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Poly(vinylidene fluoride)-*b*-poly(styrene) Block Copolymers by Iodine Transfer Polymerization (ITP): Synthesis, Characterization, and Kinetics of ITP

David Valade, Cyrille Boyer, Bruno Ameduri,* and Bernard Boutevin

Laboratoire de Chimie Macromoléculaire, UMR (CNRS) 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France

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ABSTRACT: The syntheses of poly(vinylidene fluoride)-*b*-poly(styrene) (PVDF-*b*-PS) block copolymers, from the iodine transfer polymerization (ITP) of styrene, in the presence of PVDF−I, are presented. In a first step, considering that the radical polymerization of vinylidene fluoride can lead to two different isomeric oligomers, bearing either $-CH_2I$ or $-CF_2I$ end groups, the kinetics of ITP of styrene in the presence of two chain transfer agents, $C_6F_{13}-CH_2CF_2-I$ and $HCF_2-CF_2CH_2-I$, were achieved as model reactions. The characterization of sampled aliquots by ^{19}F NMR spectroscopy could monitor the average degree of polymerization in number (DP_n) vs styrene conversion ($\alpha_{Styrene}$). ITPs of styrene with both these chain transfer agents showed two opposite behaviors, also confirmed by MALDI−TOF spectroscopy and SEC chromatography. (i) on the one hand, in the presence of $C_6F_{13}-CH_2CF_2-I$, the controlled character of ITP of styrene was evidenced (a linear dependence of DP_n vs $\alpha_{Styrene}$ was observed), theoretical DP_n values were close to those of the targeted ones, with low polydispersity indexes (PDI = 1.5) and the transfer constant value was assessed ($C_{Tr} \cong 1$); (ii) on the other hand, using $HCF_2-CF_2CH_2-I$ as the chain transfer agent, ITP of styrene did not occur since only a direct initiation for the polymerization of styrene was noted, with DP_n value higher than the targeted one and a broad polydispersity distribution (PDI > 2). In a second part, PVDF-*b*-PS block copolymers were synthesized via a two step-procedure, ITP of VDF in the presence of $C_6F_{13}I$ as the chain transfer agent leading to $C_6F_{13}(VDF)_n-I$ oligomers and, subsequently, ITP of styrene using those latter oligomers as macromolecular chain transfer agents. These block copolymers were characterized by ^{19}F and ^1H NMR and MALDI−TOF spectroscopies, and by SEC chromatography. Their morphological and thermal properties were also studied by atomic force microscopy (AFM) and by differential scanning calorimetry (DSC), respectively.

Introduction

Fluorinated polymers are well-known because of their outstanding properties,[1,2] such as surface tension, hydrophoby, lipophoby, and good thermal, physical, and chemical stabilities making them suitable materials for high-technology industry. These polymers are usually synthesized by radical (co)-polymerization of fluorinated alkenes (such as tetrafluoroethylene, vinylidene fluoride, chlorotrifluoroethylene, trifluoroethylene, etc.). However, these fluorinated alkenes do not copolymerize with other commonly used monomers such as styrene or acrylates[2,3] because these latter ones are more reactive. As a matter of fact, well-architectured fluoropolymers (alternated, graft, or block copolymers) are few, and it is still a challenge to prepare them since most fluorinated polymers are not miscible or compatible with hydrogenated ones. This kind of well-architectured fluorinated copolymers has received much attention since their chemical structure brings new physical and thermodynamical properties. Interestingly, these polymers have found many applications such as adhesives and sealants, surface modifiers for fillers and fibers, cross-linking agents for elastomers, additives for resin gelation and hardening, compatibilizers, stable emulsions of homopolymers blends that can be used in recovery and recycling plastic waste, and nanostructured materials.[4] Although block copolymers can be prepared from nonradical techniques, such as living ionic polymerization,[5] their synthesis from radical polymerization have been investigated with much interest. First, conventional radical polymerization and telomerization have led to block copolymers.[2,6] Second, the preparation of block copolymers by radical controlled polymerization had been achieved a decade ago and is now one of the most used methods. A radical polymerization can be named "controlled" when the three following conditions are fulfilled:

(i) The controlling species must be quickly consumed and this rate must be faster than that of the propagation.

(ii) The polymeric chain must be created in a short time and not in the course of the polymerization as in the traditional process.

(iii) The dormant and living species must exchange rapidly.

Iniferter (*ini*tiation−trans*fer*−*ter*mination) method,[7,8] nitroxide-mediated polymerization (NMP),[9] atom transfer radical polymerization (ATRP),[10−12] or metallocene-catalyzed polymerization,[8,13] reversible addition−fragmentation chain transfer (RAFT),[14] iodine transfer polymerization (ITP),[15−17] or reverse iodine transfer polymerization (RITP)[18] allow to produce a large variety of block copolymers.[19] However, a few studies have been carried out on the synthesis of fluorinated block copolymers from these processes. Nevertheless, using radical controlled polymerization as iodine transfer polymerization (ITP), this type of copolymerization becomes possible, leading to the formation of block copolymers.[19,20] Discovered in the late 1970s[15,21] but studied with much interest since the mid-1990s, controlled radical polymerization is based on adding in a polymerization medium a species able to react with active centers by reversible termination[9,15,21,22] or by transfer.[16,23,24] Hence, an equilibrium occurs between the living radicals (or active species) and dormant (or nonpropagating) species. Nowadays, iodine transfer polymerization of fluorinated alkenes is a technique industrially used by various companies involved in fluorine chemistry (such

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* To whom correspondence should be addressed: Telephone: +33-467-14-43-68. Fax: +33-467-14-7220. E-mail: bruno.ameduri@enscm.fr.

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Table 1. Overview of Fluorinated Block Copolymers Synthesized from Different Methods[a]

method	initiator, catalyst or chain transfer agent	structure of block copolymer
	Radical Polymerizations	
iniferter	thiuram	P*t*BuMA-*b*-PTFEMA[30], PS-*b*-PFOA[31], PDMAEMA-*b*-PFOA[32]
	tetraphenyl ethane	PTFEMA-*b*-PS[33]
ITP	R_FI	P(fluoroalkene)-*b*-P(fluoroalkene)[15,16,25,34]
ATRP	PVDF−I	PVDF-*b*-PMMA[29]
	PVDF−CCl_3	PVDF-*b*-PS, PVDF-*b*-PMMA, PVDF-*b*-PEA[11]
	P(VDF-*co*-HFP)-CCl_3	P(VDF-*co*-HFP)-*b*-PS,[27,28] P(VDF-*co*-HFP)-*b*-PMMA[27]
		PS-*b*-PFA,[35] PMA-*b*-PFA,[36] PFAS-*b*-PS,[37] P*t*BuMA-*b*-PFAEM[38]
RAFT	aromatic dithioester	P(VC_2-*co*-MA)-*b*-PFA[39]
NMP	P_M-TEMPO (M = S or FAS)	PFAS-*b*-PS,[40] PS-*b*-PFAS, PS-*b*-PFA[41]
telome-rization	PFPE-I	PFPE-*b*-PVDF, PFPE-*b*-P(VDF-*co*-HFP)[42]
	PFPE-Br	PFPE-*b*-PVDF,[43,44] PFPE-*b*-P(VDF-*co*-HFP), PFPE-*b*-PTFE[43]
	DBTFE	PVDF-*b*-PSu[45]
	Nonradical Polymerizations	
cationic	CF_3SO_3H	PVE-*b*-PPFVE[46]
	$ZnCl_2$	PVE-*b*-PFVE[47]
	X/$scCO_2$	PFVE-*b*-PHVE[48]
	PTFE-OH	PTFE-*b*-PCL[49]
anionic	*sec*-BuLi/1,1-diphenyl ethylene	PS-*b*-PFAS,[50] PS-*b*-SFPI[51]
	BuLi/LiCl	PMMA-*b*-PFMA,[52] PS-*b*-PBD/R_F[53]
	1,1-diphenyl-3-methyl pentyllithium/LiCl	P*t*BuMA-*b*-P(2-FBSMA)[54]
		PFAS-*b*-PI[40]
		fluorination by HFPO of PS-*b*-PI[55]
metathesis	C_8F_{17}	PTFE-*b*-PE[56]
GTP	MMTP	PMMA-*b*-PFMA,[57] PTHPMA-*b*-PFMA[58]
ROMP		PFPE-*b*-PCL[59]
polycondensation		PDSB-*b*-PHEO[60]
		P(A/R_F)−PU[61]

