

## Recent advances in the controlled radical (co) polymerization of fluoroalkenes and applications therefrom



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### ABSTRACT

Since late 1970s, extensive studies on controlled (or *pseudoliving*) radical polymerizations (CRP) have been reported, especially from mid-1990s. Though many works have been investigated, the unexpected scientific growth of CRP contrasts with few commercially available products derived from these techniques. But, for fluoropolymers, the situation appears reversed since iodine transfer polymerization of fluoroalkenes already yielded commercially available thermoplastic elastomers as soon as 1984. These proceedings display a brief overview of CRP of fluorinated monomers (with a real challenge for gaseous fluoroalkenes such as vinylidene fluoride, chlorotrifluoroethylene, 3,3,3-trifluoropropene, hexafluoroisopropylene, perfluoromethyl vinyl ether). These monomers can be (co)polymerized via the iodine transfer polymerization or from techniques that involve either borinates or xanthates (named MADIX). These technologies enable one to generate copolymers that exhibit well-defined architectures, such as telechelic, block and graft copolymers and open up *High Tech* applications such as potentially non-bioaccumulable surfactants, elastomers endowed with low  $T_g$ s and that can be crosslinked, thermoplastic elastomers which can be used in a wide range of temperatures, fuel cell membranes being processed either by casting or by reactive extrusion.

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## 1. Introduction

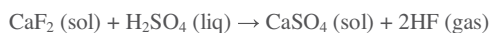
Fluorinated (co)polymers [1–5] are remarkable niche specialty macromolecules because of (i) their unique combination of exceptional properties (mainly linked to the low polarisability, the strong electronegativity, and the small Van der Waals radius (1.32 Å) of the fluorine atom, and to the strong C–F bond (that bond energy dissociation worths 485 kJ/mol) and (ii) their wide variety of morphologies that range from plastomeric, elastomeric, thermoplastic, to thermoplastic elastomeric, so that they can have a semi crystalline or totally amorphous structure. Hence, fluoropolymers that contain a high fluorine contents in the polymeric backbone display high thermal, chemical, aging and weather resistances, unique inertness to solvents, hydrocarbons, acids, and to alkalies, and exhibit low flammability, refractive index, dielectric constants, and low moisture absorption while polymers bearing a perfluorinated dangling group exhibit surface

energy (oil and water repellency). Furthermore, the strong C–F bond provokes a crucial effect on the improvements of resistances to oxidation and hydrolytic decompositions.

Most fluorochemicals arise from calcium fluoride (also called fluor spar, fluorite, or fluor mineralis) [6]. Major resources are located in South Africa, China, and Mexico [6]. Addition of sulfuric acid onto that mineral leads to acid fluoride (Scheme 1) that further enables fluorination or various (chlorinated) intermediates to get fluorocompounds.

For all such exceptional properties above, these specialty macromolecules [1–5] have found many applications in High Technologies areas: automotive industries (ca. 300 g of fluoropolymers per car) fluids for transmission [5] and in components of fuel cells and lithium ions batteries, 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 [5,6]), petrochemical (pipes and coatings as liners), microelectronics, chemical engineering (high performance membranes [7]), textile treatment, building (paints and coatings resistant to UV and to graffiti and stone protection, especially coatings of old monuments for the Cultural Heritage [8]), and

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**Scheme 1.** Preparation of acid fluoride from calcium fluoride.

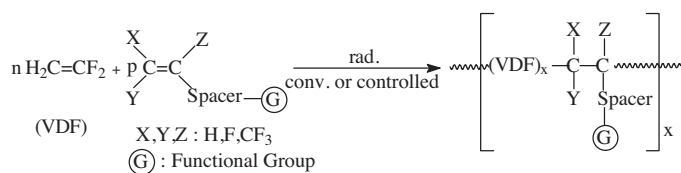
optics (core and cladding of optical fibers [9]). In spite of their high price (related to the cost of the small scale of fabrication, the purification and production of the gaseous monomers, and to unusual processes of polymerization, such as in suspension or dispersion with specific surfactants or emulsifiers), these polymers have known major developments in modern “high-tech” technologies.

As a matter of fact, fluorinated homopolymers may display various limitations: (i) high crystallinity (PTFE is *ca.* 95% crystalline) thus induces a poor solubility in common organic solvents, and (ii) difficult curing or crosslinking. [10] Thus, a further generation of fluorinated macromolecules, copolymers [4,5,10–12], has been extensively developed from the 1950–1960s without displaying such homopolymers’ disadvantages. Actually, these copolymers are based on a mixture of various comonomers that insert side chains or bulky groups (which further induce a certain disorder in the macromolecule) enabling to decrease or suppress the high crystallinity of the homopolymer. According to the function brought by the functional comonomer, the resulting copolymers (Scheme 2) exhibit various challenging properties and thus can find valuable applications in specific areas.

