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Use of Iodocompounds in Radical Polymerization

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Contents

1. Introduction

Iodocompounds are highly attractive as potential intermediates for the synthesis of various organic and macromolecular molecules because of the ability of the iodine atom to be a good leaving atom. In addition, they are efficient transfer agents in radical polymerization. In fact, the ability of the iodine atom to transfer onto growing macromolecular chains allowed the development of such compounds. An important class of iodocompounds employed as chain transfer agents (CTAs) are the fluorinated iodocompounds, R_FI. These compounds could be obtained in good yield by simple addition of either HI or ICl onto fluorovinylic monomers. These fluorinated CTAs enabled both initiation of the polymerization under UV, thermally or in the presence of redox catalysis, and transfer of the iodine atom onto the growing chains. Oligomers of low molar masses could then be obtained.

Then, in the late 1970s, Tatemoto[1] opened the route to the iodine transfer polymerization (ITP). Hence, by using an initiating radical, iodofluorocompounds could enter in a controlled process, based on a degenerative transfer (DT). This real breakthrough was first realized with fluoroolefin monomers but was rapidly extended to other common nonhalogenated vinyl monomers. For specific applications, nonfluorinated CTAs were preferred. Some iodoalkanes, such as iodoform, were then investigated in the ITP process. Recently, reverse iodine transfer polymerization (RITP), another DT process, was discovered by us and is based on the use of molecular iodine.

It was thus of interest to deeper summarize the synthesis and the use of iodinated derivatives involved in telomerization, ITP, and RITP, and these are the objectives of this review, divided in four main parts.

The first part reports the syntheses of such iodocompounds, fluorinated and nonfluorinated ones. The structural requirements are also investigated for further efficient transfer reactions. The following parts describe their uses in several radical processes, i.e., telomerization, ITP, and RITP. A wide range of vinyl monomers (halogenated and nonhalogenated) have been involved in these radical techniques. Then, syntheses of well-architectured copolymers (especially block

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Ghislain David was born in Sete, France, in 1975. He obtained his Ph.D. degree in 2002 at the University Montpellier II (National School of Chemistry of Montpellier), working in the laboratory of Professor Bernard Boutevin on the synthesis of telechelic oligomers and their applications for the synthesis of TPEs. In 2003, he obtained a postdoctoral research position in emulsion polymerization, done in the laboratory of Pr. R. G. Gilbert (KCPC, Sydney) and with the collaboration of Dow Chemicals. Then, in 2004, he joined the laboratory of Pr. B. Boutevin to do postdoctoral research on CRP of vinyl phosphonates, with the collaboration of Rhodia Chemicals. His research interest mainly covers the preparation of controlled architectured polymers by CRPs (ATRP, ITP, and RITP) of original monomers in organic and aqueous media.

Boyer Cyrille was born 1978 in Orange (France). In 2005, he received his Ph.D. from the University of Montpellier II after four years of research focused on the area of the well-architectured graft copolymers based on a “grafting onto” process, under the direction of Professors J. J. Robin and B. Boutevin. In addition, he studied the CRPs to obtain original copolymers. He also obtained a nonpermanent lecturer position. Since October 2005, he has had a postdoctorate position in collaboration with Dupont Performance and Elastomers (Willmington, United States) dealing with the synthesis of original fluorinated elastomers.

Jeff Tonnar was born in Luxembourg, Luxembourg, in 1979. He graduated from the National School of Chemistry of Montpellier in France in 2004. Since October 2004, he has been doing his Ph.D. studies under the direction of Dr. P. Lacroix-Desmazes in the laboratory of Professor Bernard Boutevin. His research covers iodine-mediated polymerization [(reverse) ITP], especially in dispersed aqueous media (suspension, miniemulsion and ab initio emulsion polymerization).

Directeur de Recherches at CNRS, Bruno AMEDURI leads the Fluoropolymers and Energy team at the Laboratory of Macromolecular Chemistry of ENSCM. His main interests focus on the synthesis and the characterizations of fluorinated monomers (including cure site monomers and telechelics), telomers, and copolymers for various applications such as surfactants, elastomers, and fuel cell membranes. Coauthor of one book, 16 reviews and chapters of books, more than 120 peer review publications, and coinventor of 20 patents, he is also a member of the American and French Chemical Societies and is a member of the Editorial Board of the Journal of Fluorine Chemistry and European Polymer Journal.

Patrick Lacroix-Desmazes was born in Caen, France, in 1968. He graduated from the National School of Chemistry of Montpellier, France, in 1992. He obtained his Ph.D. degree in 1996 at the University Claude-Bernard Lyon I, working in the laboratory of Professor Alain Guyot on the use of macromonomers as stabilizers in dispersion polymerization in polar media. After postdoctoral research on suspension polymerization, done with BP Chemicals in Wingles in 1997, he joined the laboratory of Professor Bernard Boutevin as a CNRS research scientist. In 1999, he developed RITP, a promising method for controlled/living radical polymerization. He received his Habilitation Degree in 2004. He was awarded the 2004 Innovative Research ADER Award in collaboration with Solvin Company. His research interest covers living radical polymerizations, including in dispersed media, as well as the synthesis and use of polymers in liquid or supercritical carbon dioxide.

Professor Bernard Boutevin earned his Chemical Engineering degree from the School of Chemistry in Montpellier (France) and then received his Ph.D. in 1975 from Montpellier University, where he became a CNRS researcher. The topics of his research first concerned telomerization: kinetics, chemical modifications, and their use in architectured polymers (block and grafted copolymers). The concept was first applied to fluorinated monomers, and it represents almost half of his scientific articles. Nowadays, his research is directed toward telechelic oligomers, and all of the methods of living radical polymerization are investigated (NMP, ATRP, ITP, RITP, and RAFT) in order to prepare original architectured polymers such as block, grafted, gradient, or alternated. In addition, phosphonated and siliconated monomers and (co)polymers are of increasing interest. Prof. Boutevin has supervised more than 100 Ph.D. students and published two books, more than 400 peer review articles, 25 reviews or chapters of books, has been invited to more than 35 international conferences, and is coinventor of more than 100 patents. In addition, more than 10 products coming from his research group have been or are marketed by companies. He is also a consultant for many companies, including Elf Atochem (now Arkema), and he was a consultant for Dow-Corning (United States) and Daikin (Japan). He is a member of the American Chemical Society and Groupe Français d’Etudes et d’Applications des Polymères and also President of the Scientific Council of the School of Chemistry.

copolymers) are described. Finally, iodocompounds are commonly utilized in an industrial scale for the synthesis of various commercially available intermediates (fluorotelomers, fluorinated alcohols, and fluorinated acrylates) or products used as surfactants, fire-fighting foams, surface modifiers, and thermoplastic elastomers (TPEs). These applications are highlighted in the last part.

2. Synthesis of Iodinated Compounds Used in Radical Polymerization

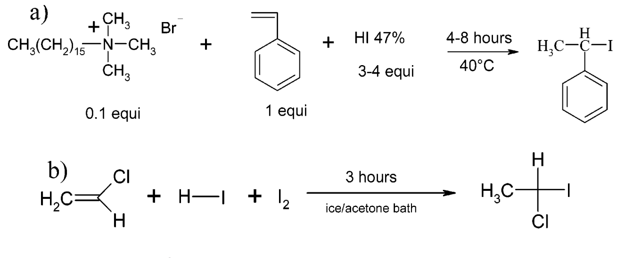
This section aims at summarizing the whole range of iodinated CTAs, which were investigated in a radical process. Some examples of CTA syntheses are described. Noteworthy, iodinated CTAs can be classifed into two different groups: the fluorinated ones and the nonfluorinated ones. Despite the high number of publications on the syntheses of CTAs, only three different pathways have been described so far to obtain iodinated CTAs: the addition of HX onto vinyl monomers, the addition of ICl onto fluoroalkenes, and the nucleophilic substitution. ω-Iodofluorinated CTAs can also be prepared by telomerization of fluoromonomers with iodinated transfer agents. However, this last synthetic strategy will be developed in section 3.2. Finally, the synthesis of iodinated CTAs by a radical pathway through the use of molecular iodine as a radical scavenger will be presented in section 4.4.

2.1. Addition of HX onto Monomers

The addition of HX (X = Cl, Br, I) to monomers has attracted the interest of many investigations.[2−5] One of the most exciting surveys has involved vinyl ethers for their living cationic polymerization. The combination of HI/I_2 was described as a very effective initiator/coinitiator system for this type of polymerization and was used to synthesize well-defined telechelics,[6,7] macromonomers,[8,9] and block copolymers.[10] Similarly, fluorinated vinyl ethers have also been used successfully by Vandooren et al.[11] The first step in such a polymerization involves the addition of HI onto the double bond yielding the corresponding 1-(1-iodoethoxy)alkane: $H_3C-CHI-OR$. As a matter of fact, the use of such a kind of monoadduct has also offered interesting research in the field of radical polymerization.

Although HI seems to behave as a good cocatalyst in the polymerization of styrene (Sty),[11,12] the additions of HX to Sty,[13−15] to MMA,[16] or to ethyl acrylate[11] also led successfully to the formation of the $CH_3CR_1R_2X$ monoadduct. For instance, Gaynor et al.[13] used this method to synthesize 1-phenyl ethyl iodide from hydriodic acid and Sty, the quaternary ammonium behaving as a phase transfer catalyst (reaction a of Scheme 1). Another example was suggested by Bak et al.[17−19] for the synthesis of 1-chloro-1-iodoethane (reaction b of Scheme 1) from the additions of HI onto vinyl chloride,[18] while that onto vinylidene fluoride (VDF)[20] was also successfully achieved. Although 1-iodo-1-chloroethane was involved in controlled radical polymerization (CRP) of vinyl chloride,[18] to our knowledge, no similar ITP has been done on VDF.

Scheme 1. Synthesis of Alkyl-Iodinated CTAs by Addition of HI

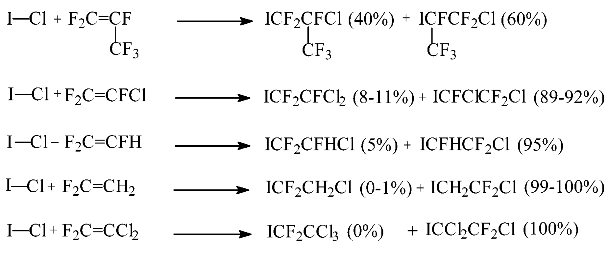


2.2. Addition of Iodine Monochloride onto Fluoroalkenes

Unlike the addition of I−F onto fluoroalkenes, which led to scarce research,[21,22] the addition of iodine monochloride (ICl) onto these halogenated olefins has been achieved by many authors.[23−28] However, in the case of asymmetric alkenes, these authors paid little attention to the presence of nonexpected byproduct arising from the reverse addition. Taking into account that the polarity of iodine monochloride is $^{\delta+}I{\cdots}Cl^{\delta-}$ and regarding polar, ionic, and steric effects, the formation of reverse isomer cannot be neglected.

For this reason, the comparison of the reactivities of various fluoroalkenes, such as chlorotrifluoroethylene (CTFE),[24] trifluoroethylene (TrFE),[29] VDF,[25] hexafluoropropylene (HFP),[23] and 1,1-difluorodichloroethylene,[23] was deeply studied in the presence of iodine monochloride. In most cases, the different radical initiations (photochemical, thermal, and the use of redox catalysts or radical initiators) were investigated and the following results are summarized in Scheme 2. Interestingly, it is observed that the lower the fluorine content of the fluoroalkene, the higher the selectivity.

Scheme 2. Reactivity of Various Fluoroalkenes with Iodine Monochloride

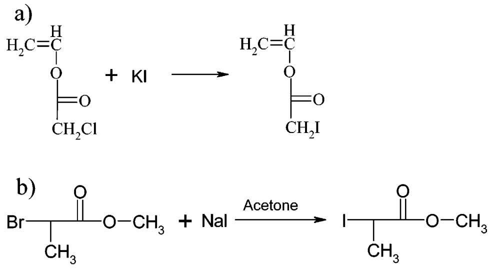


The monoadduct was obtained in all cases, leading to original activated telogens containing CF_2I or better, a CFClI end group.[23,24] The addition of ICl to 1,1-dichlorodifluoroethylene was found to be regioselective[23] as in the case of the addition onto CTFE[24] (Scheme 2). The use of a catalyst (e.g., iron) affects the yield and the amount of byproduct. HFP requires heat, unlike other monomers.[23] Hence, the decreasing reactivity series about ICl can be suggested as follows: CTFE > TrFE > VDF > $CF_2 = CCl_2$ > HFP.

2.3. Nucleophilic Substitution

The nucleophilic substitution of the corresponding chlorinated or brominated molecules can involve an iodide salt (reaction a of Scheme 3). Teodorescu[30] explained the synthesis of vinyl iodoacetate by reaction of vinyl chloroacetate with an iodide salt. A similar route was used by Iovu and Matyjaszewski[31] who synthesized methyl-2-iodopropionate from the methyl-2-bromopropionate in acetone (reaction b of Scheme 3).

Scheme 3. Synthesis of Alkyl-Iodinated CTAs by Nucleophilic Substitution



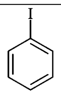
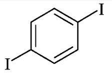
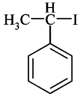
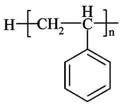
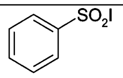
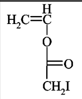
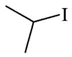
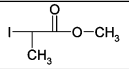
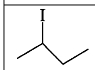
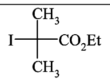
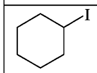
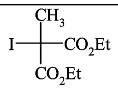
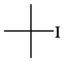
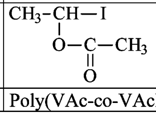
Unlike fluorinated CTAs, most nonfluorinated transfer agents[15,18,19,30−46] are rather easy to synthesize and their chemical structure enables an easy transfer of the iodine atom to the propagating polymer chain while the resulting radical is stabilized by either inductive/polar or resonance effects. Such reasons, their low price, their solubility in organic solvents, and the good control results make them an obvious choice for many different applications (Table 1).

2.4. Structural Requirements of CTAs

Some structural requirements have to be taken into account for efficient transfer of alkyl iodides. Indeed, because the propagating chain must first abstract the iodine atom from the transfer agent, the chemical structure of R−I transfer agent is quite important. To ensure that there is no great variation in free energy, one usual way lies on the preparation of a transfer agent that mimics the propagating chain end.[47] In the case where the transfer of the iodine atom from the transfer agent to the propagating radical involves no change in free energy, the transfer reaction is thermodynamically neutral (DT).[13,48] Preferably, the C−I bond should be labile enough[31] to allow an easy transfer of the iodine atom to the propagating radical. To this aim, the R group should stabilize the resulting radical through inductive or resonance effects.

Starks,[36] in his comprehensive study of the telomerization reactions, explained that the activity of telogens toward chain transfer depends on both the nature of the atom being abstracted (the decreasing order has been proposed as follows: I > Br > Cl ∼ H) and the other substituents on the telogen that stabilize the telogen radical (the decreasing series was suggested as follows: CN ∼ CO_2R > Br ∼ Cl > F > CH_3 > H). It is also evidenced that primary end groups are less effective[44] than secondary ones. Therefore, head to

Table 1. Nonfluorinated Iodocompounds Used as CTAs

Transfer Agent	Ref.	Transfer agent	Ref.
CI_4	13		13,17,36
CHI_3	13,34,35,37,38		13
CH_2I_2	13,36,38	1,4-bis(2-iodoethyl)benzene	13
CH_3-I	13		13,16,47
$ClCH_2$-I	17,35		15
CH_3-CHCl-I	17-19		39
CH_2I-CH_2I	17	$NCCH_2$-I	13,17,40,41
nC_8H_{17}-I	42	EtO_2CCH_2-I	31,40,44,45
nC_3H_7-I	13,36	 $H_2C{=}CH{-}O{-}C({=}O){-}CH_2I$	30
	13,17,36	 $I{-}CH(CH_3){-}C({=}O){-}O{-}CH_3$	31
	17	 $I{-}C(CH_3)_2{-}CO_2Et$	40
	17	 $I{-}C(CH_3)(CO_2Et)_2$	40
	13	 $CH_3{-}CH(I){-}O{-}C({=}O){-}CH_3$	38,41,46
POE-OC(O)-CH_2I	33,305	Poly(VAc-co-VAcI)	32

head additions tend to decrease the transfer rate, by changing a secondary end group into a less effective primary end group.

Thus, a wide range of iodinated transfer agents can be prepared. Nevertheless, it must be emphasized that these molecular iodinated compounds are often UV light- and heat-sensitive and can be prone to decomposition under storage. Consequently, special care should be paid to purify them prior to use.

Preferably used transfer agents include iodoform, 1-phenyl ethyl iodide, ethyliodoacetate, and iodoacetonitrile (Table 1). Those transfer agents fit well to the best structural requirements. They all possess a labile carbon−iodine bond, and the radical resulting from the abstraction of the iodine atom is stabilized either by inductive/polar effect or by resonance effect. For example, while iodomethane or diiodomethane[13] did not lead to a good control of the polymerization, iodoform[13,34,35] behaved as a successful transfer agent. Both supplementary iodine atoms in iodoform induced a very strong inductive effect, which lowers the activation energy and allows the rate of transfer to be comparable to the rate of propagation. In 1-phenyl ethyliodide and iodoacetonitrile, the delocalization of the radical after the abstraction of the iodine atom stabilizes the resulting radical and enables an easier abstraction of the iodine atom.

Concerning fluorinated CTAs, perfluoroalkyl iodides R_FI have been used as telogens with most fluoroalkenes. Extensive kinetic research on the synthesis of monoadducts was performed by Tedder and Walton.[49] From various results of the literature,[21,50−52] the decreasing reactivity scale about R_FI may be proposed as follows: VDF > TFE > $F_2C = CFH$ > HFP > CTFE. For less reactive monomers, the more electrophilic the telogen radical is, the more difficult the reaction is. This reaction is deeply investigated in the next section corresponding to the telomerization reactions of fluoroalkenes in the presence of fluorinated CTAs.

2.5. Conclusion

This section depicts the whole range of iodinated transfer agents and especially their syntheses. Iodinated transfer agents can be either fluorinated or nonfluorinated ones. The syntheses are rather simple and usually consist of an addition of HI or ICl onto a vinylic double bond. However, unlike nonfluorinated monomers, their addition onto fluoroalkenes often leads to two isomers. Interestingly, it was observed that lowering the fluorine content of the fluoroalkenes increases the regioselectivity.

Finally, another way for obtaining iodinated compounds consists of replacing the halogen atom (Br or Cl) of the molecule by an iodine atom by reaction with an iodide salt. However, this last method cannot be applied to fluoro compounds due to the strong inductive withdrawing electronic effect of the fluorine atoms. Such a nucleophilic substitution is also highly difficult to carry out onto precursors bearing tertiary carbons in α-position of the halogen atom. Hence, the competitive elimination of HX often occurs and cannot allow their use as CTA in radical polymerization.