[a] Key: *t*BuMA, *tert*-butyl methacrylate; TFEMA, trifluoroethyl methacrylate; S, styrene; FOA, 1,1-dihydro-perfluorooctyl acrylate; DMAEMA, 2-dimethylaminoethyl methacrylate; MMA, methyl methacrylate; EA, ethyl acrylate; HFP, hexafluoropropene; FA, F-acrylate; VC_2, vinylidene chloride; MA, methyl acrylate; FAS, fluoroalkoxy styrene; PFPE, perfluoropolyether; TFE, tetrafluoroethylene; DBTFE, 1;2-dibromotetrafluoroethane; Su, sulfone; VE, vinyl ether; PFVE, perfluorovinyl ether; FVE, fluorovinyl ether; CL, caprolactone; SFPI, semifluorinated polyisoprene; FMA, 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl methacrylate; BD, 1,3-butadiene; FBSMA, 2-(*N*-methyl perfluorobutane sulfonamido) ethyl methacrylate; I, isoprene; HFPO, hexafluoropropene oxide; E, ethylene; MMTP, 1-methoxy-2-methyl-1-trimethylsilyloxy-1-propene; THPMA, tetrahydropyranyl methacrylate; HEO, hexaethylene oxide; A, amide and PU, polyurethane. ITP, ATRP, RAFT, NMP, GTP, and ROMP mean iodine transfer polymerization, atom transfer radical polymerization, reversible addition−fragmentation transfer, nitroxide mediated polymerization, group transfer polymerization and ring-opening metathesis polymerization.

as Daikin, Dupont de Nemours, and Solvay Solexis) to produce original fluorinated block copolymers bearing hard and soft sequences known as thermoplastic elastomers (TPEs).[2,16,23,25,26] However, few studies report the use of this technique to prepare fluorosegment-*b*-hydrogenated block copolymers, generally based on using halogenated species bearing cleavable C−Cl, C−Br, and C−I bonds:

(i) Destarac et al.[11] used PVDF−CCl_3 telomers (synthesized from the radical telomerization of VDF in the presence of chloroform) to produce PVDF-*b*-MMA and PVDF-*b*-PS block copolymers. Later, Shi and Holdcroft[27,28] described the synthesis of segmented copolymers also by ATRP process. These authors proposed the synthesis of first block by radical cotelomerization of VDF and hexafluoropropene (HFP) in the presence of chloroform to lead to a trichloromethyl-terminated poly(VDF-*co*-HFP) telomers, which exhibit molecular weights up to 25 000 g mol^{-1}. Then, as above, these cotelomers behaved as efficient initiators for the ATRP of styrene (S), of methyl methacrylate (MMA), or styrene sodium sulfonate (SSS), to form a series of poly(VDF-*co*-HFP)-*b*-PS or poly(VDF-*co*-HFP)-*b*-PSSS block copolymers.

(ii) PS-*b*-PVDF-*b*-PS tribloc copolymers were proposed by Zhang et al.[10] from a telechelic dibrominated (Br−PVDF−Br), which was prepared by radical telomerization of VDF in the presence of 1,2-dibromotetrafluoroethane. In the second step, these α,ω-dibrominated telomers initiated the ATRP of styrene.

(iii) A similar approach was used by Jo et al.[29] to synthesize PVDF-*b*-PMMA and PMMA-*b*-PVDF-*b*-PMMA block copolymers. The synthesis of iodio-terminated PVDF was performed by telomerization of VDF in the presence of $C_nF_{2n+1}-I$ (n = 4, 6 or 8) or $I-C_pF_{2p}-I$ (p = 4 or 6), as the CTAs. The authors used the iodine extremities of PVDF to polymerize MMA by ATRP process leading to block copolymers. They used CuI, sometimes difficult to eliminate. They showed that PVDF bearing $-CH_2I$ end group was less reactive than $-CF_2I$ functions. Thus, further efforts would have been deserved to investigate the synthesis of such diblock copolymers containing PVDF.

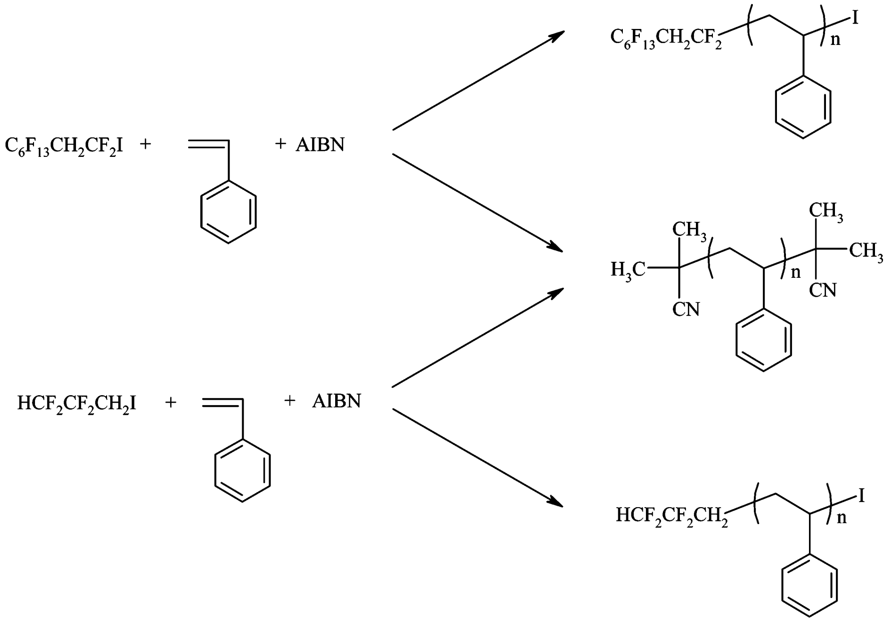
Other synthesis of fluorinated block copolymers have been reported and Table 1 summarizes different strategies.[11,15,16,25,27−61]

In our approach, an original route was chosen, resulting from the synthesis of fluorinated block copolymers prepared by sequential ITP. First, a polyvinylidene fluoride containing an iodo end-atom (PVDF−I) block was synthesized followed by the end-capping of a second block based on poly(styrene). The first part was already reported,[62] while this present investigation concerns the preparation of PVDF-*b*-PS block copolymer from PVDF−I. However, as previously shown,[63] these PVDF−I macroinitiators exhibit two isomeric end groups, $-CH_2CF_2-I$ and $-CF_2CH_2-I$, for which ITP of styrene has never been attempted. This is why two chain transfer agents (CTAs) were used, $HCF_2-CF_2CH_2-I$ and $C_6F_{13}-CH_2CF_2-I$ as models of PVDF−I, to mimic both possible end groups generated in the course of ITP of vinylidene fluoride (Scheme 1 in Supporting Information).[62] Second, that strategy was extended to the synthesis of various PVDF-*b*-PS blocks copolymers, the morphological and thermal properties of which, have also been investigated.

