-bromo-3,3,4,4-tetrafluorobut-1-ene (BDFO),[172] act as efficient initiators that bear $C_6F_{12}Br$ side groups to obtain PVDF-*g*-PS graft copolymers achieved by ATRP of styrene. Interestingly, the linear molar masses of the produced PVDF-*g*-PS graft copolymers versus the styrene conversion relationship (Figure 6) and narrow polydispersity indices (starting from 2.1 for poly(VDF-*co*-BDFO) random copolymers) evidenced a controlled behavior of that graft copolymerization.[168]

5.2.5.4. From the C−F Cleavage by ATRP. Though C−F bond is quite stable (ca. 486 kJ mol^{-1}), ATRP of methacrylates was reported by a group at MIT to be surprisingly successful from the cleavage of the C−F bond in PVDF to produce PVDF-*g*-poly(methacrylates)[156] graft copolymers. This was claimed by the authors without significant spectroscopic evidence. Indeed, if that grafting occurs, it can be anticipated that it arises rather from the cleavage of the less stable C−H in methylene and not in the more stable C−F bond of difluoromethylene site of VDF as reported by these authors. This weaker C−H bond is known to induce a poorer chemical resistance of PVDF than that of perfluoropolymers (e.g., PFTE, FEP, MFA, or PFA) (for example, the acidic hydrogen atoms along the chain are reactive in strongly basic media, leading to the formation of fluoride salt byproducts).[1−6]

From a similar process, these authors[157] also reported the synthesis of PVDF-*g*-PPEOMA graft copolymers by ATRP of PEOMA from PVDF. Although this preparation is quite surprising for the same above 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[158] which synthesized PVDF-*g*-PSSA and PVDF-*g*-poly(sulfopropyl methacrylate) graft copolymers with maximum degrees of grafting of 25 and 35 wt %, respectively. The IEC values, water uptakes, and proton conductivities were 0.45 and 0.63 mequiv g^{-1}, 33.4 and

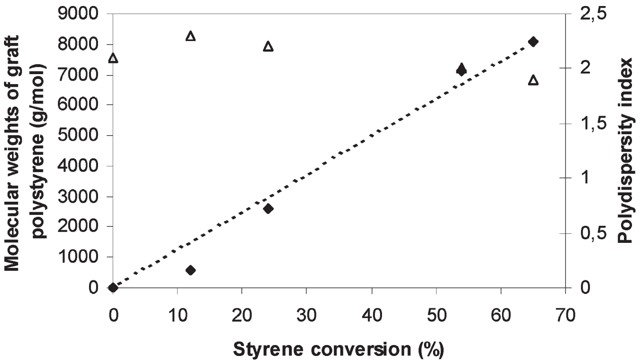


Figure 6. Dependence of molecular weight (◆) and polydispersity index (Δ) of PVDF-*g*-PS copolymer versus styrene conversion for the ATRP of styrene from poly(VDF-*co*-BDFO) copolymers as the macroinitiator. $[DMF]_0$:$[styrene]_0$:$[macroinitiator]_0$:$[HMTETA]_0$:$[Cu^{I}Br]_0$ = 500:100:10:0.5:0.5; 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 from ref 168.

46.8 wt %, and 0.007 and 0.015 mS cm^{-1}, respectively. However, as in the above studies, neither the ^{19}F NMR spectra nor the SEC chromatograms were provided while the ^{1}H NMR spectra were not convincing (from the intense signals assigned to the high amount of solvent(s) and an unexpected broad signal was observed instead of characteristic quintet centered at 2.9 ppm, assigned to methylene groups of VDF).

Nandi's group[159] also used ATRP of (*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) in the presence of PVDF as the initiator to synthesize PVDF-*g*-PDMAEMA graft copolymers (Table 5) with increasing graft density versus increasing polymerization times (though claiming that the graft lengths were similar).

Nevertheless, this above strategy was pioneered by Chen et al.[166] and more recently revisited by Takahara's group,[167] who synthesized poly(VDF-*co*-TrFE)-*g*-poly(*tert*-BuMA),[166] poly(VDF-*co*-TrFE)-*g*-poly(acrylic acid sodium salt),[167a] and PVDF-*g*-poly(butyl acrylate)[167b] graft copolymers, respectively. As above, the absence of spectroscopic proofs is required to ensure a suitable grafting though recent NMR characterizations are under investigation.[173]

