

**USE OF FLUORINATED ORGANIC COMPOUNDS  
IN LIVING RADICAL POLYMERIZATIONS**Patrick LACROIX-DESMAZES<sup>1</sup>, Bruno AMÉDURI<sup>2</sup> and Bernard BOUTEVIN<sup>3,\*</sup>

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*Dedicated to the memory of Professor Miloš Hudlický.*

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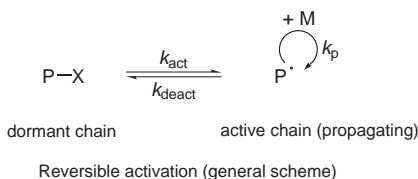
Controlled/living radical polymerization (LRP) is a field of special interest because it allows tailoring well-defined macromolecular architectures such as telechelic, block, graft or star copolymers. Since the eighties, several techniques have been reported [such as the iniferter method, nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP), iodine transfer polymerization (ITP), and reversible addition-fragmentation chain transfer (RAFT)] giving rise to a huge number of publications and patents. This review aims at illustrating the contribution of fluorinated organic compounds in this area of research through the use of fluorinated initiators (dithiocarbamates, xanthates, tetraphenylethanes, alkoxyamines, fluorinated alkyl halides, and dithioesters) or other fluorinated molecules (ligands, solvents). Another point depicts the LRP of various fluorinated monomers (methacrylates, acrylates, styrenics, and alkenes). Finally, fluorinated block and graft copolymers prepared by LRP have been reported. A review with 165 references.

**Keywords:** Fluorinated compounds; Living free radical polymerization; Iniferter; Nitroxide; Atom transfer radical polymerization; Iodine transfer polymerization; Reversible addition-fragmentation chain transfer; Fluoromonomers; Fluorinated polymers.

## 1. INTRODUCTION

Since the eighties, the international research activity in the field of controlled/living radical polymerization (LRP) has grown to a considerable extent<sup>1,2</sup>. 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 (propagating radicals), as shown in Scheme 1.

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



## SCHEME 1

General principle of living radical polymerization

nient radical polymerizations. The most popular techniques are the iniferter method<sup>3-7</sup> (where iniferter stands for INITiation-transFER-TERmination), nitroxide-mediated radical polymerization (NMP)<sup>8-11</sup>, atom transfer radical polymerization (ATRP)<sup>12-14</sup>, iodine transfer polymerization (ITP)<sup>15</sup>, and reversible addition-fragmentation chain transfer (RAFT)<sup>16-20</sup>, whose specific mechanisms are briefly summarized in Scheme 2<sup>21,22</sup>.

Fluorinated organic compounds have sometimes been used in living radical polymerization 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. This review aims at illustrating the contribution of fluorinated organic compounds in this area of research through the use of fluorinated initiators, fluorinated ligands, and fluorinated solvents. Another point depicts the LRP of various fluorinated monomers (styrenics, methacrylates, acrylates, and alkenes). Finally, fluorinated block and graft copolymers prepared by LRP are reported.

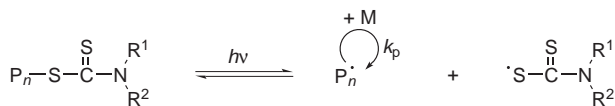
## 2. FLUORINATED MOLECULES INVOLVED IN LIVING RADICAL POLYMERIZATION (LRP)

### 2.1. Fluorinated Initiators

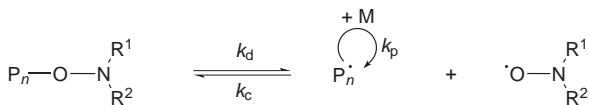
#### 2.1.1. Fluorinated Iniferters (*Dithiocarbamates, Xanthates, Tetraphenylethanes*)

Fluorinated dithiocarbamates **1** and **2** were synthesized and proved to be efficient as iniferters in the bulk photopolymerization of styrene<sup>23</sup> (Fig. 1).

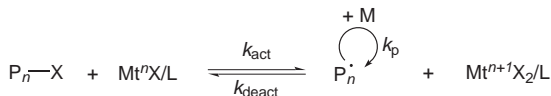
This behavior is in contrast with the results of Doi *et al.*<sup>24</sup> who have shown that a non-fluorinated dithiocarbamate homologue, butyl *N,N*-diethylthiocarbamate, was not able to control the photopolymerization of styrene because of a very slow photodissociation. These results indicate the beneficial role of the electron-withdrawing fluorine atoms on the ability of



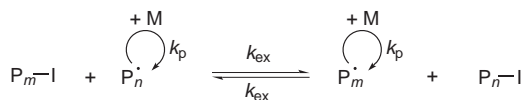
(a) Photo-iniferter method



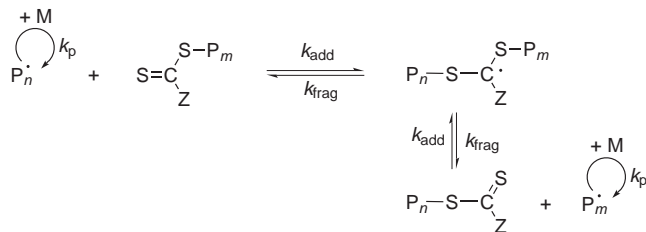
(b) Nitroxide-mediated radical polymerization (NMP)



(c) Atom transfer radical polymerization (ATRP)



(d) Iodine transfer radical polymerization (ITP)



(e) Reversible addition-fragmentation chain transfer process (RAFT)

## SCHEME 2

Specific mechanisms of the iniferter method, NMP, ATRP, ITP, and RAFT (M: monomer;  $P_n$ : propagating polymer of degree of polymerization  $n$ ;  $R^1$ ,  $R^2$ : alkyl substituents; Mt: metal; X: halogen or pseudohalogen; L: ligand; Z: alkyl or aryl substituent of dithioester species, alkoxy substituent of xanthate species or thioalkyl substituent of trithiocarbonate species)

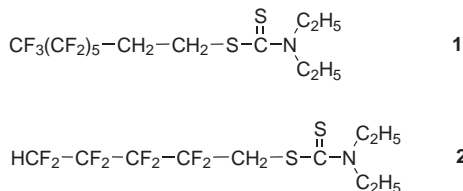


FIG. 1  
Structures of fluorinated dithiocarbamates **1** and **2**

such photo-iniferters to dissociate under UV irradiation. Moreover, in the case of **2**, kinetic analysis by  $^{19}\text{F}$  NMR showed the disappearance of the peak of the iniferter ( $\text{HCF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-}$ ) centered at  $-111.5$  ppm and the presence of a new peak at  $-113.9$  ppm which can be assigned to the polystyrene adduct. So, fluorine atoms in the  $\beta$  position in **2** could serve as a useful  $^{19}\text{F}$  NMR probe in order to determine the kinetics of initiation for the photo-polymerization of styrene or other monomers in the presence of such iniferters. Interestingly, fluorinated xanthate **3** was not able to control the photo-polymerization of styrene under similar conditions (Fig. 2).



FIG. 2  
Structure of fluorinated xanthate **3**

Tetraphenylethanes are another class of iniferters (activated by thermal activation)<sup>7,25</sup>. Fluorinated tetraphenylethane derivative **4** was used in the thermal polymerization of 2,2,2-trifluoroethyl methacrylate to yield telechelic ( $\alpha,\omega$ -difunctional) oligomers which could serve as an efficient macroinitiator to prepare block copolymers<sup>26</sup> (Fig. 3). As above, the fluorinated substituents were useful in the characterization of the polymer chain ends by  $^{19}\text{F}$  NMR.