Experimental Part

Materials. Vinylidene fluoride, or 1,1-difluoroethylene (VDF), and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay S.

Scheme 1. Synthesis of α-Fluoroalkyl Poly(styrene) by Iodine Transfer Polymerization in the Presence of $C_6F_{13}CH_2CF_2I$ and $HCF_2CF_2CH_2I$ as Different Chain Transfer Agents (CTAs)



A., Tavaux, France, and Brussels, Belgium. Perfluorohexyl iodide (99%) was kindly supplied by Elf Atochem, France. 1,1,2,2-Tetrafluoro-3-iodopropane (99%) and azobis(isobutyronitrile) (AIBN) were purchased from Aldrich Chimie, (38299 Saint Quentin-Fallavier, France). AIBN was recrystallized twice from methanol, dried at 0 °C under vacuum (0.01 mmHg) for 6 h and stored at −4 °C. *tert*-Butylperoxypivalate (TBPPI, purity 75%) and 2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane (DHBP, purity 90%) were gifts from "Akzo Nobel", Ohlin, Belgique. They were used as supplied just like acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), and methanol, from Aldrich Chimie (38299 Saint Quentin-Fallavier, France).

Analyses. The compositions and the microstructures of the oligomers obtained by iodine transfer polymerization (ITP) of VDF were determined by ^{19}F and ^{1}H NMR spectroscopies. The NMR spectra were recorded on Bruker AC 200, AC 250, and AC 400 instruments, using deuterated acetone and DMF as the solvents and trimethylsilane, TMS, (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra were the following: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 μs for ^{19}F NMR.

Gas chromatography (GC) was performed with a Delsi Instruments 330 apparatus equipped with a Shimadzu C-R6A integrator and a two meters long Carbowax 20 M (poly(ethylene glycol)) column. Nitrogen was used as the vector gas at a pressure of 1.5 bar. The analysis was performed at a oven temperature of 150 °C ($T_{\text{detector}} = 250$ °C, $T_{\text{injector}} = 230$ °C). GC was used to determine the monomer conversion throughout the polymerization. Anisole was used as the internal standard.

Size exclusion chromatography (SEC or GPC) was performed at 30 °C on a Spectra-Physics apparatus with three columns PLgel 5 μm MIXED-D, 500 Å, and 100 Å from Polymer Laboratories, and equipped with two Shodex refractive index (RI) and UV detectors. THF was used as the solvent at 0.8 mL min^{-1}. Calibration was established with poly(styrene) standards from Polymer Laboratories.

MALDI−TOF mass spectrometry was performed at "Ultraflex Bruker" (University of Montpellier II) in reflectron mode (accelerating potential of 20 kV) on a Bruker apparatus equipped with a nitrogen laser (337 nm). 2,3,4,5,6-Pentafluorocinnamic acid (PFCA) was used as the matrix and sodium iodide (NaI) or potassium iodide (KI) were used as the cationizing agent. The concentrations of sample and matrix solutions were 10 g L^{-1} in tetrahydrofuran, and the analyte-to-matrix ratio was 1/10 v/v. Then 1 μL of the mixture was deposited on a stainless steel target, air-dried, and introduced into the spectrometer under vacuum.

Thermogravimetric analyses (TGA) were conducted with a TA Instruments, TGA 51. A 10−15 mg sample of the copolymers was placed in a platinum pan and heated from 30 to 600 °C under air at a heating rate of 5 °C min^{-1}.

Atomic force microscopy (AFM) was performed using a multimode scanning probe microscope (Park Scientific Autoprobe CP) in intermittent-contact mode with a silicon tip. The AFM images were obtained at room temperature under air. The samples were prepared from spin-coating of the copolymer solution (in acetone) on glass substrates.

Reactions in Autoclave. Synthesis of the C_6F_{13}—CH_2CF_2—I Chain Agent Transfer. $C_6F_{13}CH_2CF_2I$ was synthesized by thermal telomerization of VDF with $C_6F_{13}I$ at 200 °C for 12 h, and this monoadduct was purified by distillation as previously reported.[64]

Synthesis of PVDF—I Oligomers. ITPs of VDF were performed in the presence of perfluorohexyl iodide as the CTA and with *tert*-butylperoxypivalate as the initiator, at 75 °C, according to a procedure described elsewhere.[62]

The sample was characterized by ^{19}F and ^{1}H NMR spectroscopy (supplied in the Supporting Information).

Synthesis of Oligo(styrene) with $M_{n,\text{targeted}} = 2000$ g mol^{-1} by Iodine Transfer Polymerization (ITP) in the Presence of $C_6F_{13}CH_2CF_2I$, as the CTA (Initial Concentration of $[\text{Styrene}]_0$:$[C_6F_{13}CH_2CF_2I]_0$:$[\text{AIBN}]_0 = 100:5:0.5$) at 70 °C. First, 10.400 g (0.100 mol) of styrene, 2.501 g (0.005 mol) of $C_6F_{13}CH_2CF_2I$, 0.164 g (0.5 mmol) of AIBN, and 20 mL of acetonitrile were placed in a 50 mL round-bottom Schlenk flask protected with an aluminum foil. The reaction medium was purged with argon for 15 min at 0 °C to remove oxygen, then sealed with a septum, and placed in an oil bath at 70 °C under magnetic stirring. Aliquots were sampled periodically, cooled in an ice bath, inhibited with hydroquinone, and then characterized by SEC and GC chromatographies and by ^{1}H NMR spectroscopy to determine the molecular weights and the styrene conversion, respectively. When the monomer conversion was close to 90%, the reaction was stopped. Acetonitrile was removed by rotary evaporation and the residue was diluted in THF. Then, the polymer was precipitated twice from methanol (the free monomer and CTA were methanol-soluble). After drying, the precipitated polymer was characterized by ^{1}H and ^{19}F NMR and by SEC. The yield of polymerization was determined by gravimetry, yield = $[m_P/(m_{Styrene} + m_{CTA})] \times 100$, where m_P, $m_{Styrene}$, and m_{CTA} stand for the weight of polymer recovered after precipitation and the initial weights of styrene and CTA (or $C_6F_{13}CH_2CF_2I$) in the reaction medium, respectively. In this present case, the yield was 95%. The ^{19}F NMR spectrum of $C_6F_{13}CH_2CF_2(styrene)_n$-I was recorded in $CDCl_3$. δ (ppm): −82.0 (m, CF_3-CF_2-); −90.0 ppm ($-CF_2CH_2CF_2-$); −112.0 ($-CF_2-CH_2-CF_2$); −121.0 ($-CF_2CF_2$-CH_2-); −123.0 ($-CF_2CF_2CF_2CH_2-$); −123.5 ppm ($-CF_2CF_2CF_2$-CF_2CH_2), −126.0 ppm (CF_3CF_2-); ^1H NMR: from 1.0 to 2.0 ppm ($-CH_2CH(C_6H_5)-$); 2.5 ppm ($-CF_2-CH_2-CH(C_6H_5)-$); 3.5 ppm ($-CF_2-CH_2-CF_2$); 4.6 ppm (CH-I); 6.8−7.2 ppm (C_6H_5).