6. Properties of Fluoropolymers Achieved by Controlled Radical (Co)polymerization

Commercial applications of controlled fluoropolymers reflect their special combination of properties:[1−5] excellent resistance to heat, fluids, oxidizing media combined with good physical properties such as energy-consuming industries, military aircraft, and petrochemical industries that require fluoropolymers for sealants, gaskets, O-rings, and lining resistant to corrosive materials. For example, aerospace propellant systems often utilize very aggresive fuels and oxidizers, which are incompatible with all currently available (co)polymers. Thus, specific designed fluoropolymers are often used in these systems due to their oxidative stability and compatibility with both oxidizers and hydrazine-type fuels. They become the most suitable materials for use in semiconductor processing equipment. In such applications, these well-designed F-(co)polymers come in direct contact with dry process chemicals and reactive plasmas. In addition, the (co)polymer is typically exposed to aggressive wet chemical environments such as sulfuric acid/hydrogen peroxide or ammonium hydroxide/hydrogen peroxide/ultrapure deionized water mixtures and offer the best resistance in such media.

Many strategies enabled to synthesize well-designed fluorinated polymers or copolymers by controlled radical (co)polymerization. Such well-architectured copolymers can find many applications, and at least eight main types can be distinguished:

(i) For thermoplastic elastomers involved in seals, gaskets, and O-rings applications, Dai-el and Tecnoflon[106−109] are commercially available products marketed by Daikin and Solvay Solexis, exhibiting block structures. They 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_gs and T_ms. Various strategies applied by different companies have already led to commercially available block copolymers, regarded as the first ones produced by CRP on an industrial scale. However, lowering their T_gs is still a challenge, which is inherent to the T_g of the elastomeric block always higher than −33 °C (although the 3M[174] and Solvay-Solexis[72] companies have recently produced original statistic cross-linkable terpolymers endowed with T_g values below −40 °C).

(ii) For surfactant applications, though a few designed molecules have already been obtained, it is expected that more and more compounds containing a hydrogenofluorinated block will be synthesized since key weak points can be interestingly inserted to enable a cleavage or a possible metabolized or enzymatically degradation: for example, the methylene groups of VDF units in the oligo(VDF) groups or the methylene or methyne groups in TFP units of oligo(TFP) telomers. Hence, fluorinated surfactants based on VDF or 3,3,3-trifluoropropene (TFP) can lead to potentially non-bioaccumulable products as useful alternatives to PFOA and PFOS surfactants.[145,146]

(iii) In the field of membranes, various approaches have led to different types of membranes from block or graft copolymers (mainly for microfiltration[154,155] (for water purification) or for fuel cell (for clean sources of energy)). Regarding the latter application, Xu et al.[175] noted that the conductivities of the block copolymers are considerably higher than those of the random copolymers of sulfonated polystyrene possessing similar IECs and more chemically stable than those obtained from preirradiated PVDF or poly(VDF-*co*-HFP) copolymers followed by grafting PS (which is further sulfonated into PSSA). However, under NMP of styrene from irradiated PVDF membranes quenched with TEMPO, better electrochemical properties[153] and thermal stabilities were noted. Additionally, Holdcroft's team[144,163] compared the electrochemical properties of the membranes processed from poly(VDF-*co*-HFP)-*b*-PSSA block and poly(VDF-*co*-CTFE)-*g*-PSSA graft copolymers, and they noted that the "grafted membranes" possess a significant higher percolation threshold than the "diblock membranes" (this statement correlates with water uptake values). This is in good agreement with specific micro- or nanostructures such as lamellae or, better, in gyroids as reported by Liebler.[176] Interesting results were also obtained by Chung's group[91,92] via the original CRP procedure involving boron species.

(iv) For rechargeable lithium ion batteries, quite a few works have been proposed, besides Liu et al.,[177] who prepared nanoporous membranes from PVDF-*g*-PPEOMA graft copolymers endowed with satisfactory electrochemical properties or other graft PVDF-based copolymers[178] for polymer electrolytes.

(v) For coatings, especially protective metal coatings, block copolymers have brought satisfactory solutions.[136]

(vi) For optical storage devices.[15]

(vii) For medical and dental items.[16]

(viii) For piezoelectrical devices[179] from original 1-iodohydrogenofluoroalkyl or 1-iodo-1*H*,1*H*,2*H*,2*H*-hydrogenofluoropolymers.

Other applications concern the compatibilizers for polymer alloys which comprise a hydrocarbon polymer and a fluorine-containing polymer, a dispersant for fluorine-containing paints, a carrier for electrophotography, and an electrostatic charge adjusting or fusion preventing agent for toner particles. Further, blends of fluoropolymers with other polymers nanocomposites and recyclability features will also contribute to their continuing success in many engineering and aggressive service environments.