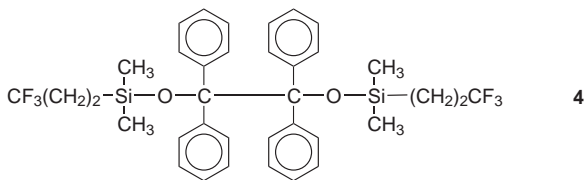


FIG. 3  
Structure of fluorinated tetraphenylethane-type iniferter **4**

### 2.1.2. Fluorinated Alkoxyamines and Nitroxides (for NMP)

#### 2.1.2.1. Fluorinated Alkoxyamines

Alkoxyamines are often synthesized by atom transfer radical addition<sup>27</sup>. Interestingly, alkoxyamine **5** (Fig. 4) was prepared by taking advantage of the lability of the carbon-iodine bond under UV irradiation<sup>28</sup> to generate a carbon-centered radical which could be trapped by nitroxide radical in order to form the desired alkoxyamine<sup>23</sup> (Scheme 3). Copper metal was intro-

duced to react with free iodine. Lastly, heptane was chosen as solvent to induce precipitation of CuI so that the alkoxyamine can be isolated by simple filtration and evaporation of the solvent.

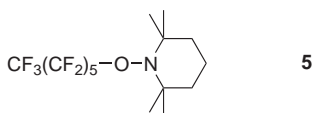
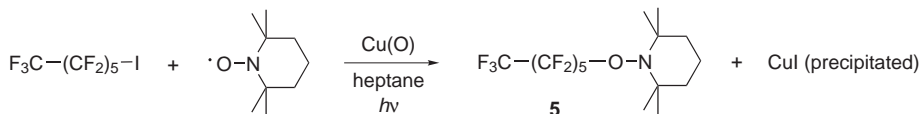


FIG. 4  
Structure of alkoxyamine 5



SCHEME 3  
Synthetic route for alkoxyamine 5

Fluorinated alkoxyamine **5** was tested in bulk polymerization of styrene at 140 °C, but showed a very low initiator efficiency. This is consistent with the behavior of the non-fluorinated homologue alkoxyamine (hexyl-TEMPO) which was shown not to dissociate below 180 °C<sup>29</sup>. However, the effect of fluorine atoms on the stability of this alkoxyamine was not elucidated. The possible strength of the C–O bond, by analogy with other alkoxyamines bearing electronegative groups<sup>30–32</sup>, would deserve further investigations.

### 2.1.2.2. Fluorinated Nitroxides

Although the synthesis and characterization of several fluorinated nitroxides was reported<sup>33–42</sup>, only a few (**6–10**) of them were studied in NMP (Fig. 5).

Nitroxide **6** is extremely reactive compared to dialkyl nitroxides: it adds to unsaturated systems<sup>43,44</sup> and readily abstracts hydrogen to form the corresponding hydroxylamine<sup>44–46</sup>. It forms very strong C–O bond that is not favorable to living radical polymerization. Also, nitroxide **7** leads to a more stable alkoxyamine than its non-fluorinated homologue (di-*tert*-butyl nitroxide, an efficient nitroxide in NMP)<sup>47</sup>. Nitroxides **8**, **9** allowed the control of the polymerization of styrene and butyl acrylate<sup>48</sup>. Moreover, better results were obtained with **9** compared with the nitroxide bearing hydrogen

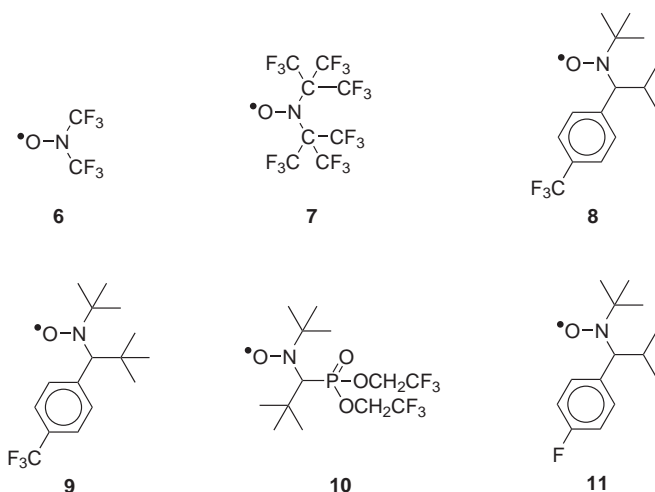


FIG. 5

Structures of fluorinated nitroxides **6–11** studied in nitroxide-mediated radical polymerization (NMP)

atom instead of the  $\text{CF}_3$  group. In this case, the electron-withdrawing effect of the  $\text{CF}_3$  group is likely to counterbalance the steric effect caused by the bulky *tert*-butyl substituent. Finally, nitroxide **10** leads to a rather poor control of polymerization of styrene<sup>49</sup>, in contrast to its non-fluorinated homologue which is known to be a very efficient control agent in NMP<sup>50,51</sup>. It was not settled whether the poor control resulted from decomposition of the nitroxide (due to steric hindrance) or from the electron-withdrawing effect of fluorine atoms.

In another study, the fluorinated nitroxide was mainly used to prepare fluorine-labeled polymers on solid support for targeted applications (nitroxide **11**)<sup>52</sup>.

### 2.1.3. Fluorinated Alkyl Halides (*C–X* Cleavage, *X* = *Cl*, *Br*, *I*) (ATRP)

The use of polychloroalkanes as initiators in ATRP of styrene, methyl methacrylate and methyl acrylate in the presence of  $\text{CuCl}/2,2'$ -bipyridine was extensively investigated by Destarac *et al.*<sup>53–58</sup>. Electron-withdrawing substituents turned out to increase the efficiency of the initiation and even to induce multifunctional initiation as shown in the case of fluorinated polychloroalkanes such as  $\text{CCl}_3\text{CH}_2\text{CF}_2\text{Cl}$  and  $\text{CCl}_3\text{CF}_3$ . Moreover,  $\text{CCl}_3$ -capped vinylidene fluoride telomers promoted fast initiation related to propagation in ATRP<sup>59</sup>.

Perfluoroalkylsulfonyl chlorides and bromides were also used as initiators in Cu-based catalyzed polymerization of hydrocarbon and fluorocarbon monomers. In the case of styrene and methyl methacrylate, the results suggested that a living radical polymerization mechanism occurs<sup>60</sup>.

A bromine-terminated poly(vinylidene fluoride), which was prepared by radical telomerization of vinylidene fluoride with 1,2-dibromotetrafluoroethane, was used as a difunctional initiator in the polymerization of styrene in the presence of CuBr/2,2'-bipyridine<sup>61</sup>. It was found that molecular weights of the polymers increased linearly with styrene conversion and polydispersities were low, suggesting the formation of a triblock copolymer in a living fashion.

Another symmetrical fluorinated difunctional brominated initiator Br-R-C(Et)(R<sub>F</sub>)-Z-Br, with Z = -C(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>- and R<sub>F</sub> = -CH<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>-S(CH<sub>2</sub>)<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>-CF<sub>3</sub>, was prepared by condensation of 2-bromo-2-methylpropionyl bromide and a fluorinated diol HOCH<sub>2</sub>C(C<sub>2</sub>H<sub>5</sub>)(R<sub>F</sub>)CH<sub>2</sub>OH. This initiator was used in ATRP in the presence of CuBr/pyridine-2-carbaldehyde *N*-pentylimine as catalyst to prepare polymers with improved surface properties<sup>62,63</sup>.

Iodoperfluoroalkane CF<sub>3</sub>(CF<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>I was used as initiator in ATRP of MMA with Cu(I)salt/bipyridine catalysts<sup>64</sup>. However, further experiments with poly(vinylidene fluoride)-capped iodine macroinitiators led to a low initiator efficiency because the propagation rate was much faster than the initiation rate. Similar results were obtained in our group with CF<sub>3</sub>-(CF<sub>2</sub>)<sub>5</sub>-I as initiator and CuX/pyridine-2-carbaldehyde *N*-pentylimine as catalysts (X = Br, I), with or without addition of Cu<sup>0</sup>, in ATRP of methyl methacrylate and styrene<sup>23</sup>.