Synthesis of Oligo(styrene) with $M_{n,targeted}$ = 2000 g mol^{-1} by Iodine Transfer Polymerization (ITP) of Styrene in the Presence of $HCF_2CF_2CH_2I$ (Molar Ratio of $[Styrene]_0$:$[HCF_2CF_2CH_2I]_0$:$[AIBN]_0$ = 100:5:0.5) at 70 °C. The same procedure as above was used in the presence of $HCF_2CF_2CH_2I$. In the present case, the yield was 91%.

^{19}F NMR spectroscopy of $HCF_2CF_2CH_2I$ was carried out in deuterated acetone (δ (ppm)): −111.0 ppm (tt, $-CF_2CH_2I$); −136.0 ppm (dm, HCF_2). ^1H NMR: 4.0 ppm (q, CF_2CH_2I); 6.5 ppm (tt, HCF_2).

^{19}F NMR spectroscopy of $HCF_2CF_2CH_2(styrene)_n-I$ deuterated acetone, δ (ppm): no signal was observed. ^1H NMR: 1.0−2.0 ppm ($-CH_2CH(C_6H_5)-$); 6.8−7.2 ppm (C_6H_5).

Synthesis of PVDF-*b*-PS Block Copolymers. PVDF-*b*-PS block copolymers were synthesized, sampled, purified, and characterized according to the procedure used for the synthesis of oligo(styrene) described above, with 1.780 g (1.74×10^{-2} mol) of styrene, 10.00 g (8.77×10^{-3} mol) of $C_6F_{13}(CH_2CF_2)_{10}I$, 0.164 g ($8.77 \times 10^{-4}$ mol) of AIBN and 20 mL of DMF. The functionality in iodine was assessed by taking into account the integral of CH−I signal centered at 4.6 ppm and that of CH_2 in $C_6F_{13}CH_2CF_2$, as follows:

$$\text{functionality}^{\text{iodine}} = \int -CH(C_6H_5)-I/(\int C_6F_{13}CH_2CF_2/2)$$

In the course of the polymerization, it was noted that the functionality decreased with the styrene conversion.

Results and Discussion

1. Iodine Transfer Polymerization of Vinylidene Fluoride. This present study uses the iodine transfer polymerization (ITP). The ITP process is described in Supporting Information. The synthesis of PVDF−I oligomers was carried out at 75 °C, initiated by *tert*-butyl peroxipivalate (TBPPI), in the presence of $C_6F_{13}CH_2CF_2I$ as the chain transfer agent, and 1,1,1,3,3-pentafluorobutane as the solvent. After 1 h, the conversion of VDF (α_{VDF}) was close to 80%. After work up and purification, these polymers were characterized by ^1H and ^{19}F NMR spectroscopies, showing the presence of both end groups, $-CF_2I$ and $-CH_2I$ hence confirming a previous study.[62] Consequently, because of the different reactivities of these end groups, it was worth using two chain transfer agents (CTAs) representing the possible terminations of PVDF−I oligomers: $HCF_2-CF_2CH_2-I$ and $C_6F_{13}-CH_2CF_2-I$. Hence, two model reactions were investigated for the iodine transfer polymerization of styrene from both CTAs (Scheme 1).

From this technique, we synthesized different oligomers with various molecular weights (see Table 4). It was observed that the proportion of polymer bearing -CF_2I end groups decreased when molecular weight or DP_n increased. This evolution is in agreement with a previous study[62]. Indeed, because of the structural asymmetry of vinylidene fluoride, it was noted that inversions occurred, to each monomer addition onto a growing chain, although the addition of the macroradical onto a = CH_2 site of VDF was more often observed[63]. Yet, as the $-CH_2-I$ bond is less reactive than $-CF_2I$, oligomers bearing the $-CH_2I$ end group were inactive, while oligomers bearing the $-CF_2I$ extremity were able to be reactivated for further insertion of VDF units.

2. Model Reaction of ITP of Styrene. ITP of styrene in the presence of $C_6F_{13}I$ as the CTA has already been reported[65] in miniemulsion. However, to our knowledge, the efficiency of the CTA regarding the environment of the iodine atom has never been investigated. Thus, it was of interest to consider $C_6F_{13}-CH_2CF_2-I$ and $HCF_2-CF_2CH_2-I$ as two different chain transfer agents involved in ITP of styrene in solution. In fact, in the former CTA, the presence of both electron-withdrawing fluorine atoms in α position to the iodine end-atom makes the carbon−iodine bond very labile[2] while the latter CTA, bearing a $-CH_2I$ end group, was expected to be less reactive because of the higher stability of the CH_2-I bond.

2.1. ITP of Styrene in the Presence of $C_6F_{13}CH_2CF_2I$ and $HC_2F_4CH_2I$. The ITP of styrene with $C_6F_{13}CH_2CF_2I$ was carried out at different temperatures (65, 70, and 80 °C), in the presence of AIBN as the radical initiator and acetonitrile as the solvent, for 8 h. At the end of the reaction, the polymer was precipitated from methanol to remove unreacted CTA, styrene, and oligomers having very low molecular weights, and then it was dried and characterized by SEC, by ^1H, ^{13}C, and ^{19}F NMRs, and by MALDI−TOF spectroscopies.

Starting from two different CTAs ($C_6F_{13}CH_2CF_2I$ and HC_2F_4-CH_2I) involved in various concentrations, and, as a consequence, different targeted degrees of polymerization, oligostyrenes bearing an ω-fluoroalkyl group showing various molecular weights were obtained (Table 2).

As shown in a previous work[63] that reports the ITP of VDF, both CTAs above exhibit different reactivities while they contain isomeric −VDF−I end groups. Whereas $C_6F_{13}-CH_2CF_2I$ has the same reactivity as that of $C_6F_{13}I$ in PVDF−I, showing a good control of molecular weight (M_n) with a narrow polydispersity index (PDI), $HC_2F_4CH_2I$ exhibits a lower reactivity. Both ITPs of styrene in the presence of these CTAs are detailed separately below.

2.1.1. Synthesis of Oligo(styrene) by ITP of Styrene Involving $C_6F_{13}-CH_2CF_2-I$ as the CTA. ITP of styrene in the presence of $C_6F_{13}-CH_2CF_2-I$ as the CTA led to various oligo(styrene)s bearing a $C_6F_{13}-CH_2CF_2$ α-group. The resulting purified $C_6F_{13}-CH_2CF_2-PS-I$ oligomers were analyzed by different methods. First, the microstructures were characterized by NMR spectroscopy. For example, the ^{19}F NMR spectrum of these oligomers (Figure 1) evidences the $C_6F_{13}-CH_2CF_2-$ end group by the presence of signals centered at (i) −82.0 ppm (assigned to CF_3-), (ii) between −120.0 and −130.0 ppm [attributed to CF_2s in $CF_3(CF_2)_4-CF_2-CH_2CF_2-CH_2-CH$-$(C_6H_5)-$], (iii) at −112.0 ppm (corresponding to $-CF_2-$ in $C_5F_{11}-CF_2-CH_2-CF_2-PS$), and (iv) from −88.0 to −92.0 ppm (attributed to $-CF_2-$ in $C_5F_{11}-CF_2-CH_2-CF_2-PS$).