In most cases, the resulting radical from the scission of iodide radical, $I^\bullet$, is similar to that of a growing radical, provided by polymerization of vinyl monomers, i.e., styrenic, acrylates. This certainly enables CRPs of the corresponding monomers in the presence of iodinated transfer agents. However, in the case of nonsymmetrical fluoroalkenes, it is not obvious to direct the radical polymerization in the presence of fluorinated transfer agents since two isomers can be produced by addition onto the double bonds and one of both may slow or even stop the polymerization.

3. Telomerization Reactions

Before the occurrence of CRPs, and especially ITP, the first radical polymerizations performed in the presence of iodinated CTAs were mainly telomerization reactions. Only few studies dealt with the use of iodinated CTAs in the telomerizations of nonfluorinated monomers. Indeed, most of works aimed at synthesizing fluorotelomers in the presence of fluoroiodinated CTAs. In this part, we focus on the telomerizations of fluorotelomers with fluoroiodinated CTAs.

A lot of fluoroalkenes have been involved in telomerization reactions leading to fluorinated polymers regarded as high value-added materials, due to their outstanding properties, which open up various applications.[53−56] Such polymers show low intramolecular and intermolecular interactions, which lead to low cohesive energy and therefore to low surface energy. They also exhibit high thermostability and chemical inertness, low refractive index and friction coefficient, good hydrophobicity and lipophobicity, valuable electrical properties, and low relative permittivity. In addition, they are nonsticky, resistant to UV, aging, and concentrated mineral acids and alkalies. Hence, their fields of applications are numerous:[53,57−61] paints and coatings (for metals, wood, leather, stone, optical fibers, and antifouling), textile finishings, novel elastomers,[56] high-performance resins, membranes, surfactants and fire-fighting agents, functional materials (for photoresists or microlithography, optical fibers, and conductive polymers), biomaterials, and thermostable polymers for aerospace. It was thus worth finding a model for the synthesis of fluoropolymers in order to predict their degree of polymerization, their structure (especially the defects of chaining when the monomeric precursor is nonsymmetrical), and the mechanism of the reaction.

One of the most interesting strategies is that of telomerization. Introduced for the first time by Hanford and Joyce in 1948,[62] this reaction usually leads to low molar mass polymers, called telomers, or even to monoadducts with well-defined end groups. Such products are obtained from the reaction between a telogen or a transfer agent (X−Y) and one or more (n) molecules of a polymerizable compound M (called taxogen or monomer) having ethylenic unsaturation, under radical polymerization conditions, as follows:

$$\mathrm{X{-}Y} + n\mathrm{M} \xrightarrow{\text{free radicals}} \mathrm{X{-}(M)}_n\mathrm{{-}Y}$$

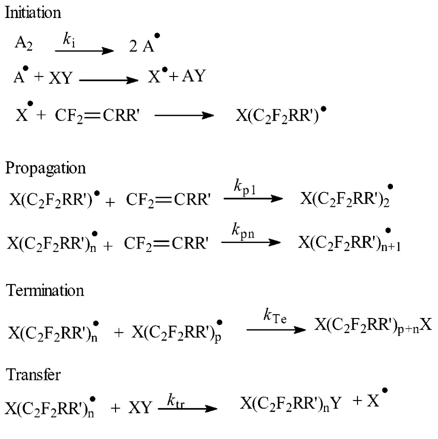
Telogen X−Y can be easily cleavable by free radicals (formed according to the conditions of initiation) leading to an $X^{\bullet}$ radical, which will be able to react further with a monomer. Telomers are intermediate products between organic compounds (e.g., $n = 1$) and macromolecular species ($n = 100$).[53] Hence, in certain cases, end groups exhibit a chemical importance, which can provide useful opportunities for further functionalizations.

The scope of telomerization was first outlined by Friedlina et al.[63] in 1966 and then improved upon by Starks in 1974.[36] Recently, we have summarized such a reaction[53] in which mechanisms and kinetics of radical and redox telomerizations have been extensively described.

3.1. Initiation and Mechanisms

A telomerization reaction is the result of four steps: initiation, propagation, termination, and transfer. These four steps have been described in previous reviews[36,64,65] and are summarized in Scheme 4 where XY, $F_2C{=}CRR'$, k_i, k_{p1}, k_{Te}, and k_{tr} represent the telogen, the monomer, the rate constant of initiation, the rate constants of propagation, termination, and transfer, respectively.

Scheme 4. General Mechanism of Telomerization



The kinetic law, regarding the reverse of the average degree of telomerization, $1/\overline{\mathrm{DP}}_n$, depends on the transfer constant of the telogen (C_{XY}), the telogen [XY], and the monomer [M] molar concentrations, as shown below taking into account both high and low average degrees of telomerization. (i) For high $\overline{\mathrm{DP}}_n$,

$$\frac{1}{\overline{\mathrm{DP}}_n} = C_{XY}\frac{[\mathrm{XY}]}{[\mathrm{M}]} \text{ with } C_{XY} = \frac{k_{tr}}{k_p} \tag{1}$$

According to eq 1, transfer constants of various telogens were determined.[66]

(ii) For low $\overline{\mathrm{DP}}_n$, the activity of transfer of a telogen in the presence of a monomer is characterized by the transfer constants (or coefficients) $C_T^{\,n}$ [65] that may be defined for each growing telomeric radical as the ratio of the transfer rate constant of the telogen k_{tr}^n to the rate constant of propagation k_p^n (eq 2):

$$C_{XY}^n = \frac{k_{tr}^n}{k_p^n} \tag{2}$$

3.1.1. Redox Catalysis

In the case of telomerization with redox catalysis (Table 2),[36,62,67,68] a metallic complex M_tL (M_t is the metal and L represents the ligand) is added. The kinetic law applied to redox telomerization depends on both the transfer constants of the catalyst and the telogen, but the former one is much greater (eq 3):

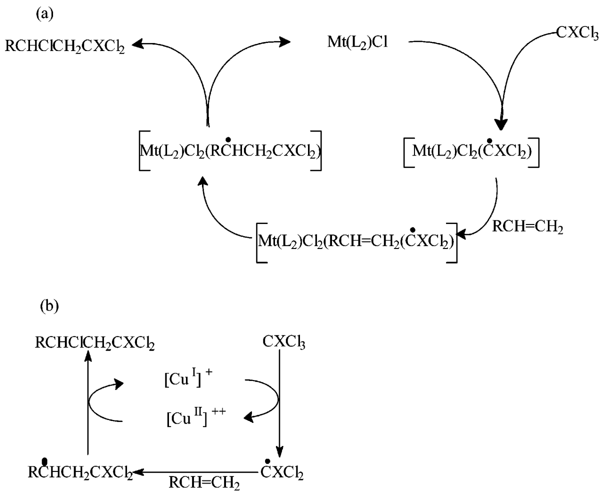
Table 2. Transfer Constants of Catalysts C_{Mt} and Telogen C_{CCl_4} with Redox Telomerization of CTFE with CCl_4[67]

nature of the catalyst	C_{Mt}	C_{CCl_4}
$FeCl_3$/benzoin	75	0.02
CuCl	700	0.02

$$\frac{1}{\overline{\mathrm{DP}}_n} = C_{Mt}\frac{[\mathrm{M_tL}]}{[\mathrm{M}]} + C_{XY}\frac{[\mathrm{XY}]}{[\mathrm{M}]} \tag{3}$$

As noted in both radical and redox mechanisms of telomerization of fluoroalkenes, termination reactions always occur by recombination and not by disproportionation (Scheme 5). In addition, it has been shown that, for the same

Scheme 5. General Mechanism in Redox and Catalytic Process: (a) Catalytic Process and (b) Redox



telogen and fluoroolefin, a radical telomerization leads to higher molar mass than those obtained from redox catalysis.

3.1.2. Thermal Initiation by Telogen Decomposition

In certain conditions, sufficient energy supplied by temperature causes scission of the X−Y bond of the telogen (Initer concept). Interesting examples concern the use of R_F-Is in which the energy of the C−I bond is 45 kJ mol^{-1}.[69]

The mechanism is rather similar to that of the radical telomerization except for the initiation step in which the radicals are produced from the telogen under temperature, as follows:

$$X{-}Y \xrightarrow[\Delta]{} X^{\bullet} + Y^{\bullet}$$

$$X^{\bullet} + CF_2{=}CRR' \rightarrow XC_2F_2RR''^{\bullet}$$

Regarding the reactivity, breakthroughs were achieved by Dolbier[69] who comprehensively reviewed the syntheses, structures, reactivities, and chemistry of fluorine containing-free radicals in solution. He also reported the influence of the fluorinated substituents on the structure stability and the reactivity of (per)fluoro-*n*-alkyl and branched chain (per)-fluoroalkyl radicals and supplied an interesting strategic overview of all aspects of organofluorine radical chemistry. In addition, this review also gives a summary of relative rates of addition of various radicals onto some fluoroethylenes and especially the following increasing series of electrophilicity first suggested by El Soueni et al.:[70] $CF_3^{\bullet} < CF_3CF_2^{\bullet} < C_2F_5CF_2^{\bullet} < nC_3F_7CF_2^{\bullet} < nC_5F_{11}CF_2^{\bullet} < (CF_3)_2CF^{\bullet} < (CF_3)_3C^{\bullet}$.

3.1.3. Cotelomerization

In cotelomerization, the problem is slightly more complex and the kinetics have been little investigated. However, the equation proposed by Tsuchida[71] relating the instantaneous $\overline{DP}_n$ vs the kinetic constants has been confirmed[72] (eq 4):

$$(\overline{DP}_n)_i = (r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)/(r_1C_{T1}[M_1][T] + r_2C_{T2}[M_2][T]) \quad (4)$$

where $[M_i]$, [T], r_i, and C_{Ti} represent the concentrations of the monomer M_i and of the telogen, the reactivity ratio of the monomer M_i ($r_i = k_{ii}/k_{ij}$), and the transfer constant of the telogen to the monomer. Furthermore, for known r_i, the conversions α_1 and α_2 of both monomers vs time could be determined.

The composition of the cotelomer, i.e., the proportion of monomer units in the cotelomer, can be predicted for known kinetic constants r_i and from $[M_i]_0$ according to the statistical theory of the copolymerization. Moreover, the probability to obtain cotelomers of well-defined composition and then the functionality of the cotelomer were calculated.

3.2. Fluoroalkenes Used in Telomerization Reactions

This section contains two main parts: The first one deals with the telomerization of most used fluorolefins (VDF, TFE, CTFE, TrFE, and HFP), and the second one deals with scarcely utilized fluoroalkenes (vinyl fluoride, 3,3,3-trifluoropropene, and 1,1-difluoro-2,2-dichloroethylene).

3.2.1. VDF

VDF (1,1-difluoroethylene or VF_2), regarded as nontoxic, nonhazardous, more safe to handle [in contrast to tetrafluoroethylene (TFE) or TrFE], and environmentally friendly (since it does not contain any chlorine or bromine atoms), can easily polymerize under radical initiation.[73] In addition, it is a nonsymmetrical alkene and its propagation may lead to a certain content of defect (i.e., tail to tail or head to head) of VDF chaining. Many authors have investigated the telomerization of VDF.[53] Almost all kinds of transfer agents have been used, requiring various means of initiation: thermal, photochemical, or from systems involving redox catalysts or radical initiators.[68] Table 3 summarizes the different initiation ways for the telomerization of VDF with alkyl iodides.[25,67,74−94]

Table 3. Telomerizations of VDF with Iodinated Transfer Agents[a]

telogen	method of initiation	structure of telomers	refs
ICl	various initiations	$ClCF_2CH_2I$	25
HI	thermal	CH_3CF_2I	91
CH_3I	UV	$CH_3CH_2CF_2I$	90
CF_3I	UV, 28 days/RT	$CF_3(VDF)_1I$	89
	UV/0−100 °C	$CF_3(C_2F_2H_2)I$	88
	UV/140 °C	$CF_3CH_2CF_2I$ (major) $CF_3CF_2CH_2I$ (minor)	85
	TBPPI	$CF_3(VDF)_nI$; $n = 10−30$	87
CF_2HI	UV	$HCF_2CH_2CF_2I$	86
iC_3F_7I	185−220 °C	$iC_3F_7(VDF)_nI$; $n = 1−5$	79−81
nC_3F_7I	20 h/UV/140−210 °C	$nC_3F_7(C_2F_2H_2)I$	85
$(CF_3)_3CI$	thermal	$(CF_3)_3C(VDF)_nI$, $n = 1, 2$	84
C_4F_9I	230 °C/15 h	$C_4F_9(VDF)_nI$	83
	AIBN, $scCO_2$	$C_4F_9(VDF)_nI$; $n = 1−9$	82
	$FeCl_3$/Ni	$C_4F_9CH_2CF_2I$	79, 80
$C_pF_{2p+1}I$, $p = 1−8$	180−220 °C	$C_nF_{2p+1}(VDF)_nI$; low n	79−81
$C_5F_{11}CFICF_3$	180−190 °C	$C_5F_{11}CF(CF_3)(CH_2CF_2)_nI$	79
$ClCF_2CFClI$	181 °C/26 h	$ClCF_2CFCl(VDF)_nI$	78
ICH_2I	DTBP/130 °C	$ICH_2{-}CH_2CF_2I$ (91%)	77
ICF_2I	LTA/70 °C	$ICF_2CH_2CF_2I$	76
$I(C_2F_4)_nI$, $n = 1−3$	180 °C or rad	$I(VDF)_p(C_2F_4)_n(VDF)_qI$; variable $p + q$	75
PFPE-I	DTBP, 140 °C	diblock $PFPE(VDF)_nI$; $\bar{n} = 5−50$	74

[a] Abbreviations: RT, room temperature; sc, super critical; DTBP, di-*tert*-butyl peroxide; LTA, lead tetraacetate; TBPPI, *tert*-butylperoxy pivalate; and PFPE, perfluoropolyether group.

Almost all R_FIs and α,ω-diiodoperfluoroalkanes (IR_FIs) were successfully utilized in thermal telomerization of VDF. One of the pioneers of such work was Hauptschein et al.[95] (who used CF_3I, C_2F_5I, *n*-C_3F_7I, *i*-C_3F_7I, $ClCF_2CFClI$, and $ClCF_2CFICF_3$ at 185−220 °C) leading to high telogen conversions. Later, Apsey et al.[81] and Balagué et al.[79,80] used *i*-C_3F_7I and linear $C_nF_{2n+1}I$ ($n = 4, 6, 8$) telogens, leading to telomeric distributions, with a better reactivity of the former branched transfer agent. We have shown that, while the monoadduct exhibits only the structure $R_FCH_2CF_2I$, the diadduct is composed of two isomers,[79,80] while the triadduct had a rather complex structure.[96]

Usually telomeric distributions are obtained in good yields, with more or less high $\overline{DP}_n$ according to the nature of the telogen (and especially the electrophilicity of the radical generated), and the experimental conditions (initial pressures, [VDF]/[telogen] molar ratios, and temperatures).

Various iodinated telogens have been used in the radical initiation reaction: $ClCH_2I$, CH_2I_2,[85] CH_3I,[90] CF_3I,[87] $ClCF_2$-$CFClI$,[78] C_4F_9I,[82] and $I(C_2F_4)_nI$ (with $n = 1, 2$, and 3). C_4F_9I was used in the telomerization of VDF in the presence of AIBN in supercritical carbon dioxide as the solvent.[82] More recently, VDF telomers obtained from CF_3I were characterized by ^{19}F nuclear magnetic resonance (NMR) spectroscopy and by matrix-assisted laser desorption ionization time-of-flight MS (MALDI-TOF MS)[87] as the first example on a perfluoroaromatic matrix and were silver cationized (Figure 1). Interestingly, the assessment of the average molar mass in number and in weight ($\bar{M}_n = 1240$ and $\bar{M}_p = 1250$, respectively, which also confirmed those obtained by ^{19}F NMR spectroscopy) enabled us to demonstrate that narrow polydispersity indices (PDI = 1.09) were obtained.

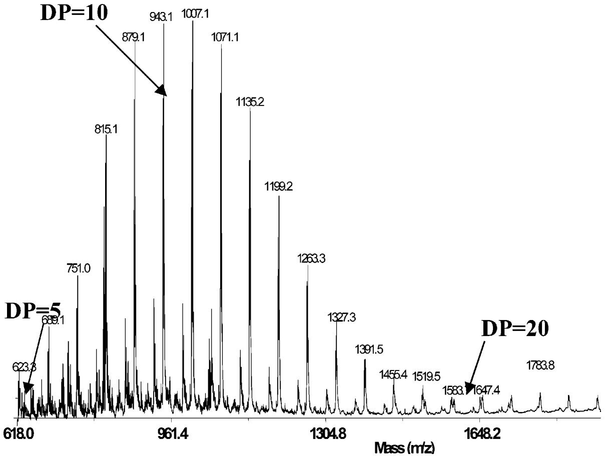


Figure 1. MALDI-TOF MS of PVDF obtained by radical telomerization of VDF with CF_3I.[87]

Similarly, electron spray ionization was realized on VDF[97] and CTFE[98] telomers. The photoinduced telomerization of VDF was pioneered in 1954 by Haszeldine[89] who used CF_3I as the transfer agent leading to the monoadduct. Cape et al.[85] studied the same reaction at 140 °C for 12 h and determined the Arrhenius parameters for the addition of $CF_3^\bullet$ radicals to both sites of VDF. The activation energy of the isomer $CF_3CH_2CF_2I$ was about three times higher than that of $CF_3CF_2CH_2I$. VDF and I−Cl were photolyzed producing ICH_2CF_2Cl as the sole product in fair yield.[25] This monoadduct was characterized from ^1H and ^{19}F NMR spectra of CH_3CF_2Cl, obtained after reduction with $SnBu_3H$.

Few studies were realized on redox telomerization from C_4F_9I and $FeCl_3$/Ni; only $C_4F_9CH_2CF_2I$ was obtained in a 55% yield.[79,80] The structure of this monoadduct is the same as that produced by thermal initiation. Such a selectivity was confirmed by Chen and Li[76,99] who obtained $ICF_2CH_2CF_2I$ from ICF_2I in the presence of lead tetraacetate.

3.2.2. TFE

TFE is obviously the most used monomer in telomerization because of the best compromise between its good ability to polymerize (in comparison to other monomers) and the properties of the perfluorinated chains obtained. Furthermore, because of its symmetry, there are no problems of regioselectivity or defects in chaining. However, it is the most difficult to handle because of its hazardous behavior toward oxygen and under pressure.

Whatever the ways of initiation, successful results have been obtained involving all kinds of telogens.[53] A summary of the literature is listed in Table 4 corresponding to photochemical, thermal, radical, redox, and miscellaneous initiations.[20,23,27,49,51,85,100−116]

For the industrial scale, thermal telomerization appears the most widely used, probably because of the thermal stability of the fluorinated telomers produced. Moreover, it is well-recognized that the good reactivity with redox catalysts leads to low molar mass telomers, as for thermal initiation at high temperature. On the other hand, thermal initiation at low temperatures and chemically induced radical telomerization provide telomers with high $\overline{DP}_n$ and wider polydispersities.