#### 2.1.4. Fluorinated Alkyl Iodides (ITP)

Iodine-containing compounds have been used for a long time as chain transfer agents in telomerization<sup>65,66</sup>. Fluorinated alkyl iodides such as CF<sub>3</sub>-(CF<sub>2</sub>)<sub>5</sub>-I, and to a lower extent CF<sub>3</sub>-(CF<sub>2</sub>)<sub>5</sub>-(CH<sub>2</sub>)<sub>2</sub>-I, were reported to be efficient telogens<sup>67</sup>. However, the living character of the polymerization carried out in the presence of alkyl iodides was reconsidered<sup>15,68,69</sup>. A large variety of branched or linear perfluoroalkyl iodides or  $\alpha,\omega$ -diiodoperfluoroalkanes<sup>70</sup> have been involved in iodine transfer polymerization (ITP)<sup>71</sup> or in stepwise cotelomerization of fluoroalkenes<sup>72</sup>. A more extensive description is given in Section 3.3.

Fluorinated alkyl iodide C<sub>6</sub>F<sub>13</sub>I was also used to perform ITP of styrene in aqueous emulsion and miniemulsion<sup>73,74</sup>. In conventional batch emulsion



polymerization, the efficiency of the transfer agent was low, resulting in molecular weights higher than expected. This is explained by a slow rate of diffusion of the hydrophobic perfluorinated transfer agent through the water phase, from the monomer droplets to the active latex particles. This problem was overcome in miniemulsion polymerization, for which the transfer agent is directly located in the polymer particle.

### 2.1.5. Fluorinated Chain Transfer Agents (for RAFT)

#### 2.1.5.1. Xanthates

*N,N*-Dialkyldithiocarbamates were known to be efficient iniferters upon UV irradiation but behave as poor transfer agents in the RAFT process. However, Mayadunne *et al.*<sup>75</sup> and Destarac *et al.*<sup>76</sup> found that the conjugation of the lone electron pair of the nitrogen atom with carbonyl or aromatic groups makes the dithiocarbamates useful in the RAFT process. Like dithiocarbamates, xanthates were also initially restricted to photo-iniferter process (except for a few monomers such as vinyl acetate where the RAFT process was claimed to operate<sup>77</sup>). Similarly to the extension of the RAFT process for dithiocarbamates, Moad *et al.*<sup>18</sup> and Destarac *et al.*<sup>78,79</sup> noticed that the reactivity of xanthates could be tuned by using electron-withdrawing substituents on the alkoxy moiety, as illustrated with fluorinated xanthates **12–14** (Fig. 6). Such fluorinated xanthates have higher apparent chain transfer constants than their non-fluorinated homologues, and become useful RAFT agents.

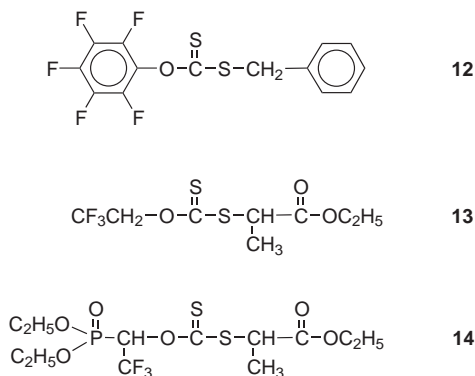


FIG. 6 Structures of fluorinated xanthates **12–14** used in RAFT process

It must be mentioned that symmetrical and nonsymmetrical fluorinated trithiocarbonates such as  $\text{CF}_3\text{SC(S)SCF}_3$  and  $\text{CH}_3-(\text{CH}_2)_3-\text{SC(S)S}-(\text{CF}_2)_5-\text{CF}_3$  have been synthesized but they were not tested in living radical polymerization<sup>80,81</sup>.

### 2.1.5.2. Dithioesters

$\omega$ -Perfluorinated dithioesters were synthesized and successfully used in RAFT process to prepare polymers and block copolymers bearing a fluorinated end-group (Fig. 7)<sup>82</sup>. Dithioesters **15**–**18** were synthesized by reacting phenylmagnesium bromide with carbon disulfide, followed by nucleophilic substitution on the appropriate brominated compounds. Dithioester **18** suf-

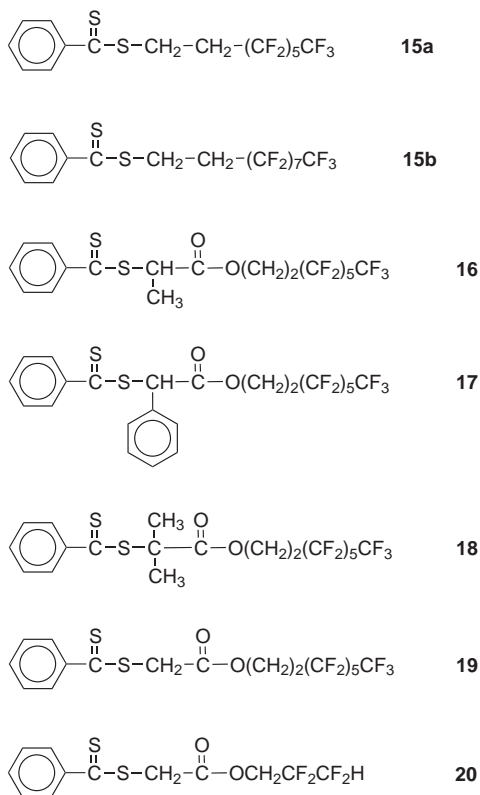


FIG. 7

Structures of fluorinated dithioesters **15**–**20** used in RAFT process

ferred from degradation at 105 °C for seven days (lack of CS<sub>2</sub>). Alternatively, dithioesters **15** were synthesized by a convenient and straightforward transesterification reaction between the corresponding fluorinated thiol R<sub>F</sub>(CH<sub>2</sub>)<sub>2</sub>SH and a commercially readily available dithioester, (thiobenzoylthio)acetic acid<sup>83</sup>. Dithioesters **19** and **20** resulted from the direct esterification of the commercial (thiobenzoylthio)acetic acid with the corresponding fluorinated alcohol<sup>23,82</sup>. Polymerization of styrene showed the following trend in the control of the polymerization **20** > **19** > **15**. Dithioester **20** with the shorter spacer between the ester group and the fluorinated moiety (methylene instead of ethylene spacer) led to a lower polydispersity index, indicating the beneficial effect of the electron-withdrawing fluorine atoms on the activity of the chain transfer agent for this structure<sup>23</sup>. Otherwise, in polymerization of styrene, methyl methacrylate, ethyl acrylate, and with butadiene, dithioester **17** gave the most promising results and a decreasing efficiency series of dithioesters was suggested (**17** > **16** > **19** > **15**), as expected from steric and electronic effects (methyl or phenyl substituents)<sup>82</sup>.

## 2.2. Other Fluorinated Molecules Involved in LRP

### 2.2.1. Fluorinated Ligands (ATRP)

The use of different nitrogen-based ligands in copper-mediated ATRP has recently been reviewed<sup>84</sup>. Electronic and steric effects are important; reduced catalytic activity or efficiency is observed when either there is an excessive steric hindrance around the metal center or the ligand bears strongly electron-withdrawing substituents. Fluorinated ligands may fall in this category depending on the location of the fluorinated substituents relative to the complexing site. So, fluorinated ligands<sup>85</sup> such as **21**, **22** were specially designed to perform ATRP in special media, such as supercritical carbon dioxide<sup>86,87</sup> and fluorous biphasic processes<sup>88</sup> (Fig. 8). Fluorine imparts solubility in supercritical carbon dioxide. In fluorous biphasic processes<sup>89</sup>, the catalytic system is reusable upon facile separation. In these examples, the metal center is isolated from the electronic effects of fluorine.