The characteristic signal centered at −40 ppm assigned to $-CH_2-CF_2I$ end group of the CTA has undergone an upfield shift to −92 ppm, corresponding to the formation of $C_6F_{13}-CH_2-CF_2[CH_2-CH(C_6H_5)]_n-$ also showing a total conversion of the CTA. Moreover, the ^1H NMR spectrum (Figure 2) confirms the presence of the quintet assigned to the methylene in $C_6F_{13}-CH_2-CF_2-$ end groups, centered at 3.5 ppm, which does not shift, hence showing the presence of the fluorinated end group arising from the CTA. That ITP of styrene was successfully achieved as evidenced by the presence of a signal centered at 4.6 ppm attributed to $-CH(C_6H_5)-I$[66] end group while the aromatic protons were observed between 6.8 and 7.2 ppm.

Table 2. Summary of Molecular Weight Values (M_n) of Oligo(styrene)s for Various Concentrations of $C_6F_{13}CH_2CF_2I$ and $HCF_2CF_2CH_2I$ as the Chain Transfer Agents (CTAs) in the Iodine Transfer Polymerization (ITP) of Styrene Initiated by AIBN at Different Temperatures

runs	T (°C)	concentration ratios $[M]_0$:$[CTA]_0$:$[In]_0$	targeted[a] M_n (g mol^{-1})	$\alpha_{Styrene}$[b] (%)	α_{CTA}[c] (%)	M_n[d] (g mol^{-1})	SEC analysis[e] M_n (g mol^{-1})	PDI	*funct*[f] −CH−I (%)
1	70	100.0:0.0:2.5		95			40 000	2.20	0
				CTA: $C_6F_{13}-CH_2CF_2-I$					
2	70	100.0:5.0:0.50	2580	95	94	1880	2100	1.55	96
3	70	100.0:3.3:0.33	3660	91	90	3460	4100	1.65	97
4	70	100.0:2.5:0.25	4680	95	96	4750	5200	1.70	91
5	80	100.0:2.5:0.25	4680	89	88	4500	4800	1.50	85
6	65	100.0:2.5:0.25	4680	92	90	4800	4800	1.50	90
7	70	100.0:1.0:0.10	10 900	90	88	8800	10 900	1.70	
				CTA: $HCF_2-CF_2CH_2-I$					
8	65	100.0:5.0:0.50	2300	93	0		30 000	2.10	
9	70	100.0:5.0:0.50	2300	91	0		31 000	2.10	
10	70	100.0:3.3:0.33	3340	95	0		33 100	2.15	
11	70	100.0:1.0:0.10	10 630	90	0		38 800	2.10	
12	80	100.0:5.0:0.50	2000	90	0		33 000	2.12	

[a] M_n = ([Styrene]$_0$/[CTA]$_0$) × $M_{styrene}$ + M_{CTA} (M_{CTA} = 242 g mol^{-1} for $HCF_2CF_2CH_2I$ and M_{CTA} = 510 g mol^{-1} for $C_6F_{13}CH_2CF_2I$). [b] Assessed by ^{1}H NMR. [c] Determined by ^{19}F NMR. [d] Assessed by ^{1}H NMR. [e] Determined by SEC (with PS standards and by means of a UV detector). [f] Determined by ^{1}H NMR from the equation $functionality^{iodine} = \int -CH(C_6H_5)-I/(\int -CF_2CH_2CF_2/2)$, where $\int$ represents the integral of the corresponding signal.

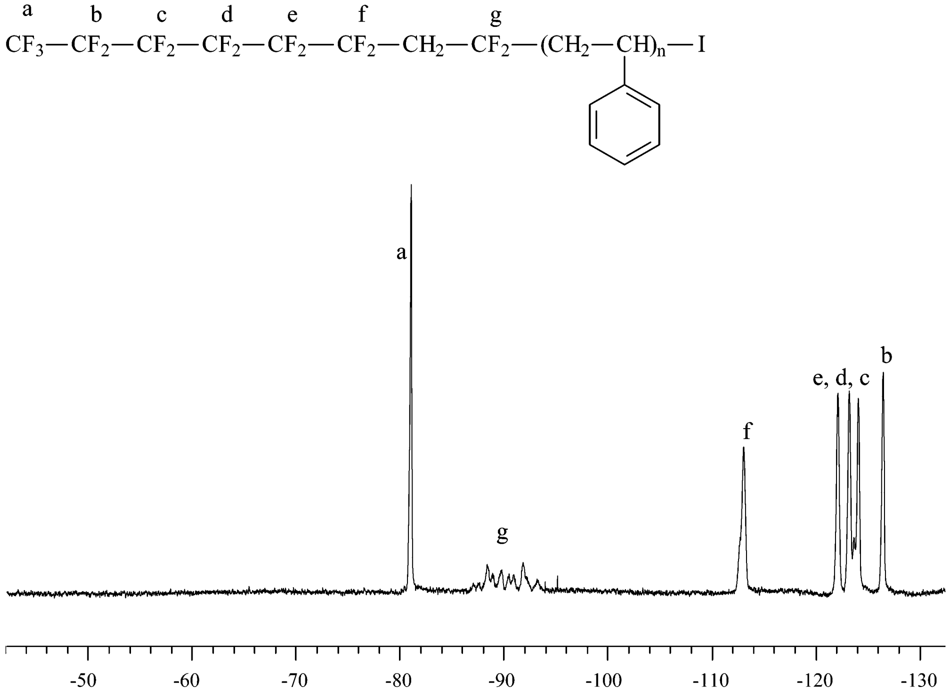


Figure 1. ^{19}F NMR spectrum of $C_6F_{13}-CH_2-CF_2-PS-I$ oligomers (run no. 4, Table 2) obtained by iodine transfer polymerization (ITP) of styrene in the presence of $C_6F_{13}-CH_2-CF_2-I$ as the chain transfer agent (400 MHz, deuterated DMF). Experimental conditions: iodine transfer polymerization (ITP) of styrene performed in the presence of $C_6F_{13}CH_2CF_2I$ at 70 °C in acetonitrile; molar ratio [Styrene]$_0$:[$C_6F_{13}-CH_2-CF_2-I$]$_0$:[AIBN]$_0$ = 100.00:2.50:0.25.

Second, the kinetics of the ITP of styrene was monitored by SEC, the chromatograms of which show two signals centered at about 17 and 20 min (Figure 1 in Supporting Information). The first one is attributed to oligomers while the second one corresponds to the CTA. It was noted that, in the course of the polymerization, the intensity of the former signal increased while the latter one decreased and even disappeared after 8 h, which confirms the consumption of CTA and the efficient radical polymerization of styrene.