Table 4. Telomerizations of Fluoromonomers with Iodinated Transfer Agents

fluoromonomer	telogen	conditions	refs
TFE	CF_3I	UV	100
	C_3F_7I	190−240 °C	51
	$I(C_2F_4)_nI$	230 °C	101
	C_2F_5I	Cu/80 °C	102
CTFE	$ClCF_2CCl_2I$	140 °C	23
	$ClCF_2CFClI$	UV	27
	CF_3I	UV	103
TrFE	$(CF_3)_2CFI$	$h\nu$	104
	$(CF_3)_2CFI$	γ-rays	105
	CF_3I	$h\nu$	106
	$C_nF_{2n+1}I$ ($n = 4, 6, 8$)	180−190 °C	107
HFP	CF_3I	UV	49
	$ClCF_2CFClI$	200 °C	108
	$C_4F_9(C_3F_6)I$	250 °C	109
	$IC_2F_4CH_2CF_2I$	210 °C	110
Vinyl fluoride	CF_3I	UV	85
	$(CF_3)_3I$	UV	111
TFP	CF_3I	UV	20
	CF_3I	225 °C	20
	$C_6F_{13}I$	DTBP	112−114
	$(CF_3)_2CFI$	DTBP	112−114

3.2.3. CTFE

The telomerization of CTFE with iodinated telogens has been investigated by many authors.[21−23,52,117] To increase the reactivity of the telogens having C−I groups, the authors have introduced one or two chlorine atoms into the iodinated extremity. The synthesis of these new products is by addition of IX (X being Cl or F) to chlorofluoroalkenes as shown in Scheme 6. Another special mention is stressed for the addition of IBr onto CTFE that led to the formation of four products: expected $ICFClCF_2Br$, $BrCFClCF_2I$, and unexpected ICF_2CFClI and $BrCF_2CFClBr$.[118]

Scheme 6. Synthesis of New Transfer Agents by Addition of IX onto Chlorofluoroalkenes

$$ICl + Cl_2C{=}CF_2 \longrightarrow ICCl_2CF_2Cl + \text{traces of } Cl_3CCF_2I$$

$$IF + Cl_2C{=}CF_2 \longrightarrow ICCl_2CF_3 + \text{traces of } Cl_2CFCF_2I$$

$$IF + ClCF{=}CF_2 \longrightarrow ICFClCF_3 + \text{traces of } ICF_2CFCl_2$$

Thus, versatile telogens have been produced with an increased activation of the cleavable bond. In fact, in 1955, Haszeldine[27] already observed a kind of controlled character of the telomerization of CTFE according to the following reaction:

$$ClCF_2CFClI + F_2C{=}CFCl \rightarrow Cl(CF_2CFCl)_nI$$

However, no deeper investigation was carried out to check whether (DP_n) vs conversion showed a linear relationship and narrow PDIs. Nonexhaustive studies dealing with the telomerization of CTFE with these above telogens are summarized in Table 4.

In contrast to the telomerization of TFE with R_FIs, the addition of these telogens to CTFE has not been fully investigated. This may be explained by the fact that the $R_F(CF_2CFCl)_nI$ telomers produced are more efficient telogens than the starting R_FI transfer agents (as seen in the previous section) since CFCl−I bond can even be more easily cleaved than CF_2−I bond. Table 4 sums up the results in the literature.

When CF_3I is used as the telogen, two isomers can be produced since the addition of $^{\bullet}CF_3$ radical onto CTFE[103,119] led to CF_3CF_2CFClI (mainly, 90%) and $CF_3CFClCF_2I$. Interestingly, Gumbrech and Dettre[120] used a mixture of $(C_2F_5CO_2)_2$ and CHI_3 (as a iodine donor) to obtain of $C_2F_5(C_2F_3Cl)_nI$ telomers, although a rather high $\overline{DP_n}$ (ca. 13) was observed.

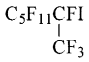
Redox catalysis provides lower molar mass telomers. However, some transfers from the catalyst (CuCl, $CuCl_2$, or $FeCl_3$) occurred and led to byproducts.[121] It can be concluded from all of these results that the reaction between R_FI and CTFE is very complex and difficult to perform successfully.

3.2.4. TrFE

One of the most known developments of this monomer concerns its interesting copolymers with VDF for piezoelectrical properties. Unlike the above fluoroalkenes extensively used in polymerization and telomerization, TrFE has been investigated in telomerization by few authors (Table 4).[104−106] Although both XCF_2CFHY and $XCFHCF_2Y$ isomers have been produced in most cases, Bissel[26] investigated the redox telomerization of TrFE with iodine monochloride and observed the selective formation of $ClCF_2CFHI$ as the sole product. When thermal or photochemical initiations were used, this isomer was the major product (95−97%) but the reverse $ClCFHCF_2I$ was also observed.[29]

With regards to the reactivity of free radicals produced from various telogens [especially (per)fluoroalkyl iodides] to TrFE, the electrophilic character of the (per)fluoroalkyl radical generated has a great influence on the proportion of reverse adduct. It was noted that the higher its electrophilicity, the higher the amount of “normal” isomer as shown in the thermal telomerization of TrFE with various fluoroalkyl iodides (Table 5).

Table 5. Thermal Telomerization of TrFE with Various Fluoroalkyl Iodides Transfer Agents and Percentages of R_FCF_2CFHI Reversed Adducts

Transfer agent	Amount of normal adduct (%)	Amount of reversed adduct (%)
$C_4F_9CH_2CF_2I$	60	40
C_4F_9I	75	25
$(CF_3)_2CFI$	90	10
 $C_5F_{11}CFI(CF_3)$	93	7

3.2.5. HFP

HFP is known to be telomerized or polymerized with difficulty. Nonexhaustive results illustrating telomerizations of HFP are listed in Table 4.[49,122,123] Among transfer agents involving a C−I bond, for trifluoroiodomethane, the wavelength λ plays an important role on the telomeric distribution since at $\lambda < 3000$ Å only $CF_3C_3F_6I$ was formed whereas at higher wavelengths, the two first telomers were produced.[111] An interesting comparison between photochemical and radical initiations was made by Low et al.,[124] who studied the competitive addition of CF_3I to HFP and ethylene (E) at different temperatures (up to 170 and 189 °C from di-*tert*-butylperoxide and UV-induced reactions, respectively). These authors noted that in all cases $CF_3C_2H_4I$, $CF_3(C_3F_6)I$, and $CF_3(C_3F_6)C_2H_4I$ were formed. The two last products are composed of two isomers, the normal one ($CF_3CF_2CFICF_3$) being produced in a higher amount than the reverse one ($(CF_3)_2CFCF_2I$). They also observed that the higher the temperature, the higher the yield of these three products, and that below 140 °C, photochemical initiation was more efficient. Above this temperature, radical initiation led to better results. In addition, from UV-induced reaction, $CF_3(C_3F_6)I$ was always produced in the higher amount whereas the contrary was noted in the other process. By thermal initiation, except for ICl, which led to both normal CF_3CFICF_2Cl and reverse $CF_3CFClCF_2I$ isomers at 98 °C, with sometimes up to 40% of reversed adduct,[23] most other transfer agents required higher temperatures, especially higher than 200 °C.

The most interesting results, however, come from R_FIs or IR_FIs for which the terminal CF_2−I group has a lower bond dissociation energy than that of CF_2−Br. The pioneer of such investigations from 1958 was Hauptschein[95] who used CF_3I, C_3F_7I, and $ClCF_2CFClI$ as the transfer agents. The originality of such thermal telomerization is that the mechanism of this reaction does not proceed by propagation. The authors suggested that the mechanism is composed of a succession of addition steps according to Scheme 7.

Scheme 7. Telomerization of Hexafluoropropene in the Presence of nC_3F_7I[95]

$$n\text{-}C_3F_7I + F_2C{=}CFCF_3 \longrightarrow n\text{-}C_3F_7CF_2CFICF_3$$
$$n\text{-}C_3F_7CF_2CFICF_3 + F_2C{=}CFCF_3 \longrightarrow n\text{-}C_3F_7[CF_2CFCF_3]_2I \text{ and so on}$$

Among other fluorinated transfer agents, R_FCFClI telogens are more reactive than R_FCF_2I as shown by Hauptschein[95] or by Amiry et al.[22] Tortelli and Tonelli[101] and Baum and Malik[108] have shown the stepwise mechanism. However, we could not confirm the work of Haupstchein who showed that the thermal addition of *i*-C_3F_7I to HFP was as successful as that of linear transfer agents.[95] In our work, this telogen reacted with HFP in a low conversion, up to ca. 30% at 250 °C.[109] To confirm this result, the telomerization of HFP with the sterically hindered $C_4F_9(C_3F_6)I$, carried out at 250 °C for 48 h, led to 8% of $C_4F_9(C_3F_6)_2I$, although this was not in good agreement with Hauptschein’s results[95] in which better yields were obtained.

The nature of the autoclave greatly influences the formation of byproducts since for a vessel made of nickel, the addition of CF_3I to HFP led mainly to $(CF_3)_3CI$, whereas a similar reaction in a Hastelloy vessel did not yield any byproduct.

Thermal initiation appears the most efficient, especially for R_FI and IR_FI. The telomeric distribution is limited to the first two or three telomers, while the monoadduct is composed of two isomers, the amount of which depends on the temperature and the electrophilic character of the telogenic radical.

Interestingly, Tortelli and Tonelli,[101] Baum and Malik,[108] and more recently Boulahia et al.[125] succeeded in telomerizing HFP with IR_FIs leading to normal $I(C_3F_6)_x(CF_2)_nI$ and “false” $I(C_3F_6)_y(CF_2)_n(C_3F_6)_zI$ adducts (where x, y, or $z = 1$ or 2). Another unexpected example concerns the radical telomerization of HFP with $ICF_2CF_2CH_2CF_2I$ (i.e., the monoaduct from IC_2F_4I with VDF), which selectively led to $ICF_2CF_2CH_2CF_2CF_2CFICF_3$.[110]

Hence, apart from redox catalysis for which only one investigation has been reported, several types of initiation are possible when reacting HFP with various transfer agents. Usually, however, the reaction is rather selective since low molar mass telomers are produced.

3.2.6. Other Fluoroalkenes

Telomers of vinyl fluoride (Table 4) were obtained by Rondestvedt[126] who added $C_4F_9IF_2$ (prepared by reacting C_4F_9I onto Cl_3F) as the catalyst at 120 °C while telomers of 3,3,3-trifluoropropene (TFP) (this monomer was prepared for the first time by Haszeldine[127] by dehydroiodination of $F_3CCH_2CH_2I$) have led to more investigations. Nowadays, this fluoroolefin is commercialized by the Great Lakes (now Chemtura) Company, and more recently, extensive work has been carried out to produce original telomers of TFP with various CTAs (branched or linear R_FIs,[112−114] diethylhydrogenophosphonates, thiols, and methanol lead to the best yields). This confirms previous works from CF_3I under thermal or photochemical initiation, the latter being more selective than the former.[20] Low et al.[124] investigated this reaction under UV radiation at various temperatures and obtained a mixture of normal and reverse isomers for the monoadduct. They observed that a higher proportion of reverse derivative was formed at higher temperatures. In addition, they noted the formation of higher adducts above 175 °C.

The reactivities of $CF_3CH{=}CF_2$ and $CF_3{-}CF{=}CH_2$ with CF_3I have been compared by Haupstein et al.[128] Only the latter olefin leads to telomers, useful for hydraulic fluids, lubricants, and heat transfer media.[128] Similarly, $C_2F_5CF{=}CF_2$ has been telomerized thermally by Paciorek et al.[129] who suggested a probable mechanism. Longer perfluoroolefins, or perfluoroalkyl vinyl ethers, investigated by Paleta's group, mainly[130−132] led to monoadducts, as for the radical addition of R_FI onto $C_5F_{11}CF{=}CF_2$.

An interesting study concerns the addition of iodine monochloride to this olefin, producing exclusively $ClCF_2CCl_2I$ isomer at −10°C (Scheme 6). However, at higher temperatures and in the presence of iron as the catalyst, the Cl_3CCF_2I isomer was also produced, and the formation of chlorinated product $ClCF_2CCl_3$ was also observed under these conditions.[23] Surprisingly, the telomerization of 1,2-dichloro-1,2-difluoroethylene has never been achieved from iodinated transfer agents.

3.2.7. Cotelomerization

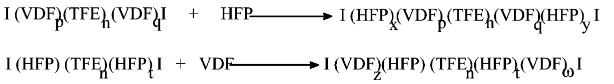
Interesting commercially available fluorinated copolymers are known for their excellent properties; most of them have been synthesized for use as elastomers[56] or thermoplastics.[133] The literature is abundant on the radical copolymerization of two fluorinated olefins or copolymerization of fluoroalkenes with nonhalogenated monomers (e.g., vinyl ethers[134,135]), regarded as electron withdrawing and electron donating, respectively. However, few articles or patents report the cotelomerization of fluoromonomers. Brace[136] provided interesting reviews on the radical addition of R_FIs to different kinds of monomers. In fact, two alternatives are possible as follows: either direct cotelomerization according to a kind of batch procedure or step-by-step or sequential addition. A few examples are given below.

Cotelomers produced by cotelomerization of CTFE and VDF seem to have attracted much interest because they constitute interesting models for Cefral, Foraflon, Kel F, or Solef copolymers.[56] First, Hauptschein and Braid thermally cotelomerized these olefins with CF_3I or $ClCF_2CFClI$[137,138] leading to cotelomers of random structure $ClCF_2CFCl[(CTFE)_n(VDF)_p]I$ where $n + p$ varies in the range of 3−20 depending on experimental conditions.

Furukawa[139] used R_FIs and IR_FIs as telogens for the synthesis of high molar mass cotelomers. Fluoroiodinated transfer agents were also used in ITP in a controlled way and have enabled Daikin,[140] Ausimont[141] (now Solexis), and DuPont[142] to produce novel fluorinated copolymers with targeted molar mass and narrow polydispersities.

Tatemoto and Nakagawa[143] started from iC_3F_7I under peroxide initiation to cotelomerize VDF and HFP, useful for the preparation of block and graft copolymers. Haupstchein and Braid[144] studied the cotelomerization of HFP and TFE with IC_3F_6Cl at 190−220 °C and obtained various molar mass cotelomers depending on initial molar ratios of the reactants.

Scheme 8. Synthesis of Poly(TFE-ter-VDF-ter-HFP) Terpolymer by Step-Wise Cotelomerization



$$I(VDF)_p(TFE)_n(VDF)_qI + HFP \longrightarrow I(HFP)_x(VDF)_p(TFE)_n(VDF)_q(HFP)_yI$$

$$I(HFP)(TFE)_n(HFP)_tI + VDF \longrightarrow I(VDF)_z(HFP)(TFE)_n(HFP)_t(VDF)_\omega I$$

Scheme 8 shows one typical example where the telomer formed acts as an interesting transfer agent for a further telomerization.[79] These oligo- or poly(TFE-ter-VDF-ter-HFP) tertelomers are interesting models for Dai-el, Fluorel, Kynar, Tecnoflon, and Viton elastomers.

3.3. Conclusion

This part summarizes the important number of investigations performed on the telomerization of well-known fluorinated alkenes with iodinated transfer agents. These fluorotelomers allow the synthesis of novel polymers bearing high fluorine content and hence are regarded as high value-added materials with usually exceptional properties.

The telomerization reaction appears as a powerful tool to prepare well-defined molecules, and their well-characterized end groups allow further key reactions. Although traditional polymerization media are still up to date, recent processes in clean (or green) media appear promising (e.g., in supercritical fluids). In addition, it is also an elegant model of (co)polymerization and the resulting telomers can also be used for the characterization of higher molar mass polymers. They can act as original standards for GPC or can be relevant in the assignments of chemical shifts in NMR spectroscopy (e.g., to determine the defects of chaining and the end groups in fluoropolymers[96]).

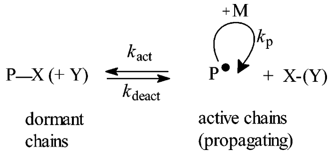
Much work still requires development and, especially, a better knowledge of the synthesis of tailor-made polymers with well-defined architecture in order to improve the properties by a better control of both the regioselectivity and the tacticity. Although many investigations on the reactivity have been extensively carried out by Tedder and Walton or by Dolbier, methods are searched for a better orientation of the sense of addition and either none or a high defect of chaining since most fluoroalkenes are unsymmetrical.

Hence, such systems should induce interesting consequences on the structures and on the properties of materials thus obtained. For example, in the case of fluoroacrylic monomers, it is well-known that the crystallization of perfluorinated chains ensures improvement of surface properties (see 5.1.2). These telomers are also interesting precursors of various fluoropolymers (such as telechelics and alternating, block, or graft copolymers).

4. ITP

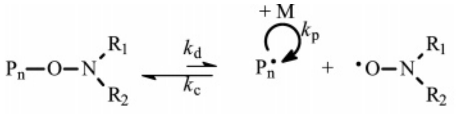
CRP includes a group of radical polymerization techniques that have attracted much attention over the past decade for providing simple and robust routes to the synthesis of well-defined polymers, low-dispersity polymers, and the preparation of novel functional materials.[145−159] The general principle 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); the rate constants are k_{act} and k_{deact}, respectively (Scheme 9).[160]

Scheme 9. General Scheme of Reversible Activation in CRP[160]

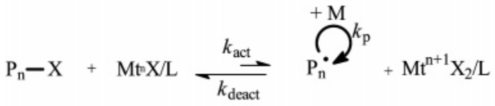


The past few years have witnessed the rapid growth in the development and understanding of new CRP methods.[149,157] The most efficient CRP methods are nitroxide-mediated polymerization (NMP) that requires alkoxyamines;[150] atom transfer radical polymerization (ATRP) involving alkyl halides, metallic salts, and ligands;[147,161−163] reversible addition−fragmentation chain transfer polymerization (RAFT) using dithiocarbonyl derivatives;[164] and ITP using alkyl iodides.[13] The respective specific mechanisms are briefly summarized in Scheme 10. It is noted that in Scheme 10c, that involves a xanthate, various authors sometimes refer to the “MADIX” process as claimed by the Rhodia Company,[165−167] which stands for macromolecular design through the interchange of xanthates.