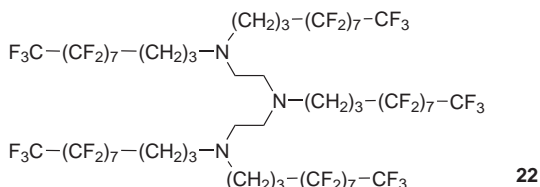
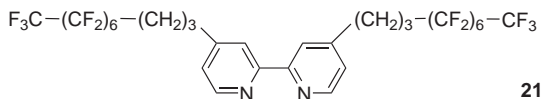


FIG. 8

Structures of fluorinated ligands **21–22** used in ATRP

### 2.2.2. Fluorinated Solvents (LRP)

Fluorinated solvents such as (trifluoromethyl)benzene were sometimes used in living radical polymerization of fluorinated (meth)acrylates to favor homogeneous conditions during the polymerization<sup>90</sup>, but investigation of the effect of the fluorinated solvent on the control of the polymerization was not the purpose of these studies although the polarity of the solvent is known to have a pronounced effect in radical polymerization (especially in ATRP)<sup>14</sup>.

As mentioned above concerning the ligands, fluorous biphasic conditions (such as perfluoromethylcyclohexane/toluene mixture) were used to propose a variant of the conventional ATRP process. In this way, the catalysts can be reused several times with reproducible results<sup>88</sup>.

## 3. LIVING RADICAL POLYMERIZATION OF FLUORINATED MONOMERS

### 3.1. Fluorinated (Meth)acrylates

Fluoroalkyl methacrylates were polymerized by iniferter method and ATRP in conventional medium<sup>26,90–93</sup>, and by ATRP in supercritical carbon dioxide<sup>86</sup> (Fig. 9). Fluoroalkyl acrylates were polymerized by iniferter, ATRP, and NMP in conventional media<sup>48,90,94–96</sup>, and by ATRP<sup>86</sup> and RAFT<sup>97</sup> in supercritical carbon dioxide (Fig. 9). In most cases, block copolymers were prepared for their surfactant properties in supercritical carbon dioxide, or for more usual aspects of fluorinated materials (such as low surface energy).

ATRP of the methacrylate with  $R_F = -CH_2C_7F_{15}$  in supercritical carbon dioxide, in the presence of methyl 2-bromopropionate as initiator and a copper-based catalyst, required the use of fluorinated ligands such as **21** to reach higher monomer conversion (83% monomer conversion instead of 64% with the non-fluorinated homologue ligand)<sup>86</sup>.

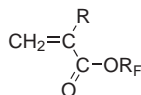


FIG. 9

Structures of fluoroalkyl (meth)acrylates used in living radical polymerizations.  $R = \text{CH}_3$ ,  $R_F = \text{CH}_2\text{CF}_3$ ,  $\text{CH}_2(\text{CF}_2)_6\text{CF}_3$ ,  $(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$ ,  $(\text{CH}_2)_2\text{N}(\text{Et})\text{SO}_2-(\text{CF}_2)_7-\text{CF}_3$ ,  $(\text{CH}_2)_2\text{OC}(\text{O})(\text{CF}_2)_6-\text{CF}_3$ ,  $(\text{CH}_2)_2\text{OC}_9\text{F}_{19}$ ;  $R = \text{H}$ ,  $R_F = \text{CH}_2(\text{CF}_2)_3-\text{CF}_3$ ,  $\text{CH}_2(\text{CF}_2)_6-\text{CF}_3$ ,  $(\text{CH}_2)_2(\text{CF}_2)_7-\text{CF}_3$ ,  $(\text{CH}_2)_2\text{N}(\text{Et})\text{SO}_2-(\text{CF}_2)_7-\text{CF}_3$

Butyl 1-fluoroacrylate (**23**) was successfully polymerized by ATRP in anisole with CuCl and CuBr as catalyst, *N,N,N',N'',N''',N'''*-hexamethyltriethylene tetramine (HMTETA) as ligand, and brominated compounds as initiators (Fig. 10)<sup>98</sup>. 1-Fluoroacrylates are particularly interesting monomers, especially when they are bearing some groups in the  $\alpha$  position with a very high fluorine content such as  $-\text{CH}_2-\text{CF}_3$ ,  $-\text{CH}(\text{CF}_3)_2$  and  $-\text{C}_6\text{F}_5$ . Indeed, these polymers show exceptional physical properties such as a very low absorption in the near infrared region, a glass transition temperature generally 30 °C higher than their methacrylic homologues, and thermal stability which is also strongly improved in a comparison with their methacrylic homologues. These properties lead to applications as polymers of high added value in areas such as materials for optics (plastic optical fibers, components for optics). For polymerization, these monomers are interesting because they are very reactive. They have the same or even higher reactivity than acrylates. Many studies were dedicated to the polymerization of these monomers by conventional radical polymerization, but nothing was reported about their polymerization by recent techniques of living radical polymerization. This is of special interest since it is known that the substitution in the  $\alpha$  position to carbonyl strongly modifies the reactivity

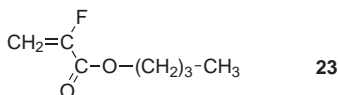


FIG. 10

Structure of 1-fluoroacrylate **23**

of acrylic derivatives. So, the successful control of butyl 1-fluoroacrylate by ATRP is of considerable importance for the living radical polymerization of this class of monomer.

### 3.2. Fluorinated Styrenics

A few fluorinated styrene derivatives were tested in living radical polymerizations. A series of 4-substituted styrenes were studied in copper-based ATRP. Electron-withdrawing groups such as in styrenes **24**, **25** have led to faster polymerizations (Fig. 11)<sup>99</sup>. A similar kinetic behavior was observed in NMP of styrene derivatives<sup>100–102</sup>. Styrene **24** was also copolymerized with methyl acrylate by ATRP to yield nanostructured materials with fluorine tag at various sites within the material<sup>103</sup>. Otherwise, fluorinated styrene **26** (a meta/para mixture) was controlled by NMP with TEMPO as nitroxide, to yield block copolymers for supercritical carbon dioxide applications<sup>94,96,104</sup>.

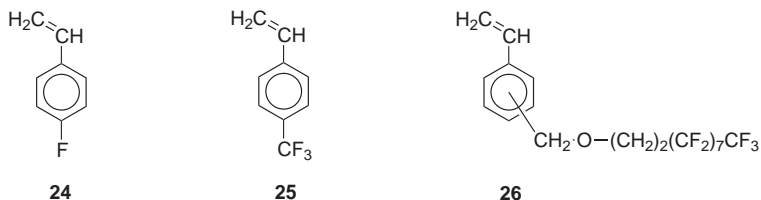


FIG. 11 Structures of fluorinated styrenes **24–26** used in living radical polymerizations

### 3.3. Fluorinated Alkenes (ITP)

According to the literature, the only examples of controlled radical polymerization of fluoroalkenes require adequate fluorinated initiators or transfer agents. The oldest method is based on the cleavage of the C–I bond that already led to industrial applications<sup>105</sup>.

The cleavage of the C–I bond, the bond dissociation energy of which amounts to 55 kcal mol<sup>-1</sup>, can be achieved by various methods<sup>106–109</sup>. Based on well-selected monomers, a method has been developed to control polymerization with alkyl iodides (iodine transfer polymerization, ITP), which can be easily applied to fluorinated alkenes. It was named “degenerative transfer” in the mid-nineties and concerned the controlled radical polymerization of butyl acrylate<sup>2,110</sup> or styrene<sup>2,110,111</sup> (not discussed in this review).