The structure of these oligomers was further characterized by MALDI−TOF spectrometry performed in reflectron mode. Figure 3 represents the mass spectrum of a PVDF-*b*-PS block copolymer that shows a series of peaks separated by m/z = 104.06 (corresponding to the molecular weight of one styrene unit). The expansion of the zone ranging from m/z = 2000 to m/z = 9000 (centered on the population containing 20 styrenic units (Figure 3)) exhibits three different series: (i) First, the expected $C_6F_{13}-CH_2-CF_2[CH_2-CH(C_6H_5)]_{20}-I/K^+$ structure (A) is located at m/z = 2630.1 (series A, theoretical value m/z = 2630.28). (ii) Second, a minor distribution at m/z = 2606.3 (series B, theoretical value m/z = 2606.8) can be ascribed to the elimination of HI in the polymeric chains of structure (A with n = 21). This loss of HI induces a vinyl terminated polystyrene and it can occur either at temperature higher than 150 °C or in the course of the MALDI−TOF analysis. This end group rearrangement was also observed in various studies[67] (e.g., when poly(styrene) contained either a bromine or a chlorine end-atom). (iii) Third, a distribution at m/z = 2604.23 is noted with a weak intensity and can be attributed to oligomers produced from the direct initiation of AIBN onto styrene. Such $(CH_3)_2(CN)C[CH_2-CH(C_6H_5)]_{24}-CH{=}CH(C_6H_5)/K^+$ oligomers can be obtained by dehydroiodination of $(CH_3)_2(CN)C$-

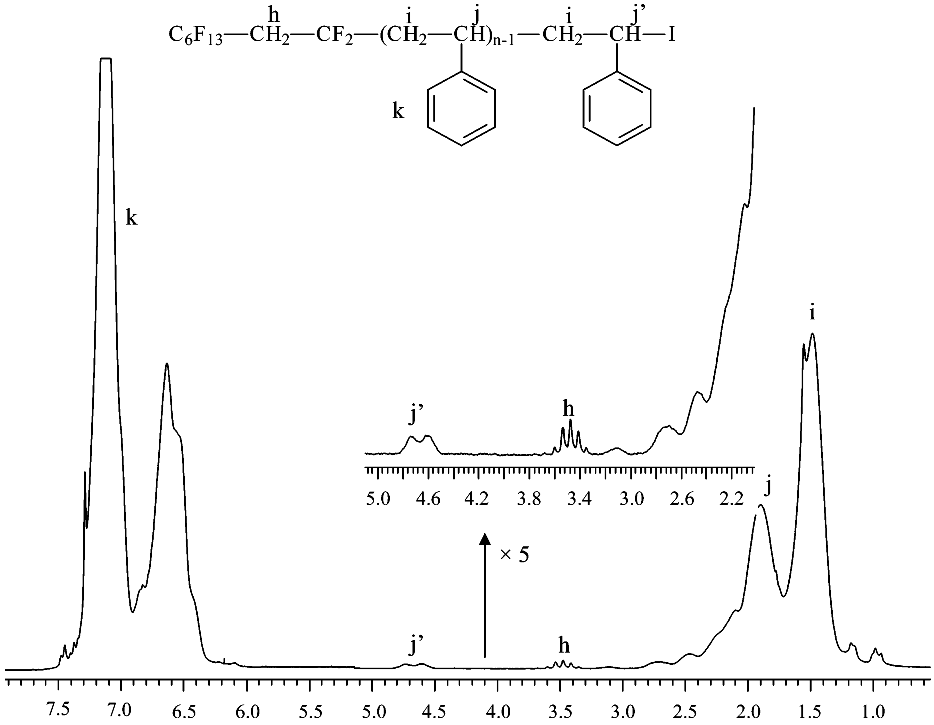


Figure 2. ^{1}H NMR spectrum of $C_6F_{13}-CH_2-CF_2-PS-I$ oligomers (run no. 4, Table 2) obtained by iodine transfer polymerization (ITP) of styrene in the presence of $C_6F_{13}-CH_2-CF_2-I$ as the CTA (400 MHz, deuterated DMF). Experimental conditions: iodine transfer polymerization (ITP) of styrene performed in the presence of $C_6F_{13}-CH_2-CF_2-I$ at 70 °C in acetonitrile; molar ratio $[\text{Styrene}]_0$:$[C_6F_{13}-CH_2-CF_2-I]_0$:$[\text{AIBN}]_0$ = 100.00:2.50:0.25.

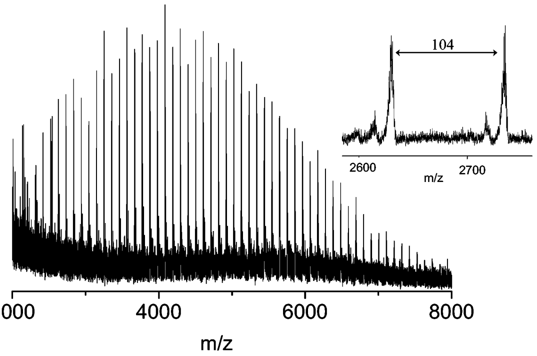


Figure 3. MALDI−TOF mass spectrum of oligo(styrene) synthesized by ITP of styrene from $C_6F_{13}-CH_2CF_2-I$ as the chain transfer agent (CTA) (run 4, Table 2). Experimental conditions: iodine transfer polymerization (ITP) of styrene performed in the presence of $C_6F_{13}-CH_2-CF_2-I$ at 70 °C in acetonitrile; molar ratio $[\text{Styrene}]_0$:$[C_6F_{13}-CH_2-CF_2-I]_0$:$[\text{AIBN}]_0$ = 100.00:2.50:0.25.

$[CH_2-CH(C_6H_5)]_{24}-CH_2-CH(C_6H_5)-I$. The absence of a peak attributed to $A-(M)_n-A$ shows that no termination reaction occurred (while it is known that styrene recombines[68]) and this demonstrates that, for ITP, the major transfer reactions that occur are more important than the termination step.

2.1.2. Synthesis of Oligo(styrene) by ITP of Styrene in the Presence of $HCF_2-CF_2CH_2-I$ as the CTA. ITP of styrene occurred in the same experimental conditions as above, involving $HCF_2-CF_2CH_2-I$, as the CTA. After reaction, the polymer was purified by precipitation from methanol. Then, the dried oligomers were characterized by different methods.

First, the ^{1}H NMR spectrum does not attest the presence of $HCF_2-CF_2CH_2-$ end group, but only those of the characteristic signals centered at 1.0 and 2.0 ppm assigned to the protons of the polystyrenic chain. In addition, signals centered at 2.4, 4.6, and 6.3 ppm corresponding to $-CF_2-C\mathit{H_2}-CH_2-CH(C_6H_5)-$ and $C\mathit{H}(C_6\mathit{H_5})-I$, respectively, were not observed. Surprisingly, the signal centered at 1.2 ppm, attributed to the methyl groups in $(C\mathit{H_3})_2(CN)C-$ (arising from the initiator fragment), confirms that the polymer results from the direct initiation of AIBN. Second, the ^{19}F NMR spectra of these resulting oligomers show the absence of the characteristic signal centered at −111 and −136 ppm attributed to the CTA signal since this one was eliminated in the precipitation from methanol. Hence, this CTA is not efficient in controlled radical polymerization of styrene by ITP, and confirms previous work when involved in the ITP of VDF.[63]

The SEC analysis indicates that this CTA does not enable to control neither the molecular weight (M_n) nor the polydispersity index (PDI). The experimental and targeted molecular weights of polymers obtained in the presence of this CTA are quite different (run nos. 8−12, Table 2). Indeed, whatever the CTA concentration in the reactional medium, the produced polymers exhibit high molecular weights ($M_n \sim 30\,000$ g mol^{-1}) and a broad polydispersity index (>2). To compare these results obtained from this CTA, the conventional radical polymerization was performed in the same experimental condition (but without any CTA) (run no. 1, Table 2): the obtained polymer presents a molecular weight close to those obtained by ITP ($M_n \sim 40\,000$ g mol^{-1}).

The poor control of that polymerization was also confirmed by the MALDI−TOF spectra which showed a wide distribution and a series of peaks separated by $m/z = 104.06$. This series corresponds to oligostyrenes resulting from the direct initiation and by classic termination (by recombination mainly), $A-[CH_2-CH(C_6H_5)]_n[CH(C_6H_5)_m-CH_2]-A$, where A represents the fragment arising from the decomposition of AIBN ($A = (CH_3)_2(CN)C-$), mainly 2-butyronitrile. It is also worth noting the absence of CTA as the chain-end of polymers.