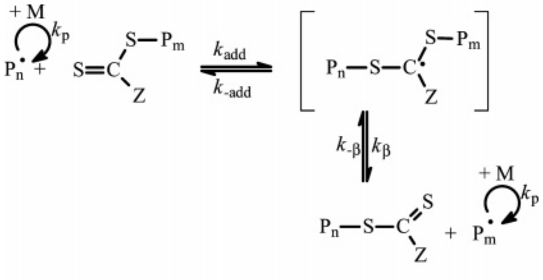
Scheme 10. Various Reversible Activation Processes Involved as Key Steps in the Process of CRP



(a) Nitroxide-mediated radical polymerization (NMP)



(b) Atom transfer radical polymerization (ATRP)



(c) Reversible addition-fragmentation chain transfer process

(RAFT and MADIX)

(d) Iodine transfer radical polymerization (ITP)

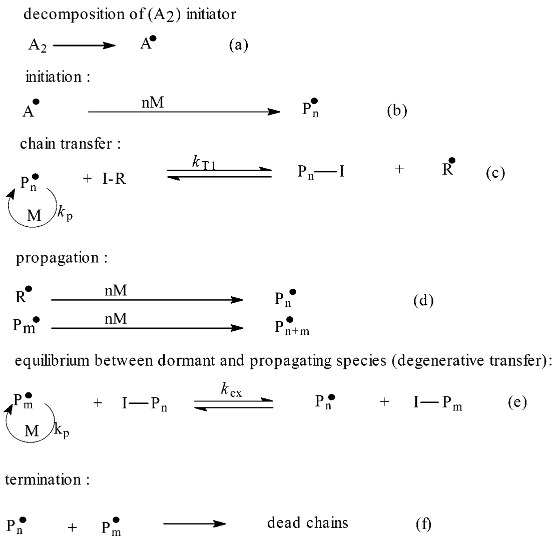
Two main mechanisms can be distinguished as follows: reversible termination (NMP, ATRP) and reversible transfer (RAFT, ITP). In reversible termination, the transient propagating radicals can recombine (irreversible termination) but it produces an excess of persistent species (nitroxyl radical, oxidized organometallic complex) (Scheme 10a,b), so that the reversible cross-termination is rapidly favored. Therefore, in reversible termination, the control of the polymerization can be achieved by the persistent radical effect.[152] In reversible transfer (RAFT, ITP), the whole process can be simplified to an exchange process with the apparent rate constant of degenerative chain transfer (DT) k_{exch} (Scheme 10c,d). In DT, the key parameters are the concentration of the transfer agent (to control the molecular weight) and the chain transfer rate constant (the higher the k_{exch} value, the lower the PDI of the polymer chains), as detailed later in this section. In reversible transfer, the RX transfer agent reacts with a propagating radical to form a P−X dormant polymer chain.[13] The expelled $R^•$ radical can then reinitiate the polymerization. The newly formed $P^•$ polymer chain can propagate or react with the transfer agent R−X or with the dormant polymer chain P−X. In reversible transfer, the concentration of the polymer chains is equal to the sum of the concentrations of the transfer agent and of the consumed initiator. Therefore, in DT, the contribution of the termination is significantly lowered under appropriate conditions (i.e., low concentration of consumed initiator).

This section focuses on the fundamentals of ITP as first called by Tatemoto[140] and then named “DT” process with alkyliodides by Matyjaszewski.[168] The mechanistic understanding of ITP is first discussed followed by the reactivity of several usual monomers toward iodocompounds in ITP.

4.1. Mechanistic Understanding of ITP

ITP is a DT polymerization requiring alkyl iodides.[13,47] ITP was developed in the late 1970s by Tatemoto et al.[1,169−171] at the Daikin Company. The mechanism of ITP with alkyl iodide is depicted in Scheme 11. The mechanism can be described as follows.[31] The initiating radical, $A^•$, generated by thermal decomposition of a conventional

Scheme 11. Elementary Steps in ITP



initiator (such as AIBN) in step a, adds onto M monomer, and the resulting radical propagates (step b). The exchange of iodine from the transfer agent, R−I, to the propagating radical, $P_n^{\bullet}$, results in the formation of the polymer alkyl iodide, P_n−I, and a new initiating radical, $R^{\bullet}$ (step c). Large differences in the stability of the reactants and products involved in step c could result in shifting the equilibrium overwhelmingly to the right [$K_{(c)} > 1$] or to the left [$K_{(c)} < 1$]. Therefore, the case when the structure of R closely looks like that of the propagating radical results in a nearly thermodynamically neutral transfer step [$K_{(c)} = 1$]. Activated transfer agents [$K_{(c)} > 1$] are preferred in order to create the dormant polymer chains early in the process. Poor transfer agents [$K_{(c)} < 1$] would result in a slow generation of new polymer chains all along the process, broadening the molecular weight distribution. In step d, $R^{\bullet}$, generated from the alkyl iodide or the $P_n^{\bullet}$, adds onto a monomeric unit and propagates. The exchange process described in step e is thermodynamically neutral because P_n and P_m propagating chains have the same structure [it is the so-called DT reaction whose corresponding equilibrium constant $K_{(e)}$ is worth 1]. As in any radical process, the termination occurs in ITP polymerization (step f). Minimizing the termination step remains essential to keep a good control of the polymerization. Ideally in ITP, to obtain polymer with a narrow molar mass distribution, the rate of exchange should be higher than that of the propagation.[13,15] The ratio between transfer and propagation rates is called transfer constant, C_T, which gives the intrinsic reactivity of the transfer agent.

Several techniques afford the calculation of C_T value. This is actually a crucial parameter to target the macromolecular architectures of the resulting oligomers. Noteworthy, this mechanism may be modified by using high temperature or UV, because the C−I bond may be cleaved to give $P^{\bullet}$ and $I^{\bullet}$ radicals. This reaction corresponds to the decomposition of the transfer agent. It was widely studied by Ameduri and Boutevin[53] concerning the synthesis of fluoro-oligomers obtained in the presence of perfluorinated iodocompounds. This process, which leads to low molar mass oligomers, has been deeply investigated in section 3.

4.1.1. Determination of the Transfer Constants

Several laws enable the assessment of the transfer constant value for conventional telomerization reactions.[172] For CRPs, such as ITP or RAFT, the assessment becomes more complex because the dormant chains also act as further transfer agents (Scheme 11). In the ITP mechanism, two different transfer reactions occur and it is necessary to well-differentiate these two reactions: (i) The first one is based on the transfer agent itself and is defined by the transfer constant C_{T1} ($C_{T1} = k_{T1}/k_p$); C_{T1} actually measures the activity of the iodinated transfer agent. (ii) The second one occurs between two polymer chains (DT) and is defined by the exchange constant C_{ex} ($C_{ex} = k_{ex}/k_p$). Unlike C_{T1}, C_{ex} is characteristic of the DT (i.e., the evolution of the molecular weight distribution vs monomer conversion). Noteworthy, an increase of C_{ex} leads to a lower PDI of the polymer chains.

Both of these constants are difficult to determine separately because the transfer reaction and the DT occur simultaneously. Nevertheless, it can be noted that if the iodinated transfer agent shows a similar structure to that of the polymer chains, C_{T1} and C_{ex} might be very close.

In the literature, different methods to obtain the transfer constants are mentioned and are reported below. However, these methods allow the determination of either C_{T1} or C_{ex}.

Determination of C_{T1}. Various methods are available to assess C_{T1}. The method of Mayo[173] is based on the determination of the molar mass (or DP_n) vs $[M]_0/[CTA]_0$ for low monomer conversion (<10%). This method is used to calculate C_{T1} of solvents or telogens, according to the following equation assuming a negligible contribution of the initiator (eq 5):

$$DP_{n,0} = [M]_0/(C_{T1} \times [CTA]_0) \tag{5}$$

where $[M]_0$, $[CTA]_0$, $DP_{n,0}$, and C_{T1} represent the initial monomer and transfer agent concentrations, the number average degree of polymerization (DP_n) at low conversion, and the chain transfer constant, respectively. This equation is usually applied for radical telomerizations.[66] However, because DT does not create new polymer chains, it means that this method can also be used in ITP to assess C_{T1} whatever the C_{ex} value. For instance, Lansalot et al.[174] used this method to determine the transfer constant of perfluorohexyl iodide in bulk Sty polymerization initiated by α,α-azobis(isobutyronitrile) at 70 °C and found a value of $C_{T1} = 1.4$.

The method of O'Brien[175] is based on the determination of the transfer agent consumption vs monomer conversion (eq 6).

$$(R_p/[M])/(R_{tr}/[CTA]) = k_p/k_{tr} = 1/C_{T1} \tag{6}$$

After integration, it gives eq 7:

$$C_{T1} = \ln([CTA]_0/[CTA])/\ln([M]_0/[M]) = \ln(1 - q)/\ln(1 - p) \tag{7}$$

where p and q are the conversions of monomer and transfer agent, respectively.

Again, because DT does not interfere with the consumption of transfer agent and monomer, this method can be used in ITP to determine C_{T1}, whatever the C_{ex} value. For instance, Kowalczuk-Bleja et al.[176] studied the polymerization of Sty initiated by AIBN at 83 °C in the presence of benzyl iodide as the transfer agent and plotted $\text{Ln}([M]_0/[M])$ and $\text{Ln}([CTA]_0/[CTA])$ vs time. Although the authors did not use these data further to assess the transfer constant, a value of $C_{T1} \cong 2$ could be calculated for this system.

An alternative method based on the evolution of the DP_n with monomer conversion p can also be mentioned[66] (eq 8):

$$C_{T1} = \ln\{1 - (p[M]_0/([CTA]_0 DP_n))\}/[\ln(1 - p)] \tag{8}$$

This latter equation holds for low values of C_{T1} (typically $C_{T1} \leq 1$) (for $C_{T1} \gg 1$, the DP_n value approaches $DP_n = [M]_0 \times p/[CTA]_0$ from low monomer conversion and, therefore, this method is not suited to calculate C_{T1} in this case). For instance, Teodorescu[30] applied this method to the polymerization of Sty initiated by AIBN in benzene at 60 °C and obtained a value of $C_{T1} = 0.46$ for vinyl iodoacetate as the transfer agent.

Determination of C_{ex}. The experimental determination of C_{ex} requires the use of a macromolecular transfer agent with the same structure as the dormant polymer chains, i.e., an oligomer with an iodinated chain end (P_0−I), to act as a DT agent in the CRP. Indeed, the use of such a macrotransfer agent P_0−I simplifies the system since $C_{T1} = C_{ex}$.

Lacroix-Desmazes et al.[177] used poly(methyl acrylate)−I oligotransfer agent in the polymerization of methyl acrylate. The degree of polymerization of the oligotransfer agent was very low ($DP_n \cong 2$) as compared to the $DP_{n,0} = 129$ determined by size exclusion chromatography (SEC) at very low conversion; therefore, the method of Mayo could be used (eq 9):

$$DP_{n,0} = [M]_0/(C_{ex} \times [CTA]_0) \qquad (9)$$

Thus, a DT constant value of $C_{ex} = 2.2$ was obtained for poly(methyl acrylate)−I at 70 °C. It is worth mentioning that the value of C_{ex} could be chain length-dependent, especially for a low degree of polymerization. Indeed, although of similar structure, the transfer constant $C_{ex,i} = k_{ex,i}/k_p$ of a transfer agent of very low degree of polymerization i could be different from the transfer constant $C_{ex,j} = k_{ex,j}/k_p$ of a transfer agent of higher degree of polymerization j. The effect of chain length dependence of k_p can be neglected because the propagating radicals involved in the transfer step are of a relatively high degree of polymerization ($DP_{n,0} = 129$ in the example discussed above and thus $k_p \cong k_{p,\infty}$).

Goto et al.[15,178] used a poly(styrene)−I macrotransfer agent of $M_{n,H-NMR} = 1900$ g mol^{-1} in the polymerization of Sty. They first employed the method of O'Brien and Gormick to determine C_{ex}. The consumption of the macrotransfer agent was monitored by the peak resolution of SEC analyses (eq 10):

$$C_{ex} = \ln([P_0{-}I]_0/[P_0{-}I])/\ln([M]_0/[M]) = \ln(1 - r)/\ln(1 - p) \qquad (10)$$

where p and r are the conversion of monomer and macrotransfer agent, respectively.

Goto et al.[15,178] have also shown that it is possible to determine C_{ex} by an alternative approach based on the analysis of the evolution of polydispersities at an early stage of polymerization. The polymerization product is viewed as an A−B diblock copolymer with subchains A and B referring to P_0−I and the incremental part of the molecule, respectively. Hence, a rather complex procedure has been used based on eqs 11 and 12:

$$Y = w_A{}^2Y_A + w_B{}^2Y_B \qquad (11)$$

and

$$[Y_B - (1/x_{n,B})]^{-1} = C_{ex}[p/(2 - p)] \qquad (12)$$

where $Y = (x_w/x_n) - 1$, $Y_K = (x_{w,K}/x_{n,K}) - 1$, $w_A = 1 - w_B = x_{n,A}/x_n$, $x_n = x_{n,A} + x_{n,B}$, and x_n and x_w are the number and weight average degrees of polymerization with K = A or B. In both cases (peak resolution and polydispersity analysis), Goto et al. obtained a value of $C_{ex} = 3.6$ in bulk polymerization of Sty at 80 °C.

4.1.2. Influence of the Values of the Transfer Constants C_{T1} and C_{ex} onto Molar Mass and Polydispersity

The number average molecular weight (M_n) is given by eq 13:

$$M_n = (p[M]_0M_{monomer})/\{(q[CTA]_0) + af([In]_0 - [In]_p)\} \qquad (13)$$

where p is the fractional monomer conversion, $[M]_0$ is the initial monomer concentration, $M_{monomer}$ is the molecular weight of the monomer, q is the transfer agent conversion, $[CTA]_0$ is the initial concentration of transfer agent, a is the mode of termination (1 for termination by combination, 2 for termination by disproportionation), f is the initiator efficiency, $[In]_0$ is the initial initiator concentration, and $[In]_p$ is the initiator concentration at p.

DT does not influence the number of polymer chains; therefore, C_{ex} has no effect on the M_n. The value of C_{T1} determines the evolution of the M_n as follows[66,179] (eq 14):

$$M_n = (p[M]_0M_{monomer})/\{[CTA]_0[1 - (1 - p)^{C_{T1}}] + af([In]_0 - [In]_p)\} \qquad (14)$$

which can be simplified if the contribution of the initiator is neglected (eq 15):

$$M_n = (p[M]_0M_{monomer})/\{[CTA]_0[1 - (1 - p)^{C_{T1}}]\} \qquad (15)$$

where C_{T1} is the transfer coefficient of the transfer agent.

For $C_{T1} = 1$, the monomer conversion equals the transfer agent conversion at any time of the polymerization ($p = q$) and M_n is almost constant ($M_n = [M]_0M_{monomer}/[CTA]_0$ if the contribution of the initiator is neglected) (Figure 2). For $C_{T1} < 1$, the M_n decreases when the monomer conversion increases because new polymer chains are continuously generated. For $C_{T1} > 1$, the M_n increases when the monomer conversion increases.

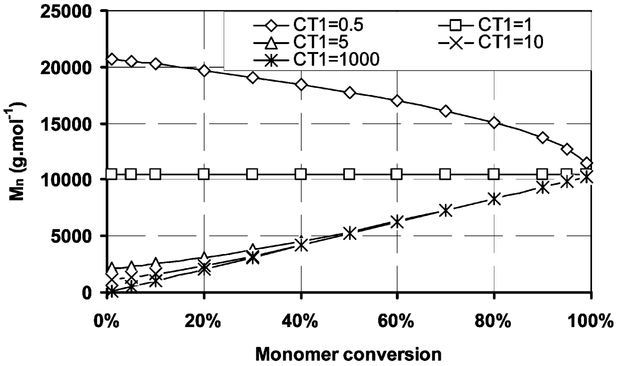


Figure 2. Evolution of molecular weight M_n with monomer conversion for different values of C_{T1} according to the equation $M_n = (p[M]_0M_{monomer})/\{[CTA]_0[1 - (1 - p)^{CT1}]\}$ (conditions: $[M]_0/[CTA]_0 = 100$, $M_{monomer} = 104$ g mol^{-1}).

It is more difficult to assess the effect of the transfer constants C_{T1} and C_{ex} on the evolution of the PDI of the polymer chains. Müller et al.[180] studied the particular case of $C_{T1} = C_{ex}$, but their equation (eq 16) can only be considered as a first approximation since it does not consider radical termination:

$$PDI = \{1+([M]_0/[CTA]_0)[2 + (2 - p)(1 - C_{ex})/C_{ex}]\}/\{p[M]_0/([CTA]_0[1 - (1 - p)^{C_{ex}}])\} \qquad (16)$$

Monteiro[179] used a numerical simulation to predict the evolution of PDI with conversion in RAFT polymerization (another type of DT polymerization) in the same particular case of a unique transfer constant value. The simulations of Monteiro matched well the equations of Müller et al. for M_n and PDI vs conversion. The results show that at a high value of transfer constant ($C_{ex} = 1000$), the PDI starts high and decreases rapidly down to 1.03, resulting in polymer chains of nearly uniform chain length (Figure 3). As the transfer constant is reduced to $C_{ex} = 5$, the PDI decreases with

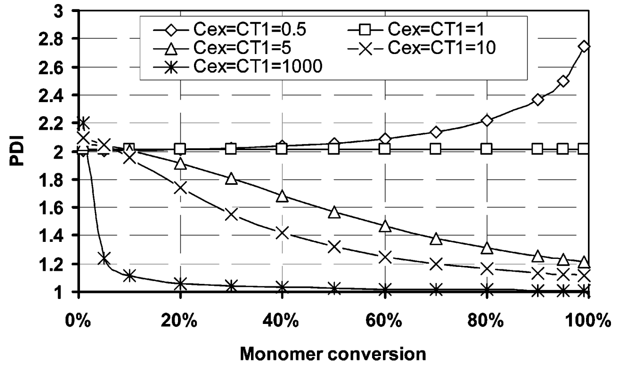


Figure 3. Evolution of PDI with monomer conversion for different values of DT constant C_{ex}, in the particular case of $C_{ex} = C_{T1}$, according to the equation $\mathrm{PDI} = \{1 + ([M]_0/[CTA]_0)[2 + (2 - p)(1 - C_{ex})/C_{ex}]\}/\{p[M]_0/([CTA]_0[1 - (1 - p)^{C_{ex}}])\}$ (conditions: $[M]_0/[CTA]_0 = 100$).

conversion at a much slower rate, finishing at 1.23. At a value of $C_{ex} = 1$, the PDI remains constant at 2 over the conversion range. Finally, at low value of transfer constant ($C_{ex} = 0.5$), the PDI remains constant at 2 for a while and then increases up to 2.5 at high monomer conversion.

Interestingly, at total conversion ($p = 1$), the PDI is given by a simple equation (eq 17):

$$\mathrm{PDI} = 1 + [CTA]_0/[M]_0 + 1/C_{ex} \tag{17}$$

which simplifies further for high values of $[M]_0/[CTA]_0$ (eq 18):

$$\mathrm{PDI} \cong 1 + 1/C_{ex} \tag{18}$$

4.2. Halogenated Monomers Used in ITP

This part is devoted to the fluorinated and chlorinated monomers involved in an ITP. Only few halogenated monomers were actually used in such a process. The literature essentially reports the ITP of VDF and of vinyl chloride.