### 3.3.1. Iodine Transfer Polymerization of Fluoroalkenes

Iodine transfer polymerization is one of the radical living process developed in the late seventies by Tatemoto<sup>15,71,105,108,112–114</sup>. Actually, it requires (per)fluoroalkyl iodides because their highly electron-withdrawing (per)fluorinated group  $R_F$  provides the lowest level of the  $CF_2-I$  bond dissociation energy. Such a C–I cleavage is possible to a lower extent for  $R_FCH_2CH_2I$ <sup>70</sup>. Various fluorinated monomers have been successfully used in ITP. Basic similarities in these living polymerization systems are found in the stepwise growth of polymer chains with each active species. The active living centre, generally located in the end groups of the growing macromolecules, has the same reactivity at any time during polymerization even when the reaction is stopped<sup>71,108</sup>. 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 follows (Scheme 4).



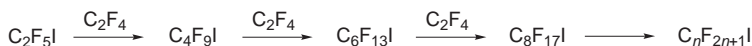
SCHEME 4  
ITP of vinylidene fluoride

Usually, molecular weights are not higher than 30 000 and yet polydispersity is narrow (1.2–1.3)<sup>71,108,114</sup>.

Tatemoto *et al.*<sup>15,71,108,109,112–114</sup> used peroxides as initiators of polymerization. Improvement is also possible by using diiodo and polyiodo compounds<sup>115,116</sup>.

Several investigations have shown that iodine transfer polymerization can occur by emulsion or solution processes. This is not described here but several articles and patents of Tatemoto are published<sup>108,109,112</sup>, using ammonium persulfate as the initiator and involving tetrafluoroethylene (TFE), vinylidene fluoride (VDF) and hexafluoropropene (HFP) as monomers. The fluoroelastomers produced by ITP can be peroxide-curable leading to commercially available Dai-El®<sup>114–116</sup> produced by Daikin. Such a polymer is stable up to 200 °C and finds many applications in high technology such as in transportation and electronics. Further investigations have led to relevant block copolymers (discussed in Section 4.1.4.).

This concept was also exploited in order to prepare “living” and well-defined tetrafluoroethylene telomers in which the telomer produced acts as another transfer agent, in Scheme 5.



SCHEME 5

ITP of tetrafluoroethylene

Such a living telomerization can be initiated either thermally or in the presence of radical initiators or redox catalysts<sup>117</sup>.

### 3.3.2. Stepwise Cotelomerization

The application of such a process allows the step by step synthesis of block copolymers either from fluoroalkyl iodides or  $\alpha,\omega$ -diiodoperfluoroalkanes. Chambers' investigations or those performed in our Laboratory have led to the extensive use of X-Y compounds with chlorotrifluoroethylene (CTFE) for the preparation of efficient transfer agents X-R<sub>F</sub>-Y with X = Y = I<sup>118</sup> or Br<sup>119,120</sup> and also X = I and Y = Cl<sup>121</sup>, Br<sup>122</sup> or F<sup>123,124</sup> (Scheme 6).



SCHEME 6

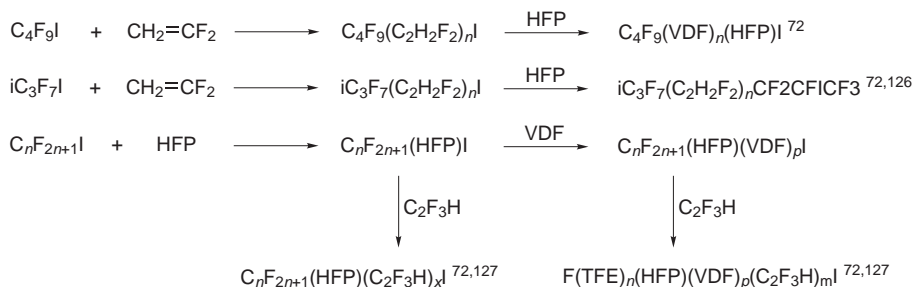
Synthesis of halogenated transfer agents

Chambers *et al.*<sup>118</sup> obtained difunctional oligomers with iodinated telogens. It has been observed, however, that from ICl or [IF], generated *in situ* from iodine and iodine pentafluoride, monoadducts were obtained as the sole products<sup>123,124</sup>. Addition of [IF] to CTFE yields CF<sub>3</sub>CFCII which was successfully used as the transfer agent for the telomerizations of CTFE, hexafluoropropene (HFP)<sup>124</sup> or for stepwise cotelomerizations of CTFE/HFP, CTFE/HFP/VDF, HFP/VDF and HFP/trifluoroethylene<sup>72</sup>. All the above cotelomers were successfully end-capped by ethylene allowing further functionalization<sup>72</sup>. In addition, the CFCII end group shows a higher reactivity than CF<sub>2</sub>I<sup>125</sup>.

Furthermore, stepwise cotelomerisation of various commercially available fluoromonomers lead also to interesting highly fluorinated derivatives as in Scheme 7.

All these cotelomers were successfully end-capped with ethylene that offered new  $\omega$ -functionalized fluorinated compounds<sup>72</sup>. In addition,  $\alpha,\omega$ -diiodofluoroalkanes also allow access to well-defined block cotelomers. Tortelli and Tonelli<sup>128</sup> and Baum and Malik<sup>129,130</sup> performed the synthesis of such telechelic products by heating iodine crystal with tetrafluoroethy-

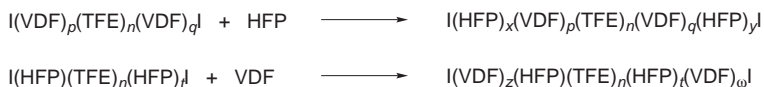




SCHEME 7

Stepwise cotelomerization of various fluoroalkenes (VDF and HFP stand for vinylidene fluoride and hexafluoropropene, respectively)

lene. Such halogenated reactants were successfully involved in telomerization of vinylidene fluoride (VDF)<sup>131</sup> or hexafluoropropene (HFP)<sup>132</sup> to form  $\alpha,\omega$ -diiodo VDF/TFE/VDF or  $\alpha,\omega$ -diiodo HFP/TFE/HFP triblock cotelomers<sup>133</sup>. These products are potential starting materials for Viton-type multiblock cotelomers<sup>132</sup> as shown in the following examples (Scheme 8).



SCHEME 8

Telomerization reactions of hexafluoropropene (HFP) and vinylidene fluoride (VDF) involving diiodides

These novel  $\alpha,\omega$ -diiodides underwent functionalizations<sup>133</sup>, especially for the preparation of original fluorinated nonconjugated dienes<sup>134</sup> (utilised in the preparation of hybrid fluorosilicones<sup>135</sup> which show excellent properties at low and high temperatures), or in original fluorinated polyesters and polyurethanes from fluorinated  $\alpha,\omega$ -diols<sup>130</sup>.

### 3.3.3. Conclusion

Even though in 1955 Haszeldine<sup>125</sup> or in 1957 Hauptschein *et al.*<sup>136,137</sup> showed a certain living nature of the radical telomerization of CTFE with  $\text{ClCF}_2\text{CFClI}$ , only the present research has attracted many academic or industrial chemists towards this fascinating area. In addition, Dear and Gilbert<sup>138</sup> or Sharp *et al.*<sup>139,140</sup> performed the telomerization of various fluoroalkenes with disulfides but they did not examine the living character of this reaction.

However, iodine transfer polymerization and stepwise cotelomerization of fluoroalkenes have shown a living character, and possible polymerization by organometallic systems, which is quite successful for nonfluorinated monomers, could be an encouraging route for these haloalkenes.

#### 4. ARCHITECTURED FLUORINATED POLYMERS BY CONTROLLED RADICAL POLYMERIZATION

Macromolecular engineering has become a useful tool for designing well-architected polymers (telechelics, cycles, networks, dendrimers, hyperbranched, gradient, star, block or graft copolymers). Although fluorinated telechelic (co)polymers have been reviewed<sup>141</sup>, the two last kinds of fluoropolymers are reported in this section.