7. Outlook and Challenges

Fluoropolymers are niche macromolecules with a few volume productions. However, they have remarkable properties, and these high-value-added materials can be used for many high-tech applications. Most fluorinated monomers can be polymerized under radical conditions, and classical processes that enable the controlled radical polymerization (CRP) of hydrocarbon monomers can be well adapted for that of fluoromonomers.

Actually, the nature of the fluoromonomers seems to play a major role for the appropriate process to use: (i) Styrenic monomers or (meth)acrylates bearing a fluorinated side group have successfully been polymerized via NMP, ATRP, or RAFT procedures. For the former monomers, although many investigations have been carried out on the CRP of pentafluorostyrene,[15] to date, the literature does not report any survey dealing with the CRP of styrenic derivatives containing a fluorine atom or a C_nF_{2n+1} group born by the ethylenic carbon atoms. This contrasts with those involving α-fluoroacrylate[49] or α-trifluoromethacrylic monomer[87] (though this latter does not homopolymerize,[180] it copolymerizes with VDF (and with VDF and HFP) under ITP process[87,88]). In addition, ATR copolymerization of 1*H*,1*H*,2*H*-perfluorooct-1-ene with methyl acrylate[67] is an interesting route to insert 1*H*,1*H*,2*H*-perfluorooct-1-ene that is difficult to polymerize. (ii) Different strategies of CRP are more appropriate for fluorinated alkenes (or for the copolymerization of various monomers). CRP of fluoroalkenes has been investigated by both industries and academia, and successful attempts involved iodine transfer polymerization (ITP)[29,59,60] (that was pioneered in the late 1970s at the Daikin Co.[29]), macromolecular design through interchange of xanthate[33,34] (MADIX) (for which a few examples have been supplied for the radical polymerization of various halogenated comonomers[93−96]), and the control by boron species.[37,91,92]

However, limitation of several processes may affect the development of such opportunities: NMP process requires alkoxyamines that are expensive and ATRP involves copper salts that are difficult to eliminate, while RAFT or MADIX systems led to polymers containing sulfur atoms that induce nasty odors and sometimes pink color. Yet, ITP seems quite interesting, and this may be the reason why since early 1980s Daiel products have been commercially available by Daikin Co. However, this company claims producing F-copolymers that can reach molar masses up to 10^6 g mol^{-1}, but the CRP of unsymmetrical fluoroolefin (such as VDF[56,60b]) indicates that defects of VDF chaining occurs as soon as 12−15 VDF units have been incorporated,[56] thus possibly limiting the reactivation of $-CF_2CH_2-I$ and making broader the polydispersities. Hence, some chemical engineering improvement (temperatures, shape of autoclave, uses of specific initiator or solvent/water) may overcome that disadvantage to get a better process of the CRP of these gaseous fluoroalkenes.

Moreover, various original well-designed architectures of these fluoropolymers have been produced. Among them, and besides alternating copolymers, three categories can be proposed: (i) block copolymers are prepared under controlled radical polymerization methods (NMP, ATRP, RAFT for styrenic or (meth)acrylates, while for F-alkenes, fluoropolymers bearing a C−X bond act as original initiators especially in halogen transfer radical polymerization (X stands for a chlorine, bromine, and an iodine atom); (ii) graft copolymers can be achieved from direct co- (or ter-) polymerization or from the polymerization of monomers in the presence of macroinitiators containing key groups (TEMPO, dithioesters, and also cleavable C−X bond); (iii) telechelics diiodoperfluoroalkanes obtained from the iodine transfer (co)polymerization of fluoroalkenes in the presence of appropriate diiodo chain transfer agents.[80] In these cases, too, the resulting fluorocopolymers have found numerous applications: for example, thermoplastics, elastomers, or thermoplastic elastomers[106−109] for aerospace, aeronautics, and automotive industries (e.g., elastomeric sealants, O-rings, gaskets which are resistant to low and high temperature, in aggressive media and in the solvents of aeronautics), microfiltration and ultrafiltration membranes, blends, and composites (even in the presence of nanofillers). Others explore the growing interest of new materials for energy (fuel cell membranes, lithium ion batteries, piezoelectrical devices, and actuators). Surprisingly, well-designed copolymers for alkaline fuel cell membranes or binders[171] have never been reported yet, and as for proton exchange membranes, it would be interesting to find out if any controlled architecture brings an added value. In that case, the resulting copolymer must be resistant to basic media. These materials required for such an emerging application will probably be prepared soon.

It is expected that new fluoropolymeric materials and new curing chemistry[5,6,134] will be developed in the future due to continued escalation at severe service conditions, improvements in broad temperature damping characteristics, and low - temperature resilience.

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

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