4.2.1. Fluorinated Monomers

On the basis of well-selected monomers, ITP can easily be applied to fluorinated alkenes. Indeed, Tatemoto et al.[181] have been succeeding since they pioneered this approach in 1980 on VDF and VDF/HFP. Noteworthy, basic similarities in this controlled polymerization system are found in the stepwise growth of polymer chains with each active species. The active propagating center, generally located in the end groups of the growing polymer, has the same reactivity at any time in the course of the polymerization even when the reaction is stopped.[148] In the case of ITP of fluoroalkenes, the terminal active bond is always the C−I bond originating from the initial iodine-containing CTA and monomer, as follows:

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

Tatemoto et al.[182,183] used peroxides as other classical initiators of polymerization in solution involving usually perfluorinated or chlorofluorinated solvents or in emulsion processes while miniemulsion was successfully chosen by Ausimont.[184] Improvement was also possible by using diiodo-[182] and polyiodocompounds.[185] Molar masses were claimed to be in the 30000−10000000 range; yet, polydispersities were narrow (1.2−1.3).[182,183]

Several investigations have shown that ITP can also occur in various processes: emulsion, solution, or later by miniemulsion.[174] This is not extensively described here, but several articles and patents of Tatemoto[143,181,186] or from DuPont[142] or Ausimont[141,187] have been reported, using ammonium persulfate as the initiator and involving TFE, VDF, and HFP as the monomers.

The first fluoroelastomers produced by ITP, which could be peroxide-curable leading to commercially available Dai-El,[186] were developed by Daikin (and now mainly by its subsidiary called Dai-Act). Such a polymer is stable up to 200 °C and finds many applications in high technology such as in O-rings and gaskets,[181,183] transportation, and electronics.

The low efficiency of $C_6F_{13}I$ as a transfer agent in emulsion polymerization 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 where the transfer agent was directly located in the polymer particle.

Iodine transfer polymerization is one of the scarce methods that makes it possible to control the polymerization of fluoroalkenes such as TFE or VDF. Iodine-containing compounds have been used for a long time as CTAs in telomerization. However, the controlled character of the polymerization carried out in the presence of alkyl iodides was revisited.[42,182,188] A large variety of branched or linear R_FIs[143] or IR_FIs[188] and even polyiodides[185] have been involved in ITP of fluoroalkenes.[53]

Recently, our team[189] extensively studied the ITP of VDF in solution by first investigating the defect of VDF chaining and then by evidencing the controlled radical behavior of such a polymerization. To this aim, ITP of VDF[189] was carried out at 75 °C in the presence of perfluorohexyl iodide ($C_6F_{13}I$) and two populations were observed, as depicted in Figure 4. The first one consists of the normal head-to-tail $-CH_2CF_2-CH_2CF_2-$ VDF chaining (major), while the second one arose from the reverse head-to-head $-CH_2CF_2-CF_2CH_2-$ addition followed by a transfer step. We showed that the $-CH_2CF_2I$ functionality regularly decreased for higher targeted DP_n and became even minor as compared to that of the $-CF_2CH_2I$ functionality from DP_{25} (Table 6). Going further, the fractionation of produced poly(vinylidene fluoride) (PVDF)−I (DP_{25}) was carried out and evidenced the absence of $-CH_2-CF_2I$ for fractions containing low DP_n telomers. To understand such a behavior, ITP of VDF was also carried out in the presence of 1,1,2,2-tetrafluoro-3-iodopropane at 75 °C. Such a CTA was chosen since it exhibited a VDF end unit ($HCF_2-CF_2CH_2-I$). In that case, the polymerization led to higher defects of VDF chaining and to uncontrolled DP_n.

Finally, the kinetics[189] of ITP of VDF were achieved in the presence of several fluoroiodinated transfer agents, i.e., perfluorohexyl iodide $C_6F_{13}I$, 1,1,2,2-tetrafluoro-3-iodopropane $HCF_2CF_2CH_2I$, and $C_6F_{13}CH_2CF_2I$. The variation of DP_n vs the monomer conversion is presented for each CTA in Figure 5.

It was noted that experimental DP_n linearly increased with VDF conversion when $R-CF_2I$ transfer agents were used, which evidenced the controlled character of the VDF radical

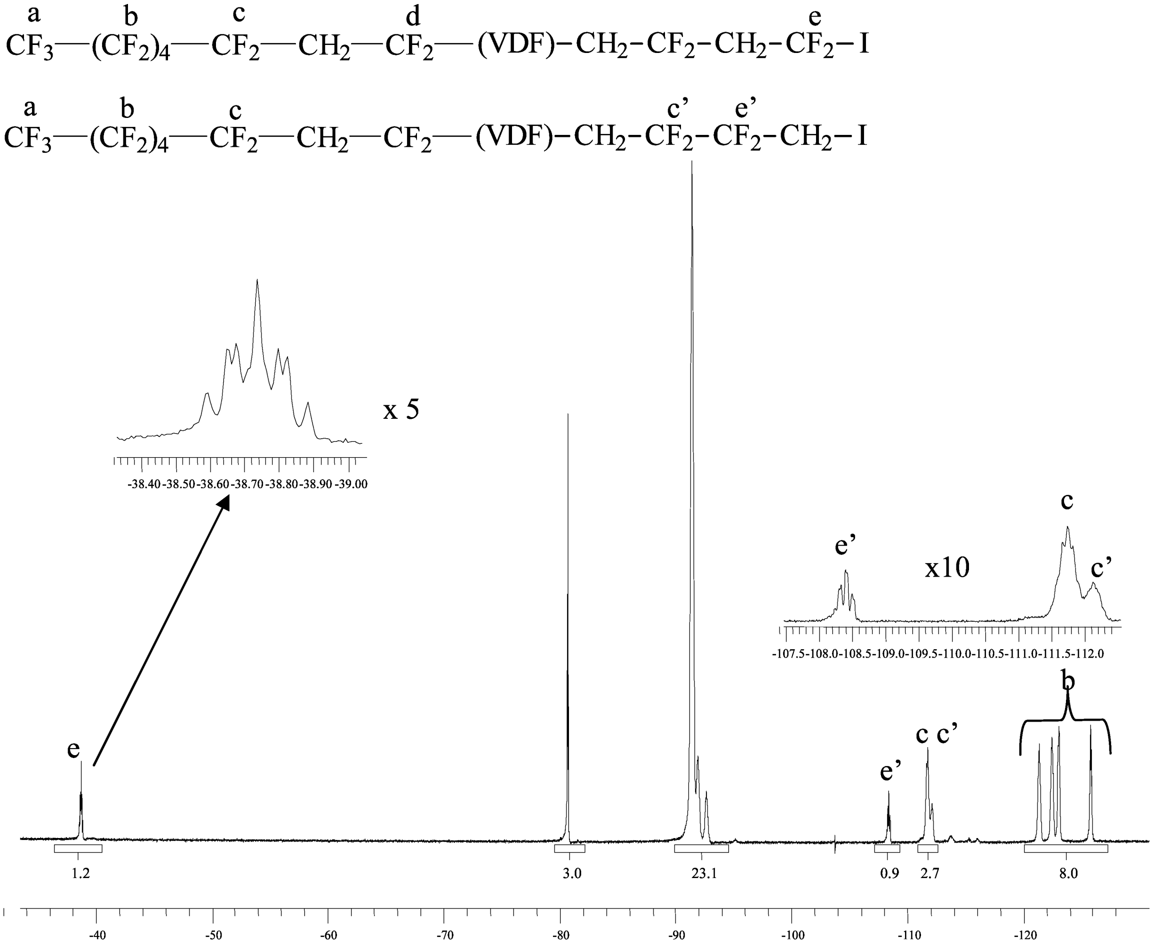


Figure 4. ^{19}F NMR spectrum of the poly(vinylidene fluoride)-I (recorded in deuterated acetone) [average degree of polymerization ($\overline{DP}_n$) = 13] obtained by ITP of VDF with $C_6F_{13}I$.[189] Experimental conditions of ITP of vinylidene fluoride with $C_6F_{13}I$: $[VDF]_0:[C_6F_{13}I]_0:[\textit{tert}\text{-butylperoxypivalate}]_0 = 100.0:6.6:0.6$ at 75 °C. Reprinted with permission from ref 189. Copyright 2005 American Chemical Society.

Table 6. Summary of Average Degree of Polymerization ($\overline{DP}_n$) for Various Concentrations in CTA (C_6F_{13}-I) for the Polymerization of VDF[189a]

run	concn ratios[b] $[VDF]_0$:[chain transfer agent]$_0$:[*tert*-butylperoxy-pivalate]$_0$	targeted $\overline{DP}_n$[c] ($\alpha = 100$)	exp $\overline{DP}_n$[d]	α_{VDF}[e] (%)	functionality$_{exp}$ −CF$_2$−I (%)		−CH$_2$−I (%)		functionality$_{theo}$
					^{19}F	^{1}H	^{19}F	^{1}H	−CF$_2$−I (%)[f]
M1	100.0:11.0:1.1	9	6	70	75	78	25	22	77
M2	100.0:10.0:1.0	10	9	90	68	65	32	35	66
M3	100.0:6.6:0.6	15	13	70	60	55	46	35	54
M4	100.0:3.3:0.3	30	25	75	28	29	72	71	29

[a] Reprinted with permission from ref 189. Copyright 2005 American Chemical Society. [b] Temperature, 75 °C. [c] Calculated by $DP_{n,0} = ([M]_0 \times \alpha)/(C_{T1} \times [CTA]_0)$. [d] Determined by ^{19}F NMR: $\overline{DP}_n = (\int CF_2^{-91.0ppm}/2 + \int(CF_2^{-38.0ppm} + CF_2^{-108.0ppm})/2 + \int CF_2^{-112.0ppm}/2)/(\int CF_3^{-82.0ppm}/3)$ and ^1H NMR $\overline{DP}_n = (\int CH_2^{2.5ppm} + \int CH_2^{3.0ppm} + \int CH_2^{3.3ppm} + \int CH_2^{3.6ppm} + \int CH_2^{3.9ppm})/(\int CH_2^{3.3ppm})$. [e] Conversion of monomer measured by gravimetry: $\alpha_{VDF} = (\text{weight}^{\text{polymer}})/(\text{weight}_{\text{monomer}} + \text{weight}_{C_6F_{13}I}) \times 100$. [f] Determined by theoretical functionality in $CF_2{-}I = (\psi)^{(n-1)}$.

polymerization. Indeed, experimental DP_n values perfectly fit with the theoretical ones (straight line). In the case of R−CH$_2$I transfer agent, a poor control of the polymerization was observed. Interestingly, the transfer constants C_{T1} were determined for each iodinated transfer agent from the O'Brien's method[175,190] presented in section 4.1.1. For R−CF$_2$I transfer agents, the transfer constants were calculated about 7.5, whereas for R−CH$_2$I, the C_{T1} transfer constant was about 0.2. However, for R−CF$_2$I transfer agents, $C_{T1} \approx C_{ex}$ because the transfer agent has a structure close to that of the dormant polymer chains. In the case of R−CH$_2$I, the process is actually a telomerization as only one transfer reaction occurs, i.e., transfer of R−CH$_2$I onto the macromolecular chain.

These values are in good agreement with the assumptions given in the mechanistic understanding of ITP (see section 4.1.2); that is, when C_{ex} is higher than 1, a controlled character is observed. These transfer constant values perfectly assess the different reactivity of −CF$_2$I and −CH$_2$I end groups; the former enable a CRP of VDF.

4.2.2. Chlorinated Monomers

Among halogenated monomers, chlorinated monomers such as vinyl chloride and vinylidene chloride have been

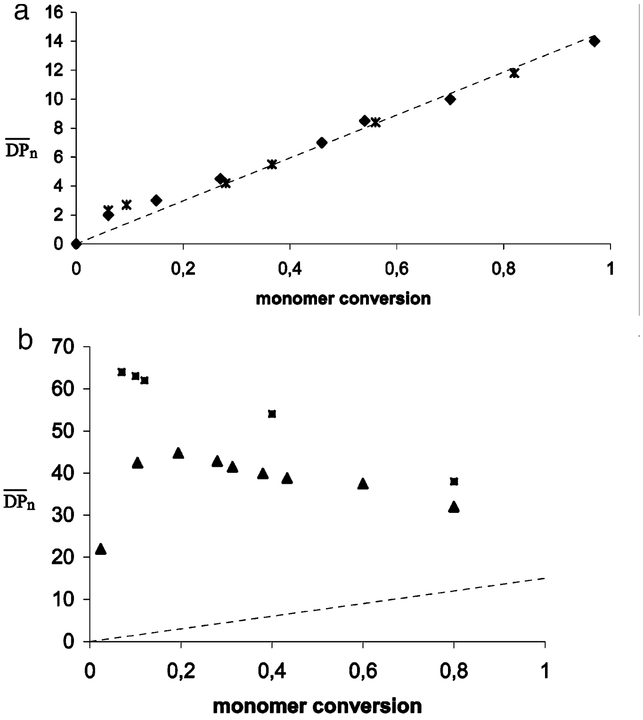


Figure 5. Variation of the average degree of polymerization in number ($\overline{DP}_n$) vs the monomer conversion for ITP of VDF performed with different CTAs and at two temperatures. (a) $C_6F_{13}I$ (◆) and $C_6F_{13}CH_2CF_2I$ (*) at 75 °C. The dotted straight line represents the theoretical $\overline{DP}_n$. (b) $HCF_2CF_2CH_2I$ at 75 °C (■) and 135 °C (▲). The dotted straight line represents the theoretical $\overline{DP}_n$.

widely used in the manufacture of industrially important polymers. Barnes[37] patented a process where iodoform (CHI_3) was used as a CTA ($C_{T1} = 0.75$) to obtain poly(vinyl chloride) (PVC) of low molar mass. Low molar mass polymers were targeted to improve the polymer solubility in solvents and to decrease the processing temperature during the fabrication of shaped articles (by molding or extrusion) or films (by solvent casting and extrusion) or for textile and paper coatings. Iodoform was used at a concentration lower than 1 wt % vs monomer to avoid delay of the polymerization but higher than 0.2 wt % to give a satisfactory reduction of the molar mass of the polymer. For instance, emulsion polymerization of vinyl chloride initiated by ammonium persulfate at 65 °C in the presence of iodoform gave a PVC latex in high yield (70%) with a lower molar mass than that arising from a reference experiment, which did not involve any iodoform. However, the iodocompound was used as a traditional transfer agent without mentioning the possible controlled nature of the polymerization.

Klinkenberg et al.[191] described the polymerization of vinyl chloride at low temperature (typically $T = -15$°C) and used secondary alkyl iodides (such as 2-iodopropane) to reduce the molar mass of the polymer ordinary formed in this temperature range. The polymerization was carried out in bulk in the presence of a redox initiating system (such as triethyl borane/hydroperoxide).

Later on, Tatemoto et al.[143] patented a process to prepare segmented copolymers, thus illustrating the controlled nature of ITP. For instance, concerning chlorinated polymers, the preparation of a poly(VDF-*co*-HFP)-*b*-PVC block copolymer is claimed in dispersed media. The first block is a fluorinated copolymer of HFP and VDF prepared by iodine transfer copolymerization in emulsion with perfluoroisopropyl iodide as the transfer agent. The iodo-containing fluoropolymer latex is then used to grow the second block of PVC by seeded emulsion polymerization.

In 1994, Bak et al.[17,18] claimed the CRP of vinyl chloride by ITP in the presence of alkyl iodides as transfer agents. The authors particularly focused on 1-chloro-1-iodoethane (see section 2.1), which was used as a transfer agent to control the molar mass and to decrease the PDI of PVC prepared by suspension polymerization. A similar process was patented by Wang et al.[192] to prepare PVC with a very low degree of polymerization.

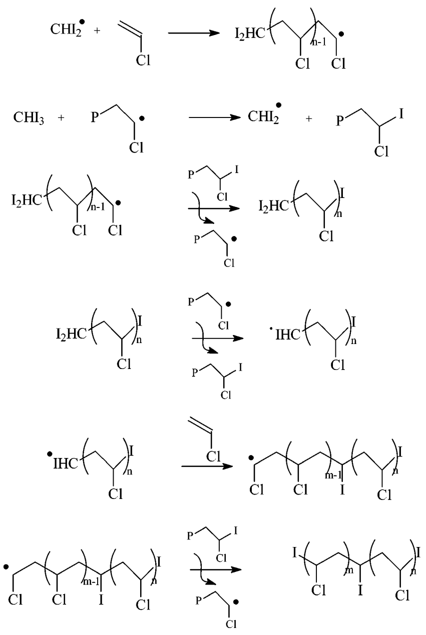
More recently, Percec et al.[153] investigated CRP of vinyl chloride and proposed a process based on the use of alkyl iodides such as iodoform (CHI_3) as the initiator in the presence of metals in their zerovalent oxidation state. This was a first step toward metal-catalyzed CRP of vinyl chloride. However, because the polymerization of vinyl chloride was dominated by chain transfer to monomer rather than bimolecular recombination, the classical persistent radical effect could not occur. Therefore, zero valence metals such as $Cu^{(0)}$ catalyzed the radical polymerization of vinyl chloride only up to 20% conversion by a combination of metal-catalyzed initiation and degenerative chain transfer processes. The process was then improved by using Cu(I) complexes at room temperature in a two-phase system containing water and tetrahydrofuran.[193] In these conditions, both $Cu^{(0)}$ and $Cu(II)X_2$ (X = Cl, I) species, required to control the polymerization, were generated in situ by the disproportionation of the Cu(I) species in water. Indeed, the low polymerization temperature for this process was the result of the single electron transfer (SET) mechanism of activation of the −CHClI dormant chains by electron donor $Cu^{(0)}$.[194,195] The SET mechanism was also possible in the absence of transition metal, for instance with sodium dithionite $Na_2S_2O_4$ or thiourea dioxide $[(NH_2)_2C{=}SO_2]$ as catalyst, in the presence of iodoform as the initiator, and sodium hydrogenocarbonate as a buffer.[196−198] The new CRP process proceeded by a combination of competitive SET and degenerative chain transfer. Authors used this combination of SET and ITP to synthesize diiodo PVC[199] (Scheme 12). Finally, the polymerization can be accelerated by using electron transfer cocatalyst such as 1,1′-dialkyl-4,4′-bipyridinium dihalides or alkyl viologens.[198,200]

Fewer reports are available on the polymerization of vinylidene chloride. Lacroix-Desmazes et al.[201,202] studied the radical copolymerization of vinylidene chloride and methyl acrylate (in 80/20 feed molar ratio) initiated by 2,2′-azobisisobutyronitrile (AIBN) in the presence of 1-phenyl ethyl iodide as the CTA. A copolymer of molar mass $M_n = 8700$ g mol^{-1} ($M_{n,\text{theoretical}} = 7100$ g mol^{-1}) and PDI = 2.06 was obtained. The poly(vinylidene chloride-*co*-methyl acrylate)−I copolymer was successfully used in block copolymerization of Sty to prepare an original poly(vinylidene chloride-*co*-methyl acrylate)-*b*-polystyrene block copolymer of $M_n = 26100$ g mol^{-1} ($M_{n,\text{theoretical}} = 25900$ g mol^{-1}) and PDI = 1.77. These results evidenced the controlled character of the iodine transfer copolymerization of vinylidene chloride and methyl acrylate.