##### 4.1. Fluorinated Block Copolymers

Block copolymers have received much attention as “novel polymer materials” with several components since they are made of different polymer blocks linked together. The reason for their importance comes from their unique chemical structure that brings new physical and thermodynamical properties related to their solid-state and solution morphologies. Frequently, block copolymers exhibit phase separation producing a dispersed phase consisting of one block type in a continuous matrix of the second block type. Their unusual colloidal and mechanical properties allow modification of solution viscosity, surface activity or elasticity and impact resistance of polymers. Thus, several block copolymers have produced a wide range of materials with tailorable properties depending on the nature and length of blocks. They have found significant applications such as adhesives and sealants, surface modifiers for fillers and fibers, crosslinking agents for elastomers, additives for resin gelation and hardening, compatibilizing agents or stable emulsions of homopolymer blends that can find applications in recovery and recycling plastic waste.

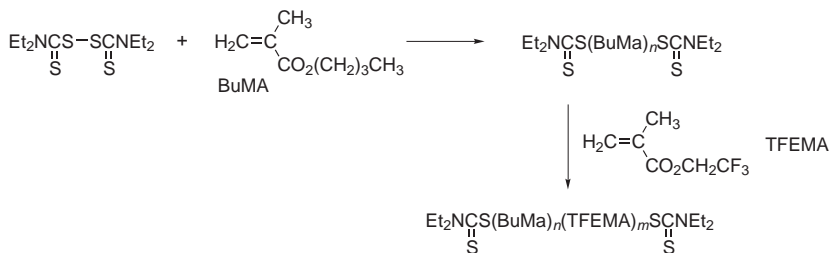
Block copolymers synthesized by radical polymerization or telomerization have been reported<sup>142</sup> and a non-exhaustive list of fluorinated block copolymers was mentioned in a recent review<sup>143</sup>. Fluorinated block copolymers can be prepared by various methods: (i) by direct radical polymerization of various nonfluorinated monomers with bis(perfluoro) azo<sup>144</sup> or peroxy<sup>145</sup> initiators, (ii) by polycondensation<sup>146</sup>, (iii) by cationic methods (e.g., by ring-opening polymerization of  $\epsilon$ -caprolactone with telechelic fluorodiols)<sup>147</sup>, (iv) by telomerization reaction of fluoroalkenes with

perfluoropolyethers bearing bromo<sup>148</sup> or iodo<sup>149</sup> end groups as transfer agents, (v) by chemical modification of side double bonds of well-defined poly(dienes) prepared by anionic polymerization<sup>150</sup>. However, all the above synthetic methods are not convenient for synthesis of radical living (co)polymers, in contrast to those depicted hereafter.

#### 4.1.1. By Iniferter Method

##### 4.1.1.1. Thiurams

A Japanese team<sup>91</sup> synthesized amphiphilic acrylic resins composed of (meth)acrylate esters and fluoroalkyl (meth)acrylates by a two-step procedure involving a thiuram disulfide as in Scheme 9.



SCHEME 9  
Copolymerization of methacrylates involving thiuram

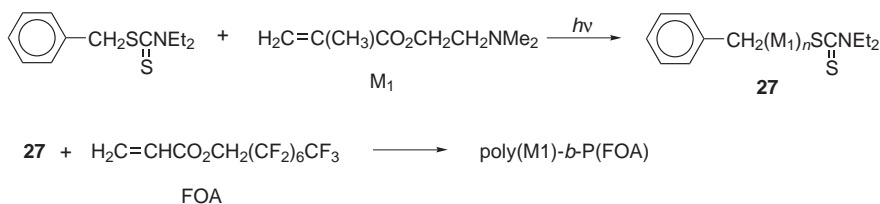
The obtained paints were resistant to acid, heat and weather.

A similar approach was used by Guan and Desimone<sup>151</sup> in radical photopolymerization of 1,1-dihydroperfluorooctyl acrylate with a telechelic polystyrene synthesized by polymerization of styrene with tetraethylthiuram disulfide.

##### 4.1.1.2. Dithiocarbamates

DeSimone and co-workers<sup>152</sup> prepared amphiphilic block copolymers (Scheme 10) by a two-step controlled radical polymerization of conventional methacrylates with fluoroacrylate from benzyl *N,N*-diethyldithiocarbamate<sup>152</sup> (under photoinitiation).

This “iniferter” controlled free radical technique made it possible to prepare surfactants used in numerous applications including the stabilization of dispersion polymerization in supercritical CO<sub>2</sub>.



SCHEME 10

Photopolymerization of (meth)acrylates from dithiocarbamate

#### 4.1.1.3. Fluorinated Tetraphenylethanes

Roussel and Boutevin<sup>26</sup> synthesized poly(TFEMA)-*b*-PS by radical polymerization of styrene with trifluoroethyl methacrylate (TFEMA) oligomers, obtained from the oligomerization of TFEMA with a telechelic fluorinated tetraphenylethane (see Section 2.1.1.). Interestingly, the efficiency of the TFEMA oligomers as macroinitiator was 85%.

#### 4.1.2. Synthesis of Fluorinated Block Copolymers by Polymerization of Fluorinated Monomers Using Alkoxyamines (NMP)

Another attempt of synthesis of fluorinated diblock copolymers was recently performed in our Laboratory by a controlled radical stepwise copolymerization involving TEMPO as a counter radical<sup>94,96,104</sup> from PS-TEMPO, the molecular weights of which were in the range from 3 000 to 10 000. Its structure is in Fig. 12.

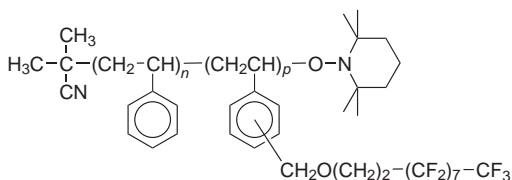


FIG. 12

Fluorinated block copolymers end-capped with TEMPO

The molecular weight of the fluorinated block was 20 000–80 000.

In the same way, poly(styrene)-*b*-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) block copolymers were obtained with molecular weights ranging from 40 000 to 60 000. Interestingly, the fluorinated CO<sub>2</sub>-philic blocks, if large enough, impart solubility in dense CO<sub>2</sub> to the diblock copolymers,

making them useful as original macromolecular surfactants in such a medium.

#### 4.1.3. Synthesis of Fluorinated Block Copolymers by Atom Transfer Radical Polymerization (ATRP)

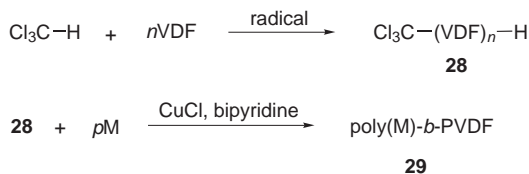
In this part, two kinds of routes for obtaining fluorinated block copolymers by ATRP can be considered: (i) the radical polymerization of a monomer with a fluorinated telomer is followed by an ATRP and (ii) two consecutive ATRP steps.

##### 4.1.3.1. Fluorodiblock Copolymer by ATRP of Nonfluorinated Monomers with Fluorotelomers as Original Initiators

As mentioned in Sections 2.1.3., 3.1. and 3.2., ATRP requires an activated C–X (X is a halogen atom) bond of the initiator.

##### 4.1.3.1.1. Telomers Containing a C–Cl Bond

A typical example is the chlorine-transfer radical polymerization (*via* a reactivated  $\text{CCl}_3$  end-group) of various monomers (styrene, MMA, methyl acrylate and butyl acrylate) initiated with VDF telomers (**28**) with  $\overline{\text{DP}}_n$  ranging between 5 and 16, as follows<sup>59</sup> (Scheme 11).