As expected, the results obtained from this CTA are totally different from those reported with $C_6F_{13}CH_2CF_2I$ and $C_6F_{13}I$ [65]

for the ITP of styrene. This result shows that the efficiency of CTA is influenced by this structure. Indeed, Gaynor et al.[66] investigated the influence of the structure of the iodinated hydrogenated transfer agents on their reactivity in iodine transfer polymerization of various monomers (acrylates and styrenics) and, in particular, the difficulty to control the radical polymerization of styrene using a CTA such as iodomethane or diiodomethane (Table 1 in Supporting Information). On the contrary, 1-phenyl-1-iodoethane, iodoform, perfluoroalkyl iodides and iodoacetonitrile led to controlled PS endowed with narrow polydispersity indexes (as low as 1.4) and with experimental molecular weights close to the targeted ones.[66] For these efficient transfer agents, the group adjacent to iodine is able to stabilize the generated radical by inductive or resonance effects. On the other hand, iodobenzene behaves as a poor transfer agent for ITP of styrene, 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 polymerization of styrene could be achieved. Such a result confirms those of Kowalczuk-Bleja et al.[69] who carried out the ITP of styrene in the presence of benzyl iodide in a controlled manner.

2.2. Assessment of the Transfer Constant Values. The DP_n and PDI were monitored vs the styrene conversion to estimate the values of the transfer and exchange constant (C_{tr} and C_{ex}).

2.2.1. Estimation of C_{tr} and C_{ex} by Evolution of DP_n and PDI. The monomer conversion was determined by both gas chromatography and ^1H NMR spectroscopy of the total product mixture. Using ^1H NMR, eq 1 enables us to assess the styrene conversion ($\alpha_{styrene}$) from the integrals of the vinylic protons ($CH_2{=}CH(C_6H_5)$) of free styrene centered at 5.2 and 5.8 ppm. The integral of the signal assigned to the aromatic protons of free styrene and of the resulting polymer was used as the internal reference since the intensity did not vary vs time.

$$\alpha_{styrene} = 1 - ([Styrene]_t/[Styrene]_0) = 1 - [(\int CH_2{=}C/2)/(\int -C_6H_5/5)] \quad (1)$$

where $[Styrene]_t$ and $[Styrene]_0$ stand for the monomer concentrations at t time and at $t = 0$, respectively, $\int CH_2$ and $\int -C_6H_5$ represent the integrals of the signals assigned to methylene and aromatic groups, respectively.

The average molecular weights, $M_{n,\ SEC}$, and polydispersity indexes, PDI, were determined by SEC chromatography. When $C_6F_{13}-CH_2CF_2-I$ was used as the CTA, $M_{n,\ NMR}$ values were assessed by ^1H NMR from the integral of the signal assigned to aromatic protons ($-C_6H_5$) and that of the signal of the protons in $C_6F_{13}-CH_2CF_2$- group centered at 3.5 ppm. It was noted that the M_n values determined by ^1H NMR and by SEC were close.

$$M_{n,NMR} = [(\int C_6H_5/5)/(\int CH_2/2)] \times M_{Styrene} + M_{C_6F_{13}CH_2CF_2I} \quad (2)$$

where the symbols have been defined above.

Figure 4 exhibits the evolution of the molecular weights, M_n, and PDI vs the styrene conversion ($\alpha_{styrene}$) at 70 °C. The evolution of M_n is not characteristic of the behavior of a controlled radical polymerization, since it is known that, in the case of that polymerization, the M_n increases linearly, while PDI is constant (or even decreases) vs $\alpha_{styrene}$ in the course of the polymerization. In our case, using $C_6F_{13}-CH_2CF_2-I$ as the CTA, it was observed that experimental molecular weights, $M_{n,experimental}$, slightly decreased with the monomer conversion, the dotted line being the theoretical line, calculated by eq 3:

$$M_{n,}\text{ theoretical} = \left(\frac{[Styrene]_0 \times \alpha_{styrene}}{[CTA]_0 \times \alpha_{CTA}}\right) \times M_{styrene} + M_{CTA} \quad (3)$$

where $\alpha_{styrene}$, α_{CTA}, M_{CTA}, and $M_{styrene}$ represent the styrene and CTA conversions and the molecular weights of CTA and styrene, respectively.

Thus, the M_n evolution (Figure 4) exhibits a character of a conventional radical telomerization. This behavior can be explained by the transfer constant, which is close to 1. Indeed, from the Bauduin et al.'s equation,[70] it is possible to simulate the evolution of the molecular weights vs the transfer constant of the CTA (see Figure 2 in Supporting Information). The values of transfer constant enable one to determine the evolution of the molecular weights (M_n) vs the monomer conversions. Two cases can be possible: if C_{tr} is low ($C_{tr} < 1$), the CTA consumption is slow, the experimental molecular weights should be high at the beginning of the reaction (experimental values quite different from the targeted ones) and should decrease vs monomer conversions. On the contrary, for high C_{tr} values ($C_{tr} \gg 1$), the experimental molecular weights should increase almost linearly vs the monomer conversion and should be close to the targeted values. The C_{tr} value has been assessed as: $C_{tr} = 1$ at 70 °C from the Bauduin et al.'s law,[70] the determination being given by Figure 2 in the Supporting Information, from plotting M_n vs the styrene conversion. This value was also confirmed by using the O'Brien and Gornick's method[71] (see paragraph 2.2.2).

The evolutions of PDI vs the monomer conversion are surprising for two reasons: (i) it is noted that they decrease

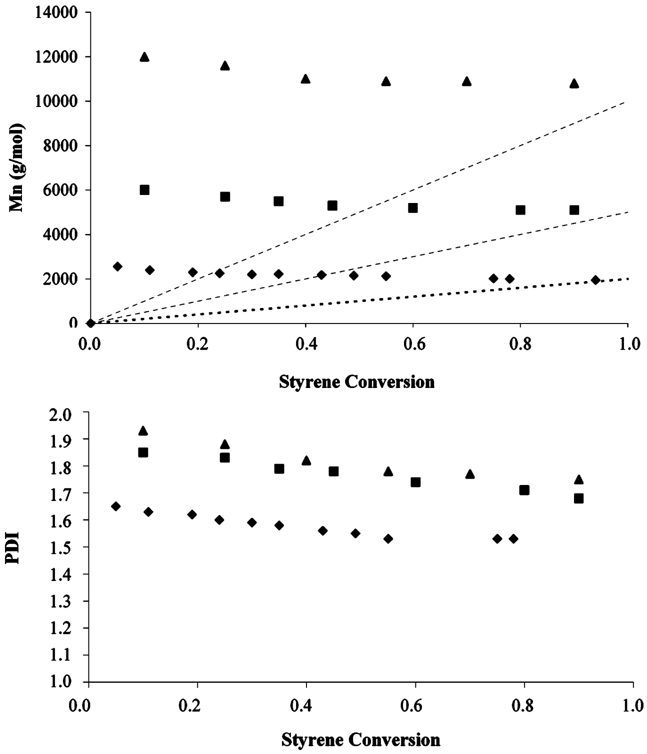


Figure 4. Molecular weight, M_n (upper figure), and polydispersity index, PDI (lower figure), vs monomer conversion in the ITP of styrene performed at 80 °C in the presence of AIBN as the initiator and $C_6F_{13}-CH_2-CF_2-I$ as the CTA. Targeted molecular weights are shown close to 2000 (◆), 5000 (■), and 10 000 g mol^{-1}(▲), with their respective theoretical straight lines.