4.3. Nonhalogenated Monomers Used in ITP

Only few nonhalogenated monomers have been successfully polymerized by ITP, mainly styrenics, (meth)acrylates,

Scheme 12. Synthesis of α,ω-Diiodinated PVC by Combination of ITP and SET[199]



and vinyl acetate (VAc). Each monomer and its derivatives need to be studied independently since their reactivity is related to an appropriate transfer agent. The optimal conditions (temperature, solvent, etc.) to reach a controlled process also vary with the nature of both the monomer and the transfer agent and are discussed below.

4.3.1. Styrenics

In the iodine-mediated DT method, Sty and its derivatives are probably the most investigated monomers. Sty was first successfully studied in bulk by Gaynor and co-workers.[13,47,48,203] These authors carried out a conventional radical polymerization initiated by AIBN or dibenzoyl peroxide (BPO) alone at 70 °C and performed the same reaction in the presence of a DT agent, namely, phenyl-ethyliodide.[48] In the first case, polymers with high molar masses were obtained (≈100000 g/mol) whereas low molar masses were observed when the transfer agent was used. However, in that latter case, the observed molar masses were higher than the expected ones. Authors attributed this behavior to an insufficient rate of DT as compared to that of the propagation. Interestingly, they also found polydispersities of about 1.4.

The same team optimized the conditions of the ITP reaction, i.e., by varying the temperature, the initiator, and the transfer agent concentrations.[47] They showed that a higher temperature (80 °C) led to an accelerating rate of polymerization for high conversions, arising from an increase of the viscosity. Finally, increasing the amount of transfer agent slowed the polymerization. Authors attributed this behavior to the generation of I_2, acting as an inhibitor in ITP.

After establishing the best conditions to perform the polymerization (i.e., initial concentrations $[A_2]_0 = 0.03$ M; $[RX]_0 = 0.1$ M), various transfer agents were used to explore their effect onto the control of the molar mass (Table 7).[13] The chosen transfer agents were iodomethanes, R_FIs, alkyl iodides, phenyl iodides, and iodoacetonitrile. By gathering molar masses, PDIs, and conversions vs time, these authors discussed the role of the R substituent in R−X (where X represents an iodine atom).

Table 7. Use of Various Alkyl Iodides for the Bulk Polymerization of Sty ($[Sty]_0 = 1$ M)[13a]

CTA $[CTA]_0 =$ 0.1 M	initiator $[Ini]_0 =$ 0.03 M	temp (°C)	time (h)	conversion (%)	M_n theo/found (g/mol)	PDI
none	AIBN	70	6	86	65500	3.7
	BPO	80	3.5	97	40500	2.1
1-PEI	AIBN	70	16	94	6580/7810	1.5
	AIBN	50	39	92	6500/7830	1.4
	AIBN	90	2	52	3670/5840	1.5
	BPO	80	4.25	83	6570/7280	1.4
iodomethane	BPO	80	3	93	7380/34500	2.1
diiodomethane	BPO	80	5.5	91	7250/20140	2.0
iodoform	BPO	80	5.5	80	6360/5120	1.4
carbon tetraiodide	BPO	80	5.5	31	2480/390	1.0
n-propyl iodide	BPO	80	3	99	7420/34050	2.2
isopropyl iodide	BPO	80	3	86	6460/33730	2.0
tert-butyl iodide	BPO	80	4.8	57	4300/25540	2.0
perfluorohexyl iodide	BPO	80	4.5	94	7440/11200	1.5
iodobenzene	BPO	80	4	98	8260/29700	2.0
1,4-diiodobenzene	BPO	80	4.25	77	6050/33620	2.0
iodoacetonitrile	BPO	80	4.5	83	6550/5800	1.4

[a] Reprinted with permission from ref 13. Copyright 1995 American Chemical Society.

Table 7 summarizes several data obtained from each transfer agent.[13] It is noted that phenyl-ethyl iodide, iodoform, R_FIs, and iodoacetonitrile led to the narrowest polydispersities for dependencies of M_n upon conversion close to the targeted molar mass. For the successful transfer agents, the R group was able to stabilize the formed radical by inductive or resonance effects. This stabilization results in a transfer comparable to the propagation for Sty, giving a suitable control. On the other way, iodobenzene behaves as a poor transfer agent related to Sty, indicating that the rate of transfer is lower than that of the propagation. However, by inserting a methylene group between the phenyl ring and the iodine atom (i.e., benzyl iodide), the control of the Sty polymerization was achieved. Kowalczuk-Bleja et al.[176] carried out the ITP of Sty with benzyl iodide at 83 °C and confirmed that this reaction proceeded in a controlled way (Figure 6).

Figure 6 shows that molar masses ranged between 1500 and 4500 g/mol for PDI values up to 1.5. Indeed, the benzyl iodide radical seems stabilized enough to undergo transfer

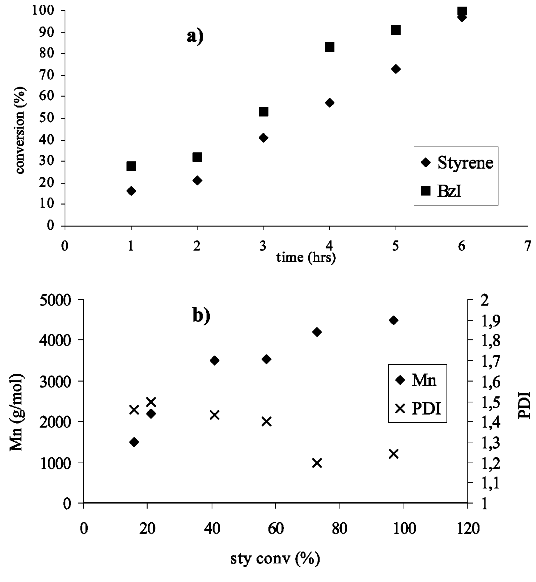


Figure 6. Polymerization of Sty in the presence of benzyl iodide (BzI)[176] at 83 °C initiated by AIBN. (a) Sty conversion vs time. (b) Molar masses vs Sty conversion. Adapted with permission from ref 176. Copyright 2004 Elsevier.

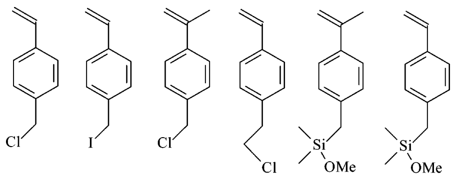
comparable to propagation for Sty. To confirm this result, Kowalczuk-Bleja et al.[176] used polystyrene, from ITP of Sty with benzyl iodide, as a macromolecular transfer agent for the polymerization of Sty. The GPC chromatogram clearly proved the chain extension and so the efficiency of benzyl iodide for DT polymerization of Sty.

In 2001, Teodorescu[30] investigated the DT polymerization of Sty by using vinyl iodoacetate (VAcI) as the transfer agent to lead to a new macromonomer. In fact, VAcI was chosen for two reasons:[30] (i) Its chain transfer ability to Sty might be similar to that of iodoacetic acid (which has a transfer constant C_{T1} of 0.8 at 68 °C).[204] (ii) In the copolymerization process, there is no incorporation of VAcI into the polystyrene backbone. The formation of the macromonomer was evidenced by ^{1}H NMR and especially by the presence of the vinylic proton. Iodine atoms were then substituted by azido groups to allow the subsequent graft copolymerization of the macromonomer with VAc.

Most studies of DT polymerization of Sty were realized in bulk and led to interesting results as shown above. Furthermore, it is noted that further work was carried out such as ITP of Sty in emulsion[174] and miniemulsion[205] polymerizations. Lansalot et al.[174] performed the emulsion polymerization of Sty in the presence of $C_6F_{13}I$ at 70 °C and obtained an unusually low efficiency of 50% for this transfer agent. They assigned such a behavior to a slow diffusion of perfluorohexyl iodide from the monomer droplets to the active particles during polymerization. Thus, the same system was carried out in miniemulsion process,[174,205] and 100% efficiency was reached especially when Sty was added continuously. Moreover, a linear increase of the molar mass with monomer conversion was observed.

In addition, some styrenic derivatives were successfully involved in the DT polymerization. It is the case for *p*-chloromethylstyrene[206] polymerized at 80 °C with iodoform as the transfer agent to give controlled polymers of M_n about 15000 g/mol. The same group also synthesized controlled polymers of methoxysilylmethylstyrene[207] by also using iodoform as a transfer agent in the same experimental conditions. Scheme 13 shows styrenic derivatives successfully polymerized by ITP.[176,206,207]

Scheme 13. Various Sty Derivatives Polymerized in ITP[176,206,207]



4.3.2. (Meth)acrylates

Only a few companies patented the polymerization of acrylates[208] and methacrylates[209−211] by using an iodinated transfer agent. Kakei et al.[208] successfully polymerized butyl acrylate by using iodoacetic acid at 60 °C, leading to carboxy-terminated acrylate. The same authors[210] claimed the DT polymerization of MMA with benzyl iodide, the resulting polymer being treated with aminopropyldiethoxymethylsilane to give an original alkoxysilyl-terminated poly(methyl methacrylate) (PMMA) having an M_n and M_w/M_n of 13000 and 1.74, respectively. These authors observed that the introduction rate of alkoxysilyl group was 91%. Dong et al.[211] claimed that *tert*-butyl iodide was an efficient transfer agent in the ITP of MMA.

However, the kinetics of ITPs of both acrylates and methacrylates have so far only been described by Gaynor et al.[13] These authors also investigated the same study for butyl acrylate, methyl acrylate, and methyl methacrylate (MMA) as for Sty, described above, in the presence of 1-phenylethyliodide. They observed an acceleration for acrylates due to a decrease of the termination rate constant over conversion, resulting in broad polydispersities. However, in the case of MMA, the molar masses did not increase with conversion evidencing that the transfer to 1-phenyl-ethyliodide was much slower than the propagation.

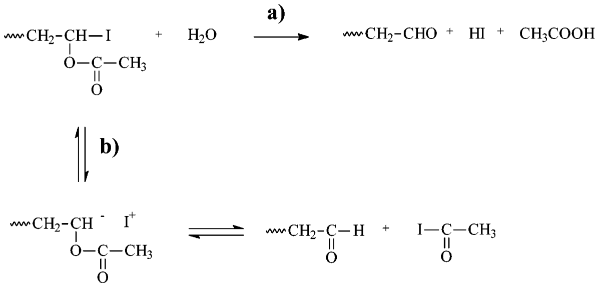
4.3.3. VAc

Unlike Sty or (meth)acrylates, the control of VAc polymerization by CRP has been so far considered highly difficult. It is especially due to high extent of transfer undergone by a highly reactive propagating radical.[212] Ueda first tried the synthesis of poly(vinyl acetate) by DT polymerization by using either iodoform[213,214] or iodoperfluorohexane.[215−217]

As a matter of fact, ATRP of VAc was proved to be efficient by Sawamoto et al.[218] These authors used an iodoalkyl transfer agent activated by employing dicarbonylcyclopentadienyliron. This catalyst, already involved in ATRP with iodides,[38,41,46,219] induced the homolysis of the C−I bond for both initiator and dormant polymer chain ends. Indeed, Sawamoto's studies involved both ATRP and ITP since the dormant chains are iodine end capped.

Finally, the DT of VAc with alkyl iodides and without any catalyst was reported by Iovu et al.[31] in 2003. Poly(vinyl acetate) with controlled molar mass and relatively narrow molar mass distributions was synthesized by using ethyl iodoacetate as the transfer agent. The influence of both initiator and transfer agent concentrations was investigated to conclude that higher concentrations of both reagents were required for a good control of the molar mass and lower polydispersities. However, authors investigated an ^{1}H NMR analysis of the chain end that revealed unstable iodo end groups of poly(vinyl acetate). Indeed, during reaction, the iodo end groups decompose into an aldehyde end group (Scheme 14a,b). The decomposition mechanism was previously demonstrated by our group[220] and by others workers.[221,222]

Scheme 14. Hydrolysis (a) and Decomposition (b) of Iodo End Group for Poly(vinyl acetate)[31]

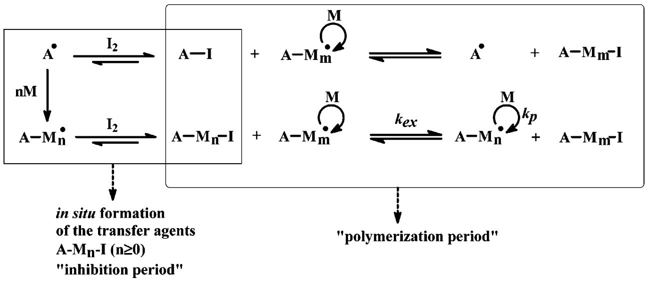


4.4. RITP

CTAs used in ITP were iodoalkyl compounds (such as 2-iodo-perfluoropropane, 1-iodo-perfluorohexane, 1-iodo-1-chloro-ethane, 1-phenylethyl iodide, methyl-2-iodopropionate, and iodoacetonitrile), which are unstable due to the weak C−I bond, and thus prone to alteration upon storage.

Furthermore, ITP of monomers involving tertiary propagating radicals (such as methacrylates) was not successful[13] because it would require iodoalkyl compounds with a better leaving group such as in ethyl 2-iodo-2-methylpropionate, although such compounds are inherently even more unstable.[223] To overcome these limitations, Lacroix-Desmazes et al.[202] have proposed a new process based on a direct reaction of radicals with molecular iodine I_2. In this way, the reversible CTA is generated in situ in the reaction mixture (Scheme 15). By analogy with the reverse ATRP process where the alkyl halide initiator (e.g., R−Cl) was in situ synthesized by reaction of radicals with the complex in the oxidized state (e.g., $CuCl_2$/ligand),[147] this new process was called RITP.

Scheme 15. Simplified Mechanism of RITP[a]



[a] A•, radical from the initiator; I_2, molecular iodine; M, monomer unit; n, mean number degree of polymerization, k_{ex}, degenerative chain transfer rate constant; and k_p, propagation rate constant.

The reactivity of iodine is complex. Iodine has been reported in different kinds of reactions. For instance, iodine can react onto double bonds,[224,225] initiate some ionic polymerizations,[226] and form acceptor−donor complexes.[227] Molecular iodine I_2 has already been reported as a strong inhibitor in free radical polymerization. For instance, Bartlett et al.[228] monitored the monomer conversion for the peroxide-induced polymerization of VAc and showed that iodine behaved as an efficient inhibitor, the polymerization being apparently totally arrested for a period in which iodine stopped two chains per molecule. A possible interpretation of the kinetics was proposed based on the formation of $I_3^\bullet$ radicals, which would react with growing chains, but this hypothesis encountered some difficulties and no molar mass data were supplied for the polymers after the inhibition period. Bartlett et al.[229] also established that iodine strongly inhibits the free radical polymerization of Sty. In addition, Ghosh et al.[230] studied the thermal polymerization of MMA initiated by AIBN in the presence of iodine, and by plotting the reciprocal degree of polymerization $1/DP_n$ vs molar ratio $[I_2]$/[monomer] in a set of experiments, they concluded that iodine (or some adducts it could give with the monomer) acts as a CTA ($C_{tr} = 6$, unfortunately expressed in terms of transfer constant of iodine); however, the evolution of monomer conversion with time was not investigated and the authors did not mention any inhibition period. On the contrary, Lissi et al.[231] also studied the thermal polymerization of MMA initiated by AIBN and emphasized that iodine was not consumed in a chain reaction but behaved as an efficient inhibitor even at extremely low concentration. However, after the inhibition period, no molar mass data of the polymers were reported. There are no discrepancies and/or contradictions between the conclusions of these studies if the whole RITP process is considered. Indeed, RITP takes advantage of the powerful inhibitor ability of iodine to generate in situ the iodinated reversible CTAs $A{-}M_n{-}I$ ($n \geq 0$) where A, M, n, and I stand for the primary radical fragment from the initiator, the monomer unit, the average number degree of polymerization, and the iodine atom,[202] respectively. The RITP mechanism can be described as a conventional free radical polymerization using an effective terminating agent. Typically, the RITP process is split into two different periods (Scheme 15). During the first period, primary free radicals $A^\bullet$ arising from the initiator react directly or indirectly (after few propagation steps) with iodine I_2 to form $A{-}M_n{-}I$ telomers. If its reaction rate constant with iodine is high (i.e., much faster than that of the propagation), as expected from the values reported in the literature for the bimolecular reaction of alkyl radicals with iodine ($k > 10^8$ L mol^{-1} s^{-1} at 25 °C),[232−234] this period lasts until the quantitative consumption of iodine. Consequently, for a high initial monomer-to-iodine ratio, the monomer conversion during this period is essentially negligible. This is the reason why this period can be called the “inhibition period”. After this inhibition period during which the iodinated transfer agents are formed, the polymerization follows the kinetics of a conventional free radical polymerization governed by degenerative chain transfer.[178] The theoretical average number degree of polymerization (DP_n) is given by eq 19 where Δ[monomer], $[I_2]_0$, and Δ[AIBN] stand for the consumption of the monomer, the initial concentration of iodine in the reaction medium, and the excess amount of AIBN used to initiate and propagate the polymerization, respectively. Δ[AIBN] can be assessed by kinetic analyses and is usually negligible as compared to the $2 \times [I_2]_0$ term. Therefore, the theoretical molar mass of the polymers prepared by RITP can be calculated by eq 20 where M_{A-I} stands for the molar mass of A−I adduct. This equation is simplified assuming a high degenerative chain transfer constant and a low fraction of dead chains. Alternatively, in the case of rather low degenerative chain transfer constant (but still higher than unity), a good approximation of the molar mass can be given by eq 20 at high monomer conversion.

$$DP_n = \Delta[\text{monomer}]/(2 \times [I_2]_0 + \Delta[\text{AIBN}]) \cong \Delta[\text{monomer}]/(2 \times [I_2]_0) \quad (19)$$

$$M_{n,\text{theoretical}} = (\text{mass of monomer}) \times \text{conversion}/[2 \times (\text{moles of } I_2)] + M_{A-I} \quad (20)$$

Several patents based on the RITP process have been recently deposited by Solvay[235−237] and Akzo.[39] Sekisui Chemical[238] reported a similar process to prepare styrenic polymers with controlled structures. In our laboratory, the RITP process was investigated by the survey of several classes of monomers. RITP has been found to be a versatile process since it efficiently provides controlled polymerization for a wide range of monomers such as vinylidene chloride, acrylates, methacrylates, α-fluoro acrylates, and Sty.[177,202] Furthermore, RITP of acrylates was successfully performed in a large variety of media (in bulk, toluene, α,α,α-trifluorotoluene, anisole, methyl ethyl ketone, butyl acetate, propylene carbonate, propionitrile, and dimethylformamide). All of the considered solvents gave a reasonable control of the final molar mass, indicating that RITP is a rather flexible and robust process. Furthermore, first results on RITP of *n*-butyl acrylate in aqueous emulsion showed that the molar mass of the polymer can be tuned, indicating that the RITP process should be applicable to heterogeneous processes,