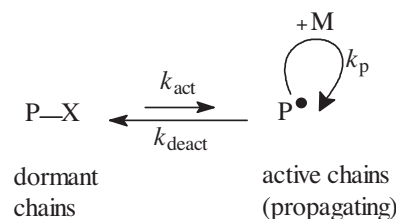
Fluoropolymers based on fluoroalkenes are synthesized from conventional radical methods of polymerization [1–6] and a few strategies of controlled radical polymerization (CRP) have successfully been applied on fluoroalkenes [13]. Actually, CRP has undergone a growing development [14] as a useful tool to precisely predict the molar masses and to control polymeric structures, as well as getting narrow polydispersities. This arises from the nature of the (macro)radicals (that have very short life times), the fast equilibrium between living macroradicals and dormant chains (Scheme 3), and to avoid termination and transfer reactions in certain conditions. Many books and reviews have reported and summarized the exceptional and inventive development of modern techniques of CRP of monomers.

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

Though many basic studies have been reported, industrial realizations have already demonstrated that such a technique is also relevant for the productions of adhesives, dispersants, lubricants, high-performance elastomers, *etc.*, and can also find much interest in novel electrical [15], optical [16], and biomedical materials [17]. More than 13,000 papers have been published on CRP over the last 20 years, and the industrial interest is based on an anticipated \$20 billion/year market for materials achieved by CRP [18]. Nowadays, fluorinated thermoplastic elastomers, based on Hard-*b*-Soft-*b*-Hard triblock copolymers, still involved in electronics, aerospace, automotive industries and medical applications [19,20], are currently produced at the industrial scale, linked by the



**Scheme 2.** Radical copolymerization of vinylidene fluoride (VDF) with fluoro-functional comonomers (where G stands for  $\text{SO}_3\text{H}$ ,  $\text{P}(\text{O})(\text{OEt})_2$ , Br,  $\text{CO}_2\text{H}$ , oligo(ethylene oxide),  $\text{Si}(\text{OEt})_3$ ,  $\text{NR}_3^+$ ) [12].



**Scheme 3.** Fast equilibrium between active macroradicals and dormant chains in the controlled radical (co)polymerization.

fascinating discovery in the late 1970s by Tatemoto working at the Daikin company [21].

Hence, it was of interest to supply more recent results on those achieved from controlled radical polymerization and this proceeding article first briefly summarizes the different strategies of CRP, then a summary of surveys on CRP of fluorinated alkenes will be briefly mentioned, taking into account that a more exhaustive review on CRP of fluorinated monomers (including styrenic and (meth)acrylic ones) was published four years ago [13]. Finally, applications of such well-designed (co)polymers will be supplied.

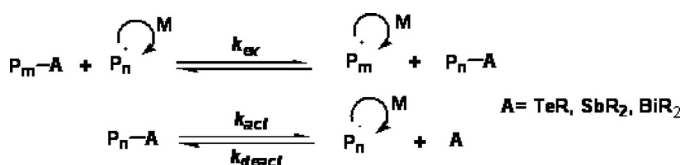
## 2. Strategies of controlled radical (co)polymerization

Since the mid-1990s, the international research activity in the field of controlled (or *pseudoliving*) radical polymerization (LRP) has considerably grown [14]. The general principle of the methods reported so far is based on a fast reversible activation-deactivation equilibrium between dormant chains (or dead chains) and active chains (or propagating radicals), as in Scheme 3.

Many textbooks and reviews (few of them are supplied below) have well summarized. One of the oldest techniques, iodine transfer (co)polymerization, was pioneered by Tatemoto [21], and was first applied on fluoroalkenes. It was followed by the iniferter method [22] (where iniferter means INITiation-transFER-TERmination) introduced by Otsu in 1982. Then, more recent ones have been reported and reviewed such as nitroxide-mediated radical polymerization (NMP) [23], atom transfer radical polymerization (ATRP) [24], reversed iodine transfer polymerization [25], reversible addition-fragmentation chain transfer (RAFT) [26] including macromolecular design *via* interchange of xanthates (MADIX) [27], organoheteroatom mediated radical polymerization [28,29] involving Tellurium (TERP), Bismuth, Antimony derivatives developed by Yamago [28] (Scheme 4), or Cobalt mediated radical polymerization (CRMP) in the presence of bis(acetylacetonato)-cobalt(II) ( $\text{Co}(\text{acac})_2$ ) [29]. In addition, CRP controlled by borinate derivatives under a recombination process from Chung [30], and more recent methods developed by Goto *et al.* [31] have already shown a great interest, briefly summarized in Scheme 5.

Though fluorinated alkenes have been involved in radical polymerization controlled by boron derivatives, [30] to the best of our knowledge, no study on TERP or CRMP have been attempted on fluoromonomers.

As known, CRP tends to avoid any termination reactions, though, as expected classical recombination/disproportionation



**Scheme 4.** Radical polymerizations mediated by tellurium, antimony and bismuth derivatives [28].

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