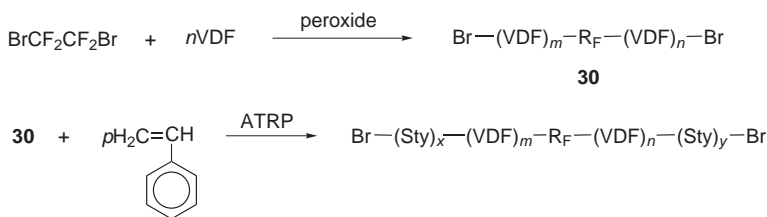
SCHEME 11

Fluorinated block copolymers by ATRP of various monomers starting from chlorinated PVDF telomers

Interestingly, whatever the VDF telomer/monomer pair, the number-average molecular weight ( $\overline{M}_n$ ) of **29** increased linearly with the monomer conversion and experimental values were close to the theoretical ones. In addition, narrow molecular-weight distributions and low polydispersities ( $\overline{M}_w/\overline{M}_n < 1.2$ ) were obtained, as evidence of a controlled radical polymerization.

#### 4.1.3.1.2. Telomers Containing a C–Br Bond

On the other hand, involving the cleavage of the C–Br bond regarded as stronger than the C–I but weaker than the C–Cl bond, two processes have been used to prepare di- or triblock copolymers. The first one, as above, is based on the controlled radical polymerization of styrene with bromine transfer<sup>153</sup> from  $\alpha,\omega$ -dibrominated intermediates **30** regarded as “macro-initiators”<sup>92</sup>. These dihalogenated compounds were prepared by telomerization of vinylidene fluoride with 1,2-dibromotetrafluoroethane<sup>154</sup>, as in Scheme 12.



SCHEME 12

Fluorinated triblock copolymers by ATRP of styrene initiated with brominated PVDF-telomers

#### 4.1.3.1.3. Telomeric Initiators Reactivated by a C–I Bond

$\alpha,\omega$ -Diiodinated PVDF telomers were synthesized to initiate the ATRP of MMA leading to a triblock PMMA-*b*-PVDF-*b*-PMMA copolymer<sup>64</sup> (Scheme 13).



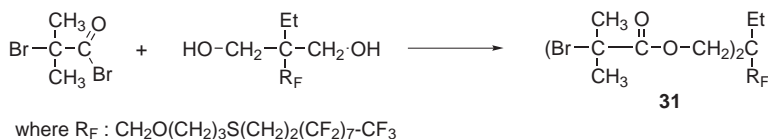
SCHEME 13

Synthesis of triblock copolymers by ATRP of MMA initiated with  $\alpha,\omega$ -diiodo PVDF

The kinetic plots ( $\ln([M]_0/[M])$  vs time) showed nearly a linear behavior, the  $\bar{M}_n$  (by NMR) of block copolymers increasing linearly with conversion.

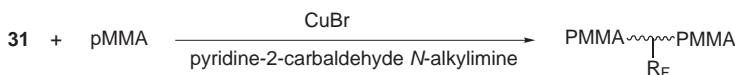
#### 4.1.3.2. Synthesis of Block Copolymers by Stepwise ATRP Processes

A fluorinated  $\alpha,\omega$ -diinitiator (**31**) was recently prepared by the condensation of a telechelic diol bearing a perfluorinated side group<sup>62,63</sup> (Scheme 14).



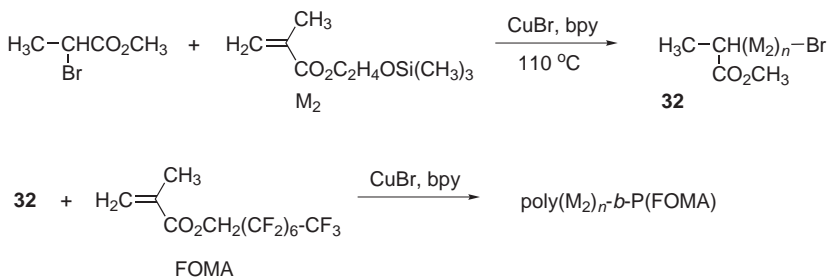
SCHEME 14  
Synthesis of  $\alpha,\omega$ -dibrominated initiator bearing a perfluorinated side group

**31** was successfully used in the ATRP of MMA (Scheme 15) leading to a PMMA having a perfluorinated side chain that exhibits a  $\bar{M}_n = 26\,000$  and PDI = 1.2. Such a perfluorinated lateral groups brought improved surface properties.



SCHEME 15  
ATRP of MMA from an  $\alpha,\omega$ -dibrominated initiator with  $\text{CF}_3(\text{CF}_2)_7$  pendant group

Similarly, Betts *et al.*<sup>155</sup> obtained amphiphilic block copolymers (Scheme 16).



SCHEME 16  
Fluorinated diblock copolymers by ATRP of methacrylates

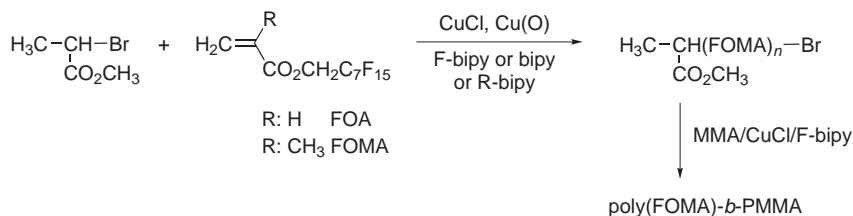
Interestingly, by atom transfer radical polymerization, various poly( $\text{M}_1$ )-*b*-PFOMA block copolymers were obtained,  $\text{M}_1$  representing MMA, 2-hydroxyethyl methacrylate, styrene, *tert*-butyl acrylate, 2-ethylhexyl acrylate with average molecular-weights ranging from 40 000 to 56 000<sup>93</sup>.

Similar investigations were carried out by Wu and Li<sup>95</sup> and Gaynor *et al.*<sup>156</sup> who prepared fluorinated diblock copolymers with improved surface properties.

Interestingly, Becker and Wooley<sup>103</sup> synthesized amphiphilic diblock copolymers containing poly(4-fluorostyrene) and poly(methyl acrylate) blocks by ATRP with CuBr and *N,N,N',N',N'*-pentamethyldiethylene-

triamine (PMDETA) as coordinating ligand, with molecular weight between 8 000 and 22 000. The block copolymers were hydrolyzed, assembled into micelles and converted into shell-crosslinked nanoparticles by covalent stabilization of the acrylic acid units in the shell.

Xia *et al.*<sup>86</sup> synthesized poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) and poly(1,1-dihydroperfluorooctyl methacrylate) (PFOMA) macroinitiators by ATRP in supercritical CO<sub>2</sub> (Scheme 17), and they found that the more CO<sub>2</sub>-philic the bipyridine ligand, the higher the fluorinated (meth)acrylate conversion.



SCHEME 17

ATRP of (meth)acrylates in supercritical CO<sub>2</sub>

The second step was also successful when 2-(dimethylamino)ethyl methacrylate (DMAEMA) was used as monomer<sup>157</sup>.

The authors also investigated the solubility of these block copolymers in CO<sub>2</sub> at various temperatures and pressures. Interestingly, at 65 °C and for 5 000 PSI (*i.e.*, 34.5 MPa), the poly(FOMA)-*b*-poly(DMAEMA) was soluble in that medium.

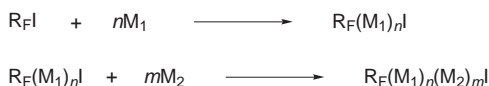
Under similar ATRP conditions, from “telechelic” ethylene bis(2-bromopropionate), poly(FOA) bearing two bromo end-groups was obtained with  $M_{n,(\text{NMR})} = 12\ 000$ . The diester was also a macroinitiator for obtaining PMMA-*b*-poly(FOA)-*b*-PMMA triblock copolymer (containing 49 MMA units)<sup>86</sup>.