Table 8. Polymerization of Methyl Acrylate by RITP ([MA] = 5.26 M) in Benzene ([Benzene] = 5.88 M) at 65 °C in the Presence of AIBN as Initiator[177a]

run	$M_{n,targeted}$ (g mol^{-1})	[AIBN]/[I$_2$]	h			α^c (%)	g mol^{-1}		PDI
			$t_{loss\ of\ coloration}$	$t_{inh,theo.}{}^b$	t_{pol}		$M_{n,theo.}{}^d$	$M_{n,exp.}{}^e$	
1	5700	1.7	26	27	45	97	5500	5700	1.79
2	10700	1.7	22	27	45	98	10500	10900	1.91
3	21100	1.7	30	27	45	98	20700	21800	1.98

[a] Reprinted with permission from ref 177. Copyright 2005 American Chemical Society. [b] Calculated by $t_{inhibition,theo.} = -\mathrm{Ln}\{1 - [I_2]_0/(f \times [\mathrm{initiator}]_0)\}/k_d$ with $k_d = 1.90 \times 10^{-5}$ s^{-1} and $f = 0.7$. [c] Determined by ^{1}H NMR in CDCl$_3$: fractional conversion $= 1 - I_1/I_2$ where the integral I_1 refers to the resonances at 6.4 ppm (H$_A$), 6.1 ppm (H$_B$), and 5.8 ppm (H$_C$) (3H, $H_AH_CC{=}CH_B-$, $J_{trans} = 17.3$ Hz, $J_{cis} = 10.3$ Hz, and $J_{gem} = 1.4$ Hz) and the integral I_2 refers to the resonances at 3.5−3.8 ppm (3H, $-OCH_3$, singlet + broad peak). [d] Calculated by $M_{n,theoretical}$ = (mass of monomer) × conversion/[2 × (moles of I$_2$)] + M_{A-I} where $M_{A-I} = M_{chain\ ends} = 195$ g mol^{-1}. [e] Determined by SEC with polystyrene standards and calculated with Mark−Houwink coefficients of polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.716$) and poly(methyl acrylate) ($K = 19.5 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.660$).

which are of major industrial importance.[239,240] For industrial developments, a long inhibition period may be crippling. Therefore, attempts were made to fasten the RITP process by increasing the temperature.[177] The results obtained with *n*-butyl acrylate showed that the inhibition period can be shortened efficiently (about 30 min at 95 °C instead of more than 15 h at 65 °C for an initial [AIBN]$_0$/[I$_2$]$_0$ molar ratio of 1.9), thus decreasing the overall time of polymerization, while keeping a good control of the final molar mass of the polymer. Tables 8 and 9 list some results of the RITP of methyl acrylate and *n*-butyl acrylate, respectively.

Table 9. Polymerization of *n*-Butyl Acrylate by RITP at Various Temperatures, 80% w/v vs Butyl Acetate as Solvent ([*n*-BuA] = 3.30 M) in the Presence of AIBN as Initiator with [AIBN]/[I$_2$] = 1.9[177a]

run	T (°C)	h		α (%)^b	g mol^{-1}		PDI
		$t_{loss\ of\ coloration}$	$t_{pol.}$		$M_{n,theo}{}^c$	$M_{n,exp}{}^d$	
1	65	>15	24	97	10300	12600	2.16
2	85	≈1.66	5	95	9500	10000	1.85
3	95	≈0.5	1	95	9200	8600	1.88

[a] Reprinted with permission from ref 177. Copyright 2005 American Chemical Society. [b] Determined by ^{1}H NMR. [c] Calculated by $M_{n,theoretical}$ = (mass of monomer) × conversion/[2 × (moles of I$_2$)] + M_{A-I} where $M_{A-I} = M_{chain\ ends} = 195$ g mol^{-1}. [d] Determined by SEC with polystyrene standards and calculated with Mark−Houwink coefficients of polystyrene ($K = 11.4 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.716$) and poly(*n*-butyl acrylate) ($K = 12.2 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.700$).

Recently, our team[241] performed the RITP of MMA. Figure 7 illustrates the controlled character of the polymerization, with PDIs of about 1.6.

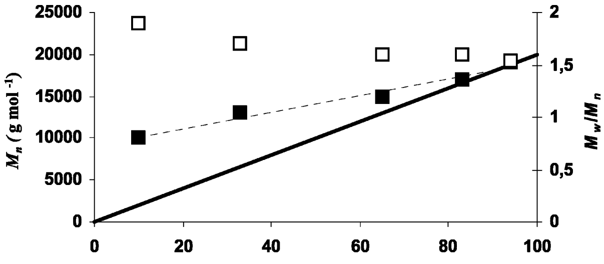


Figure 7. Polymerization of MMA by RITP at $T = 80$ °C in toluene ($M_{n,targeted} = 20\,200$ g mol^{-1}). Evolution of molar masses M_n (■) and PDI M_w/M_n (□) vs monomer conversion.[241] Experimental values determined by SEC analysis (PMMA calibration). Theoretical line (full bold line) calculated by $M_{n,theoretical} = [MMA]_0 \times M^{MMA} \times$ conversion/(2 × [I$_2$]$_0$) + M^{A-I}, where $M^{MMA} = 100$ g mol^{-1} and $M^{A-I} = M^{chain-ends} = 195$ g mol^{-1}. Adapted with permission from ref 241. Copyright 2006 American Chemical Society.

Finally, a poly(methyl acrylate)-*b*-polystyrene block copolymer ($M_{n,exp} = 13300$ g mol^{-1} and $M_w/M_n = 1.73$) was prepared by sequential RITP polymerization of methyl acrylate followed by addition of Sty.[177] The SEC analysis of the block copolymer with two detectors (refractive index and UV) showed an unimodal distribution with a visible shift toward higher molar masses as compared to the macroinitiator, confirming that most of the poly(methyl acrylate) chains were controlled and took part in the formation of the desired block copolymer. A poly(vinylidene chloride-*co*-methyl acrylate)-*b*-polystyrene block copolymer ($M_n = 20000$ g/mol, $I_p = 1.57$) was also successfully prepared by sequential RITP of vinylidene chloride and methyl acrylate followed by ITP of Sty. Hence, the controlled nature of the RITP process opens the door to a wide range of well-designed macromolecular architectures.

4.5. Conclusion

ITP was the first CRP discovered in the late 1970s. Like the RAFT polymerization, the ITP mechanism is based on a DT and requires a CTA, able to start the polymerization. The ITP mechanism is characterized by two transfer constants, C_{T1} and C_{ex}, attributed to the transfer of the CTA and the DT, respectively. Several mathematical methods, e.g., Müller's method, allow the assessment of the transfer constants, but none of them afford the simultaneous determination of both constants. These transfer constant values are of high importance because they characterize the controlled behavior of the polymerization.

Furthermore, the polymerization of most of the vinylic monomers remains efficient in the ITP process. For instance, for halogenated ones, the radical polymerization of VDF was proved to be controlled in the presence of perfluorinated transfer agent. Percec[199] also performed the CRP of vinyl chloride by a combination of ITP and SET. Concerning the nonhalogenated vinylic monomers, styrenic and acrylates were efficiently polymerized by the ITP process. The polymerization of VAc also behaved in a controlled way in the presence of alkyl iodides, but a decomposition of the iodo end groups occurs during the reaction. Only the polymerization of MMA does not show any controlled behavior in ITP. On this basis, our group developed the RITP that involves molecular iodine. Unlike ITP, RITP shows an inhibition period corresponding to the in situ formation of the alkyl iodide transfer agent. Increasing the temperature can, however, shorten this inhibition period. RITP was demonstrated to be efficient toward acrylates and MMA among others. Because it is based on simple molecular iodine, this new technique will allow soon the CRP of original monomers, which would require specific iodinated transfer agents in an ITP process.

5. Applications of Iodinated Compounds

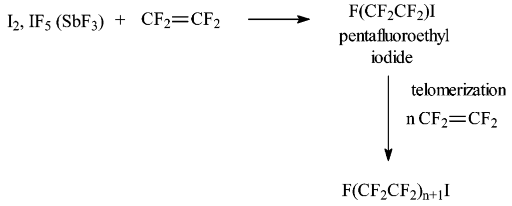
Fluorinated compounds have unique properties, such as surface activity and weak interaction,[53,242,243] which makes them suitable for a wide range of high-tech applications. These compounds are precursors of various functional intermediates bearing a perfluoroalkyl group, such as fluorinated acrylates, surfactants, etc. Indeed, on an industrial scale, the synthesis of perfluoroalkanes is possible by two processes. These processes used in the manufacturing of fluorinated surfactants are based either on electrochemical fluorination (ECF) or on telomerization.[36,53,244] In the former process (Scheme 16), the substance to be fluorinated is dissolved in hydrofluoric acid (HF) and an electrical current is passed through the media. This process, also called the “Simons’ process”, pioneered in 1957, enables the synthesis of different perfluorinated carboxylic acids, perfluoroalkanesulfonyl fluorides, and the derivatives of such products.

Scheme 16. Reaction of ECF

$$C_nH_{2n+1}SO_2F \;+\; (2n+1)F^- \xrightarrow{HF} C_nF_{2n+1}SO_2F \;+\; (2n+1)\,H^+ + (4n+2)\,e^-$$

The second process is the telomerization of TFE. Such a process is used in the industrial synthesis of perfluoroalkyliodides and of ω-perfluoro alcohol or perfluoroacid (Scheme 17). The first step concerns the synthesis of the telogen, perfluoroethyliodide, by reacting TFE onto [I−F] generated in situ from I_2 and IF_5. Telomerization of TFE results in a mixture of telomers containing an even carbon number of the general structure: $F(CF_2CF_2)_{n+1}-I$.

Scheme 17. Industrial Synthesis of Fluorotelomer Using the Telomerization of TFE with Pentafluoroethyliodide



To our knowledge, the only industrial applications of iodocompounds consist of the synthesis of fluorinated molecules or polymers, bearing a functional end group. For instance, Dupont de Nemours[245] (which bought the Atofina activities in that field), Clariant, Asahi Glass, or Daikin synthesized new organic molecules (Scheme 18) as well as fluoropolymers with remarkable properties, such as TPEs[246,247] or surfactants.[112−114,244,248]

(Perfluoro)iodocompounds lead to industrial products, following two distinct routes: (i) by direct chemical modification of (perfluoro)iodocompounds or (ii) by (controlled) radical polymerization with (perfluoro)iodocompounds as the transfer agents.

5.1. Synthesis of Fluorinated Oligomers from Iodinated Compounds

The chemical modification of perfluoroiodocompounds has led to many investigations from academic and industries and have already led to various industrial applications for surfactants, coatings, textile finishing, surface modifiers, optical fibers, etc. Nonexhaustive examples are supplied below.

5.1.1. Synthesis of New Functional Precursors

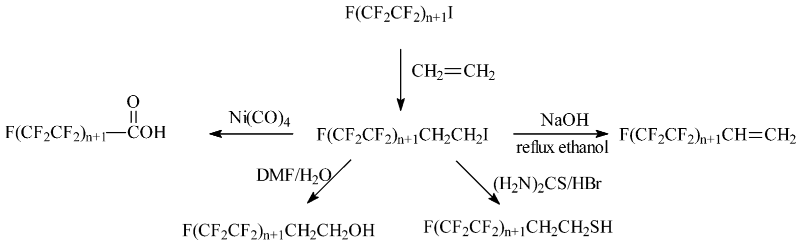
The chemical modification of iodocompounds has been widely studied by many authors. Améduri and Boutevin[53] have summarized the whole synthesis of functional precursors from perfluoroiodocompounds. For instance, the synthesis of the Zonyl type products is based on these reactions. Such compounds then undergo modifications, leading to several industrial products: Forafac marketed by Atofina in the 1980s and then sold to Dupont[249] in 2000 under the Zonyl tradename, Surflon from Asahi Glass, and surfactants from 3M,[250] Rhodia,[248] or Ciba.[251,252] Another application from these products is based on their surface properties. These compounds provide lower surface energy; higher resistance to chemicals, moisture, oil, and grease; and allow a good adhesion to other low-energy surfaces.

5.1.2. Synthesis of New Fluorinated Monomers

One of the most interesting intermediates (obtained from perfluoroiodocompounds) is fluorinated alcohol, used for the synthesis of several monomers such as fluorinated acrylates (Scheme 18). They are prepared by esterification of (meth)-acrylic acids or from (meth)acryloyl chloride with fluorinated alcohols.[253,254] Fluorinated acrylates may be used in several industrial applications[255] reported below.

Aqueous Fire Fighting Foams and Surfactants.[28,244] Many investigations were pioneered by Pittman[256−258] on aqueous fire-fighting foams (AFFFs). AFFFs were developed in the 1960s as important tools for fire extinguishers for flammable liquid fuels, such as petroleum, kerosene, etc. Commercial AFFF formulations are composed of a mixture of different fluorinated surfactants in water solution. This kind of surfactant is obtained by copolymerization of fluorinated acrylates or by chemical modification of perfluoroiodocompounds. For example, it is possible to mention industrial products, such as ZONYL by DuPont de Nemours. The Daikin Company[259] copolymerized fluorinated acrylates with acrylic acid and $Me(OCH_2CH_2)_9O_2CCMe{=}CH_2$. Our group also telomerized fluorinated acrylates with iodo-terminated polyacrylamide, previously synthesized by telomerization reaction of acrylamide in the presence of $C_8F_{17}C_2H_4I$. This block copolymer has been marketed by

Scheme 18. Synthesis of Organic Molecules from $F(CF_2CF_2)_{n+1}I$[53,245,301−304]



Atofina under the Forafac tradename[260] in the late 1980s and was then sold to Dupont in early 2000.

These fluorinated surfactants enable the formation of an aqueous film that is distributed over the whole surface of the hydrocarbon compound. Hence, these block copolymers lead to a surface tension of 28 mN m^{-1} in aqueous solution (0.1% w/w).

In addition, recent investigations have been carried out on the syntheses of original amphiphilic telomers based on TFP.[112−114] Fluorinated surfactants are also involved in (mini)emulsion copolymerization[261] of fluorinated monomers with hydrophilic monomers, such as acrylic acid. However, the most known and efficient PFOA (perfluorooctanoic acid) and also APFO (ammonium perfluorooctanoate) surfactants are toxic, persistent, and bioaccumulated and have pushed most chemical industries producing fluoropolymers to think of new alternatives via the Stewardship Program. Its goal consists of reducing of 95% the production of PFOA by 2010 and to stop it by 2015. Although the 3M company has withdrawn Scotchguard because of the toxic perfluorooctanoic anion, many hazardous issues have been thought on perfluorooctyl sulfonate. However, Wasburn et al.[262] have shown that exposure to perfluorooctanoate from consumer goods, such as treated textiles, carpets, and clothing, is not expected to cause health effects or quantifiable levels of the chemical in the blood. In addition, the same group[263] looked at the concentrations of perfluorocarbons, including PFOA-derived materials, that have accumulated in sludge in the San Franscisco Bay area. The results have shown that in domestic sludge, the concentration of PFCs ranged from 5 to 150 ng/g for all perfluorocarboxylates and between 55 and 3370 ng/g for perfluoroalkanesulfonyl-based chemicals.

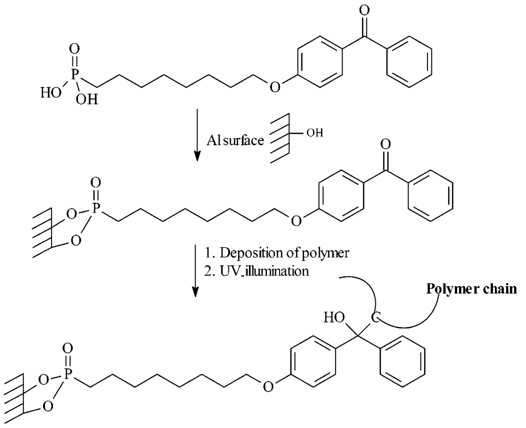
Textiles. Applications of fluorinated acrylic ester polymers to impart oil and water repellency to textiles,[264−268] such as soft furnishings and carpets, are nowadays in wide commercial use (Scotchgard produced by 3M but was withdrawn from the market a few years ago, Teflon replaced by the Zonyl by Dupont de Nemours, Foraperle by Atochem, Asahiguard by Asahi Glass, Unidyne by Daikin, etc.). For instance, Scotchguard is a block copolymer containing hydrophobic segments, such as sulfonamido-fluoroacrylic, and hydrophilic blocks, such as oligoethylene oxide.

Electronics. Fluorinated polymers are used in lithography for electronic applications. Indeed, these fluorinated compounds allow a decrease of the surface energy but also bring antiadhesive properties to the surface. For instance, Pawloski et al.[269] coated 1H,1H,2H,2H-perfluorooctyl-triethoxysilane onto the surface to obtain antiadhesive coatings. Interestingly, such coatings showed a better precision of the lithography.

Surface Modifiers. Fluorinated compounds are used to modify the surface properties of various substrates (metals, stone, leather, glass, etc.) by making them hydrophobic.[53] The surface modifiers are made of a fluorinated chain but also of a nonfluorinated one that enables the direct physical interaction with the metal surface. Hence, Bongiovanni et al.[270] proposed the synthesis of telechelic oligomers with the following structure: Rh−Rf−Rh, with Rh = $-CH_2O-CO-NH-CH_2-CH_2-O-CO-C(CH_3){=}CH_2$ and Rf = $-CF_2O-(CF_2-CF_2O)_p-(CF_2-O)_q-CF_2-$, and $p = q$.

These authors used these oligomers as a surface modifier after the photopolymerization of a hydrogenated resin. They showed a modification of the surface by adding these oligomers with 0.1% (w/w). This oligomer actually increased the hydrophobicity (as evidenced by a contact angle of 105°). This is the reason why fluorinated derivatives are also employed to limit the corrosion of anodes in batteries.[271−275] Vignaud[272] suggested the use of poly(ethylene oxide) copolymer, bearing a perfluorinated chain end [i.e., $C_6F_{13}C_2H_4(OCH_2CH_2)_nOH$], to limit the corrosion in the batteries. However, delamination occurs over time and chemical links of the polymers with the metal are required. Pahnke et al.[276,277] realized a new chemical grafting of fluorinated polymers onto aluminum. First benzophenone, bearing a phosphonic acid group, was fixed onto the metal. Then, irradiation of benzophenone followed by a radical transfer reaction onto a fluorinated acrylate monomer allowed a chemical grafting onto the surface (Scheme 19). Noteworthy, applications such as self-cleaning require highly hydrophobic surfaces, i.e., a contact angle of about 160°.

Scheme 19. Synthesis of Benzophenone Phosphonic Acid, Its Immobilization on Aluminum Surfaces, and the Attachment of Polymers[276,277]



Optics. Fluorinated acrylates monomers have been used in the synthesis of polymeric optical fibers (POF).[278−281] Hence, unlike PMMA, fluorinated polyacrylates exhibit a very low refractive index, a good thermal resistance, and a low adsorption in a wide wavelength range (from 600 to 900 nm).[282,283] Present uses of POF are mainly lightings, optical sensors, short length data links, etc.

CO_2 Technology. Poly(fluoroalkyl(meth)acrylates) belong to the limited class of polymers that are highly soluble in liquid and supercritical carbon dioxide even at a high molecular weight.[284] Because $scCO_2$ appears as an attractive alternative to organic solvents for various processes in material science, CO_2-philic polymers prepared with fluoroalkyl (meth)acrylates might be of great importance for further developments in this area.

5.2. General Applications of Polymers Obtained from Iodinated Precursors

As mentioned in section 3.2, R_FIs have been often used in telomerization of fluoroalkenes and also extended to the CRPs (section 4). Indeed, in that latter topic, one of the best examples is the use of ITP to obtain fluorinated TPEs. These TPEs are composed of two (A−B) or triblocks (A−B−A) copolymers. These A−B−A fluorocopolymers are phase segregated including an amorphous zone and crystalline domains, and they combine various advantages inducing a wide range of service temperature. These TPEs are synthesized in a two-step procedure: a novel telechelic polymer (usually an elastomeric I−soft−I block) is produced from the first step by ITP with a telechelic transfer agent ($I-R_F-$

Table 10. Main Commercially Available Fluoroelastomers (DuPont P. E. stands for DuPont Performance Elastomers)

monomers	HFP	PMVE	CTFE	P
VDF	Daiel 801 (Daikin) Fluorel (3M/Dyneon) Kynar (Arkema) Tecnoflon (Solvay Solexis) SKF-26 (Russian) Viton A (DuPont P. E.)		Kel F (Dyneon) SKF-32 (Russian) Voltalef (Arkema)	
TFE		Kalrez (DuPont P. E.)		Aflas (Asahi Glass) Viton Extreme (DuPont P. E.)
VDF + TFE	Daiel 901 (Daikin) Fluorel (Dyneon) Tecnoflon (Solvay Sol.) Viton B (DuPont P. E.)	Viton GLT (DuPont P. E.)		
VDF + TFE + ethylene	Tecnoflon (Solvay Sol.)			

Table 11. ITP of Fluoroalkenes for the Synthesis of Fluorinated Hard-b-Soft-b-Hard Triblock Copolymers (NG, Not Given)

soft block[a]	monomers in soft block (wt %)	hard block	soft/hard ratio (wt %)	°C		refs
				T_g	T_m	
$I[(VDF)_xHFP]_yI$	NG	PVDF	NG	NG	160	290
	NG	poly(E-*alt*-TFE)	NG	NG	220	290
$I[(CTFE)_x(VDF)_y]_zI$	45/55	poly(E-*co*-TFE)	85/15	−6	247	296
	45/55	poly(E-*co*-TFE)	90/10	−8	252	296
$I[(VDF)_x(FVA)_y]_zI$	NG	PVDF	NG	NG	NG	188
$I[(TFE)_xP]_yI$	55/45	poly(E-*co*-TFE)	80/20	−1	267	294
$I[(VDF)_xHFP(TFE)_y]_zI$[b,c]	56/19/25	PVDF	80/20	−12 to −15	165	141, 295
	35/40/25	poly(E-*alt*-TFE)	NG	−8	222	290
	50/30/20	poly(E-*co*-HFP-*co*-TFE)	85/15	NG	NG	297
	54/21/25	poly(E-*alt*-TFE)	80/20	−13	266	295
$I[(VDF)_xPMVE(TFE)_y]_zI$[b]	62/19/19	PVDF	80/20	−30	160	187, 295
	73/17/10	poly(E-*co*-TFE)	72/28	−33	254	294
	NG	poly(E-*co*-TFE)	NG	−13 to −15	266	141, 295
	57/23/20	poly(E-*co*-TFE-*co*-PMVE)	75/25	NG	180	187
$I[(TFE)_xP(VDF)_y]_zI$	NG	poly(E-*co*-TFE)	85/15	−13	262	294
$I[(TFE)_xE(PMVE)_y]_zI$	45/19/36	poly(E-*co*-TFE)	71/29	−16	245	294

[a] Perfluoro vinylacetic acid, FVA. [b] Additional tetrapolymerization with less than 1 mol % of $H_2C{=}CH{-}C_6F_{12}{-}CH{=}CH_2$. [c] Additional tetrapolymerization with less than 1 mol % of $H_2C{=}CH{-}C_6F_{12}{-}CH{=}CH_2/H_2C{=}CHC_6F_{12}C_2H_4I/IC_2H_4C_6F_{12}C_2H_4I$ mixture.

I) and can be further successfully utilized as an original transfer agent in a second polymerization reaction (such as ATRP or ITP reactions), as follows:

$$I{-}R_F{-}I + nM_1 + nM_2 \rightarrow I{-}[(M_1)_x(M_2)_y]_z{-}R_F{-}[(M_1)_x(M_2)_y]_z{-}I(I{-}\mathrm{soft}{-}I)$$

$$I{-}\mathrm{soft}{-}I + pM_3 + qM_4 \rightarrow I{-}[(M_3)_p(M_4)_q]_\omega{-}\mathrm{soft}{-}[(M_3)_p(M_4)_q]\omega{-}I(I{-}\mathrm{hard}{-}\mathrm{soft}{-}\mathrm{hard}{-}I)$$

where M_1, M_2, M_3, and M_4 represent (fluoro)alkenes, which can be chosen among TFE, VDF, HFP, perfluoromethyl vinyl ether (PMVE), CTFE, and also E and propylene (P).

This process can be performed in emulsion, suspension, microemulsion,[285] or solution polymerization. Various companies have already shown much interest in this research. Indeed, Daikin's pioneering works from 1979[182,286−293] were confirmed at the Dupont Company[294] (now Dupont Performance Elastomers) and at Ausimont[141,187,295] (now Solvay-Solexis), leading to commercially available Daiel, Viton, and Tecnoflon XPL, respectively. A summary of these researches and products is given in Table 10. A combination of comonomers by pair, trio, or quartet enabled the authors to obtain both soft and hard segments (Table 11).[141,187,188,290,294−297] The proportion of these comonomers gives the properties (soft or hard segment). As an example, it is reminded that a poly(VDF-*co*-HFP) copolymers containing less than 15 mol % HFP is a thermoplastic (inducing hard block), while having an HFP content higher than 15 mol % exhibits elastomeric properties.[53,298]

Table 10 lists the various commercially available elastomers based on VDF, HFP, TFE, CTFE, PMVE, and P comonomers. For example, Tatemoto[290,297] proposed the synthesis of a soft segment by using the mixture of VDF/HFP/TFE and $I{-}(CF_2)_4{-}I$ in the presence of bis(trichloroperfluorohexanoyl) peroxide in 1,2,2-trifluorotricholorethane. The obtained soft $I(HFP)_x(VDF)_y(TFE)_zI$ diiodide (molar composition 30:50:20) exhibited a number average molar mass of 3300 g mol^{-1} with a PDI of 1.27.[297] The hard segment can be composed of PVDF or Poly(tetrafluoroethylene) (PTFE), or a combination of VDF (in high amount) with HFP or CTFE, or copolymers of TFE with E, PMVE, VDF (Table 10), or a poly(E-ter-TFE-ter-HFP) terpolymer. The different compositions of the hard segment are given in Table 11. The combination of these various monomers gives different properties, such as improved thermal stability, high melting point and low glass transition, chemical resistance, or better mechanical properties. For example, the addition of E as a comonomer in the mixture allows one to reduce the cost, but also the base sensitivity of VDF-containing copolymers,[294,299] and/or the livingness of the polymerization.[296] The properties of these TPEs are influenced by the molar mass of the segments. The central elastomeric segments are obtained by ITP process. Usually, the molar mass of the elastomeric segment is about 30000 g mol^{-1} whereas the hard blocks are higher than 10000 g mol^{-1}, although Yagi et al. have already claimed molar masses of TPE up to 1000000 g mol^{-1}. The TPEs are endowed with a negative glass transition temperature (T_g < 0 °C) and a high melting temperature (T_m), ranging from 160 to 267 °C. The schematic structural morphology of TPEs sketched by Figure 8 represents the amorphous (from soft segments) and crystalline (from hard blocks) zones, the latter inducing physical cross-links.

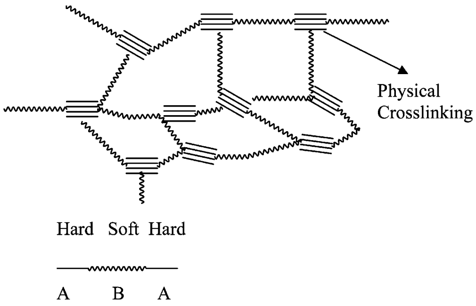


Figure 8. Schematic structural morphology of TPEs, such as Daiel, Tecnoflon XPL, or Viton GLT from Daikin, Ausimont (now Solexis), and Dupont Performance Elastomers, respectively.

To improve the properties of TPEs, Ausimont (now Solexis) has suggested adding $H_2C{=}CHC_6F_{12}CH{=}CH_2$ diene into the copolymer to lower the PDI and to favor a crosslinking. Interestingly, the compression set was increased by 13% at 120 °C. The stress at break increased from 7.8 to 10.4 MPa without any decrease of the elongation at break (Table 12).

Table 12. Properties of TPEs Copolymers Prepared with or without Bis-olefin ($CH_2{=}CH{-}C_6F_{12}{-}CH{=}CH_2$)[141,295]

polymer characteristics	copolymer (VDF/HFP/TFE: 55.9/18.2/25.9)		copolymer (VDF/PMVE/TFE: 62.1/19.1/18.8)	
	without	with	without	with
T_g (°C)	−15.1	−13.9	−29.3	−30.6
T_m (°C)	163.2	160.7	161.8	160.2
stress at break (MPa)	10.4	7.8	9.0	3.1
elongation at break (%)	452	460	384	520
compression set (120 °C for 24 h)	60	73	49	98

Furthermore, the introduction of PMVE in the soft segment did not significantly lower the T_g but increased the T_m by a few degrees.[141,294,295] Tatemoto[290,297] compared the thermal decomposition of three TPEs and showed an improved thermal stability when using exclusively the fluorine monomers as follows: (poly(E-*alt*-TFE)-*b*-poly(VDF-*co*-HFP)-*b*-poly(E-*alt*-TFE) < poly(E-*alt*-CTFE)-*b*-poly(VDF-*co*-HFP)-*b*-poly(E-*alt*-CTFE) < poly(VDF)-*b*-poly(VDF-*co*-HFP)-*b*-poly(VDF).

Thus, the fluorinated TPEs present a better stability than the conventional elastomers, such as the SBS triblock. They can be used from −30 to 250 °C (in continuous processing at 200 °C) and exhibit also other interesting properties such as a high specific volume, a low refractive index, and good surface properties. These characteristics can easily be used in high-tech areas (Table 13) such as aeronautics and aerospace (tubing, hoses,[247] rubber stoppers, O-rings and seals,[247] etc.), because they provide excellent resistance against aggressive chemical, fuels, oils, and ozone.

Another application of these triblock copolymers, obtained by ITP polymerization, concerns the compatibilizers for polymers. Table 13 gives a summary of the fields of applications from TPEs, and Figure 9 shows several examples of products obtained by ITP using R_FI transfer agents.

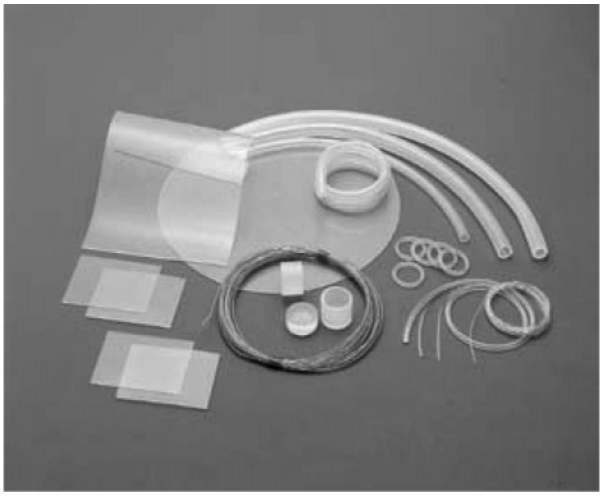


Figure 9. Several examples of items obtained by ITP, using R_FIs as transfer agents (courtesy of Daikin).

5.3. Conclusion

This subsection reports the wide range of applications found by the organic and macromolecular iodinated compounds. Interestingly, the molar masses, the functional end groups, the number, and the nature (elastomeric and thermoplastic) of the blocks target the expected properties and hence the applications.

Table 13. Fields of Applications and Items from TPEs

field of industry	molding	weather and chemical resistance	transparency	elasticity	safety	vulcanizability	mechanical properties	applications
biomedical	×	×	×	×	×			tubing, rubber stoppers, medical materials
physical and chemical equipment	×	×	×	×		×		tubing, seals, pipets
semiconductor	×	×	×	×	×	×		tubing and seals
chemical		×		×				anticorrosion paints, diaphrams, hoses, linings
food	×	×	×	×	×		×	hoses, sealing materials
electronics	×	×		×			×	wiring, sealing material
civil engineering	×	×		×				sealing materials, films, nonflammable materials
textile				×			×	coatings, filaments, fibers, water-repellant treatments
optics			×					lenses
others			×	×			×	adhesives (hot melt)

Organic derivatives have been involved as surfactants, as useful aqueous fire-fighting agents, lubricants, precursors of novel acrylates for surface modifiers used in coatings, textile, or leather finishing, or optical fibers (both cores and claddings). Block copolymers have already shown potential. However, there is an urgent need to replace toxic, bioaccumulable, and persistent PFOAs by challenging original and efficient surfactants for radical (mini)emulsion (co)polymerization of fluorinated alkenes. Such a topic has pushed many academic and industrial laboratories to be presently active in that field. In the same context, although a C_8F_{17} end group is hazardous but brings an exceptionally low surface energy, it is also necessary to find novel alternatives with C_4F_9 end groups for almost similar performances, as 3M has led the way. Another application concerns the TPEs based on the sequential CRP of a wide range of fluoroalkenes for which a suitable combination brings soft and hard sequences.

6. Conclusion

Iodocompounds, especially perfluoroalkyl ones, have been used for a long time in radical telomerization and polymerization to bring ω-perfluorinated end groups to the resulting polymers for specific properties. Although R_FIs have been mainly used for preparing telomers, these last years have witnessed the use of iodocompounds in CRP. These halogenated and especially perfluorinated telomers are valuable precursors of a wide range of fluorinated intermediates (alcohols, mercaptans, amines, allyl or vinyl derivatives, carboxylic acids, acrylates), which have already led to various applications: surfactants or monomers for textile, leather, metals, or stone protection.

In the late 1970s, the Daikin Company pioneered the use of these R_FIs or IR_FIs as CTAs in the CRP of fluorinated monomers, which further led to valuable applications. The transfer constants are often lower than those of noniodinated CTAs (CTAs involved in RAFT), which lead to higher PDIs. However, as compared to RAFT agent or xanthate derivatives, whose syntheses are often complex, iodinated CTAs are nowadays particularly interesting in the development of the CRP and certainly less expensive. This becomes particularly true when the use of molecular iodine is considered to synthesize in situ efficient iodinated transfer agents. In contrast to other CTAs, iodinated CTAs can be applied to a wide range of monomers. Iodinated CTAs indeed can be involved in universal polymer syntheses since it allows the control of various monomers such as styrenics, (meth)-acrylates, VAc, and even halogenated monomers. These parameters explain the use of iodocompounds in an industrial scale. It can be expected that their use will increase in the next decades.

In addition, the fluorinated iodocompounds are precursors of various materials endowed with remarkable properties for various applications. The fluorinated telomers lead to a wide range of intermediates bearing an ω-perfluorinated group. Such an end group brings specific properties (hydro- and oleophoby, surface modifiers, and soil repellency) that enable the resulting materials to be involved in various applications (coatings for textile, electronics, optics, AFFFs, surface modifiers, etc.).

In addition, TPEs are easily made and are versatile materials containing both soft and hard segments. Interestingly, various combinations of synthetic block microstructures are possible based on the comonomers involved in the different blocks to achieve both thermoplastic or elastomeric segments and, hence, to reach suitable T_g and T_m values. Various strategies applied by Daikin, Dupont Performance Elastomers, and Solvay-Solexis have led to commercially available block copolymers, regarded as the first ones produced in an industrial scale. However, lowering their T_g values is still a challenge, which is inherent to the T_g of the elastomeric block always higher than −33 °C (although the 3M Company recently produced an original statistic cross-linkable terpolymer endowed with a T_g of −40 °C[300]). Nevertheless, many applications of these TPEs have been found in civil and engineering materials such as hot melts, gaskets, O-rings, diaphragms of pumps, pressure sensitive adhesives, medical contact lenses, electronic chemical items, coatings for food industries, and other devices involved in high-tech industries. Hence, still many investigations deserve to be confirmed in that fascinating area, which should attract the interest of many academic and industrial researchers.

7. List of Symbols and Abbreviations

AIBN	α,α′-Azobisisobutyronitrile
ATRP	Atom transfer radical polymerization
BPO	Dibenzoyl peroxide
C_{ex}	Exchange constant
CRP	Controlled radical polymerization
C_{T1}	Transfer constant
CTA	Chain transfer agent
CTFE	Chlorotrifluoroethylene
DP_n	Number average degree of polymerization
DT	Degenerative transfer
DTBP	Di-*tert*-butyl peroxide
E	Ethylene
ECF	Electrochemical fluorination
FVA	Perfluoro vinylacetic acid
HFP	Hexafluoropropylene
IR_FI	α,ω-Diiodoperfluoroalkane
ITP	Iodine transfer polymerization
M	Monomer
MADIX	Macromolecular design trough interchange of xanthates
MMA	Methyl methacrylate
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance
P	Propylene
PDI	Polydispersity index
PMMA	Poly(methyl methacrylate)
PMVE	Perfluoromethyl vinyl ether
POF	Polymeric optical fibers
PTFE	Poly(tetrafluoroethylene)
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
R	Alkyl group
RAFT	Reversible addition−fragmentation chain transfer polymerization
R_F	Perfluorinated group
R_FI	Perfluoroalkyl iodide
RITP	Reverse iodine transfer polymerization
SEC	Size exclusion chromatography
SET	Single electron transfer
Sty	Styrene
TFE	Tetrafluoroethylene
TFP	3,3,3-Trifluoropropene
T_g	Glass transition temperature
TPE	Thermoplastic elastomers
TrFE	Trifluoroethylene
VAc	Vinyl acetate
VDF	Vinylidene fluoride (or 1,1-difluoroethylene)
Δ	Heating

8. References

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