#### 4.1.4. Synthesis of Fluorinated Block Copolymers by Iodine-Transfer Polymerization (ITP) of Fluoroalkenes

As mentioned in Section 3.3, iodine-transfer polymerization is one of the scarce methods that makes it possible to control the polymerization of fluoroalkenes such as tetrafluoroethylene or vinylidene fluoride. Because of strong CF<sub>2</sub>-Br and CF<sub>2</sub>-Cl bonds, bromine or chlorine transfer polymerizations were not observed.



The most remarkable use of the “living” polymerization is the preparation of block copolymers. A practical method for obtaining such copolymers is direct ITP of two fluorinated monomers with an efficient iodoinitiator. For instance, Tatemoto and Morita<sup>112</sup> used a mixture of VDF/HFP in the 46/54 molar ratio and I-(CF<sub>2</sub>)<sub>4</sub>-I in the presence of bis(trichloroperfluorohexanoyl) peroxide and obtained I-poly(VDF-*co*-HFP)<sub>x</sub>-C<sub>4</sub>F<sub>8</sub>-poly(VDF-*co*-HFP)<sub>y</sub>-I which exhibited a number-average molecular weight of 3300 with a polydispersity index of 1.27. This fluoroelastomer could be used for the synthesis of a block copolymer containing fluoroelastomer blocks and thermoplastic blocks (Scheme 18).



SCHEME 18

Fluorinated diblock copolymers by stepwise polymerization

M<sub>1</sub> and M<sub>2</sub> are fluorinated monomers or a group of fluoroalkenes which can be adequately selected to bring softness and hardness, respectively, leading to a thermoplastic elastomer (TPE)<sup>114</sup>. For instance, a hard segment sequence can be composed of E/HFP/TFE units in the 43/8/49 molar ratio (E is ethylene) whereas the soft part may consist of E/HFP/VDF in the 20/30/50 molar ratio<sup>116</sup>. A similar scheme can also be applied to α,ω-diiodides<sup>114,115</sup> hence leading to ABA triblock copolymers (where A and B are hard and soft blocks, respectively). These TPEs are useful as hot melts or pressure-sensitive adhesives or sealants having good chemical and ageing resistance. Furthermore, the introduction of hard segments such as alternate copolymers of TFE and ethylene, or PVDF, led to commercially available Dai-El® thermoplastics<sup>114,116</sup>.

They exhibit very interesting properties such as a high specific volume (1.90), a high melting point (160–220 °C), a high thermostability (up to 380–400 °C), a refractive index of 1.357 and good surface properties (γ<sub>c</sub> ≈ 19.6–20.5 in mN m<sup>-1</sup>). These characteristics offer excellent resistance against aggressive chemicals and strong acids, fuels, and oils. In addition, their tensile moduli are close to that of cured fluoroelastomers.

The Daikin's pioneering work was confirmed by that of the DuPont Company<sup>70</sup>.

As a model of ITP, the stepwise cotelomerization of fluoroalkenes (such as VDF, trifluoroethylene, hexafluoropropene or chlorotrifluoroethylene) was performed, taking into account that the fluoroiodo end group of the ob-

tained telomer is capable of being reactivated in a further telomerization reaction<sup>72</sup>. Interestingly, a large variety of telomers containing various polyfluorinated units exhibit amorphous to semicrystalline behavior depending on the number of difluoromethylene groups (more than six lead to crystallinity). Branches with trifluoromethyl groups decrease their crystallinity.

#### 4.1.5. Block Copolymers from the RAFT Process

Using  $\omega$ -perfluorinated dithioesters (see Section 2.1.5.2.), we synthesized poly(ethyl acrylate)-*b*-polystyrene of  $\overline{M}_n = 32\ 600$  and a PDI = 1.20 and PMMA-*b*-PS ( $\overline{M}_n = 147\ 000$  and PDI = 1.17) block copolymers bearing an  $\omega$ -perfluorinated group<sup>82</sup>.

### 4.2. Fluorinated Graft Copolymers

Graft copolymers are also interesting like block copolymers; they can be used as emulsifiers for polymer blends.

Various methods have been investigated to synthesize graft copolymers: (i) from macromonomers<sup>158</sup> (fluorinated macromonomers are scarce<sup>159</sup>); (ii) by direct copolymerization of monomers, one of which bearing peroxide side groups which do not initiate the copolymerization (one of the best examples has led to industrial product commercialized by the Central Glass Company under the Cefral® trade mark<sup>160</sup>); (iii) by chemical grafting of activated fluoropolymers (activation can be performed by electron beam<sup>161</sup> or heavy ions<sup>162</sup> or by ozonization<sup>163</sup>). However, none of these fluorinated graft copolymers are obtained by controlled polymerization.

Nevertheless, the Ausimont Company has investigated potential grafting of fluorinated polymers (PVDF or poly(VDF-co-HFP)) using a “branching and pseudo-living technology”<sup>164</sup> which involves a nonconjugated diene (e.g.,  $\text{H}_2\text{C}=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}_2$ ) and a perfluorinated alkyl diiodide (e.g.,  $\text{I}(\text{CF}_2)_6\text{I}$ ) in a terpolymerization leading to a low polydispersity index. A similar process which was not claimed pseudo-living was discovered *ca* 10 years before by Tatemoto *et al.*<sup>165</sup> in the polymerization of tetrafluoroethylene with 0.1 to 1.0 mole % of the above fluorodiene.

### 5. CONCLUSION

Organofluorinated compounds have been used in living radical polymerizations, as fluorinated initiators (dithiocarbamates, xanthates, tetra-

phenylethanes, alkoxyamines, fluorinated alkyl halides, and dithioesters), fluorinated ligands, fluorinated solvents, and fluorinated monomers. In some cases, fluorine atoms permitted to significantly improve the living process, as in the case of xanthates where fluorine atoms in the alkoxy moiety allow to tune their reactivity in the RAFT process. In general, heteroatoms offer rich possibilities in organic chemistry and should allow to further extend the potentials of living radical polymerization. For instance, phosphorus- and silicon-based compounds could be very useful in future to prospect for new living radical polymerization processes. As an illustration, the thiophosphorus compounds ( $>P(S)S-$ ), widely used in agriculture, could be efficient reversible transfer agents. In other cases, the fluorinated compounds are mainly used to impart specific properties to the resulting materials (in particular interesting surface properties, low cohesive energy, solubility properties for supercritical carbon dioxide applications, fluorine labeling). Regarding the monomers, the polymerization of fluorinated (meth)acrylics and styrenics can be well controlled by the iniferter method, NMP, ATRP and RAFT, with essentially the same restrictions as for their non-fluorinated homologues (for instance, polymerization of methacrylics cannot be controlled by NMP because of the occurrence of hydrogen abstraction reactions). In contrast, the most adequate method for living radical polymerization of fluorinated alkenes is ITP in which iodine atom acts as an interesting transfer site. As a matter of fact, modeling the bond dissociation energy between the fluorinated unit and the end groups introduced by dithiocarbamates, tetraphenylethanes, nitroxides, alkyl halides (Cl, Br, I), xanthates, and dithioesters, would deserve deep investigation. In addition, the characterization of higher-fluorinated polymers is still a challenge, especially by size exclusion chromatography because of the lack of appropriate fluorinated solvents and standards. This review has also shown that, in contrast to only one example of synthesis of fluorinated graft copolymer, several methods of preparation of fluorinated block copolymers by LRP are available. Lastly, living radical polymerization in supercritical carbon dioxide is an attractive approach since some fluoropolymers are soluble in such a medium, which makes it possible to achieve rather high molecular weights (no transfer to the solvent).

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21. In Scheme 2 (a), the example of dithiocarbamates is given for simplicity but other molecules such as xanthates  $R^1SC(S)OR^2$  also fall in this category.
22. In Scheme 2 (e), for xanthates, some authors sometimes refer to the name MADIX, which stands for Macromolecular Design Through Interchange of Xanthates, as claimed by Rhodia for this process.
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