slowly; however, they should increase vs the styrene conversion (case of conventional radical polymerization); (ii) the value is low (PDI = 1.6−1.8). This observation is explained by the exchange transfer constant (C_{ex}). It represents the transfer which occurs between two polymeric chains (called "degenerative transfer", Scheme 1 in the Supporting Information). Thus, C_{ex} is characteristic of the evolution of the molecular weight distribution (or PDI) vs the monomer conversion. Noteworthy, an increase of C_{ex} gives a lower polydispersity index (PDI) of the polymeric chains as demonstrated by Mueller et al. equation[72] (Figure 3 in the Supporting Information gives the different theoretical curves of PDI vs the monomer conversion for different C_{ex} values):

$$\mathrm{PDI} = [1 + ([\mathrm{Styrene}]_0/[\mathrm{CTA}]_0) \times (2 + (2 - \alpha_{\mathrm{Styrene}}) \times (1 - \mathrm{C}_{\mathrm{ex}})/\mathrm{C}_{\mathrm{ex}})]/[\alpha_{\mathrm{styrene}} \times [\mathrm{Styrene}]_0/([\mathrm{CTA}]_0 \times (1 - (1 - \alpha_{\mathrm{styrene}})^{C_{ex}})] \quad (4)$$

where $[\mathrm{Styrene}]_0$, $[\mathrm{CTA}]_0$, $\alpha_{\mathrm{styrene}}$, and C_{ex} represent the styrene and the chain transfer agent concentrations, the styrene conversion, and the exchange constant, respectively.

Thus, by comparison of the theoretical and experimental curves of PDI vs styrene conversion (Figure 3 in the Supporting Information), we have shown that the C_{ex} values is greater than 1 (estimated C_{ex} value was 2). According to the literature, the C_{ex} value of polystyrene (PS−I) is close to 3.2 at 80 °C[73] in the presence of oligo(styrene)−I, used as the macromolecular transfer agent, and this statement is in agreement with our observation.

The styrene concentration vs time is represented in Figure 4 in the Supporting Information, indicating that the system is a stationary state with respect to the R_p/M ratio (i.e., the slope of the $\ln[\mathrm{M}]_0/[\mathrm{M}]$ vs time) or to the polymer radical concentration ($[\mathrm{P}°] = k_p^{-1}(R_p/M)$, where k_p is the propagation rate).

2.2.2. Determination of C_{tr}. In the present case of the ITP of styrene with fluorinated CTAs, the structures of the CTA and of the P_n−I are different since the chemical environments of the iodine atoms are not the same in both species. Hence, the difference of both structures leads to a different reactivity of both species and it was worth considering two essential parameters as driving forces of ITP: (i) C_{tr}, the transfer constant, directed by the nature of CTAs, and (ii) C_{ex}, the exchange constant, relative to the growing chain.

Indeed, the comparison of the values of C_{tr} constant leads to different cases (Scheme 1).

(i) $C_{tr} \gg 1$, and two cases are possible:

- In the case where $C_{ex} = 0$, after the transfer reaction of the CTA, the obtained polymer cannot behave as a further CTA (i.e., there is no controlled character). Thus, the behavior is typical of a telomerization where the molecular weights are not controlled: for example, the telomerization of styrene in the presence of thiol as the chain transfer agent (e.g., 2-mercaptoethanol gave low molecular-weight oligomers[74]). In this peculiar case, the radical telomerization of styrene cannot lead to controlled molecular weights.
- In the case where $C_{ex} \neq 0$, the obtained oligomers can transfer. Thus, the oligomers can grow in the presence of monomer. Hence, M_n and PDI are controlled. For example, the ITP of VDF in the presence of $C_6F_{13}I$ may illustrate this case.[62]

(ii) In the case where $\mathrm{C}_{tr} \leq 1$, whatever the value of C_{ex}, the CTA is not consumed quickly. However, according to the Bauduin's et al. law,[70] the system can be regarded as a telomerization. This case can be illustrated by the ITP of styrene in the presence of vinyl iodoacetate [75] or by our study.

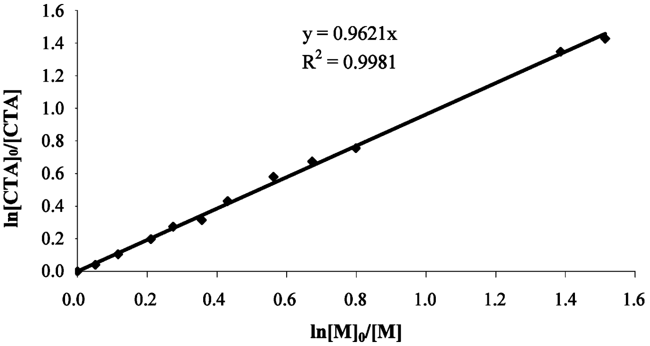


Figure 5. Kinetics plots of $\ln([\mathrm{CTA}]_0/[\mathrm{CTA}])$ vs $\ln([\mathrm{M}]_0/[\mathrm{M}])$ performed in the ITP of styrene with $C_6F_{13}-CH_2-CF_2I$, as the CTA at 70 °C for the assessment of the transfer constant of $C_6F_{13}-CH_2-CF_2-I$. Experimental conditions: iodine transfer polymerization (ITP) of styrene performed in the presence of $C_6F_{13}-CH_2-CF_2-I$ at 70 °C in acetonitrile; molar ratio $[\mathrm{Styrene}]_0:[C_6F_{13}-CH_2-CF_2-I]_0:[\mathrm{AIBN}]_0 = 100.00:2.50:0.25$.

To assess the transfer constant, C_{tr}, O'Brien and Gornick's method[71] can be used and it was required to monitor the CTA and monomer consumptions vs time. Chong et al.[76] used this method successfully to assess the C_{Tr} values of various RAFT agents for the polymerization of styrene. In the case of ITP of styrene in the presence of fluorinated CTAs, the CTA conversion was monitored from aliquots, since ^{19}F NMR allows one to quantify the decrease of the $-CF_2I$ end groups (from the integral of the characteristic signal located at −40 ppm assigned to CF_2 in $C_6F_{13}-CH_2C\mathit{F}_2-I$). The evolution of the $C_6F_{13}-CH_2CF_2-I$ consumptions vs time at 70 °C is represented by Figure 5 in the Supporting Information. The CTA conversion of $C_6F_{13}-CH_2CF_2-I$ was assessed from the ratio of the integrals of the signals assigned to $-CH_2-CF_2-I$ and $-CF_3$ (located at −82 ppm) (eq 5) in the ^{19}F NMR spectra, as follows:

$$\alpha_{\mathrm{CTA}} = 1 - ([\mathrm{CTA}]_t/[\mathrm{CTA}]_0) = 1 - [(\textstyle\int -\mathrm{CF}_2-\mathrm{I}/2)_t/(\int -\mathrm{CF}_3/3)_t] \quad (5)$$

where $(\int -CF_2-I)_t$ and $(\int -CF_3)_t$ represent the integrals of the signals assigned to CF_2I and CF_3, respectively, at t times.

Thus, the transfer constant can be assessed from eq 6:

$$C_{\mathrm{Tr}} = \ln([\mathrm{Styrene}]_0/[\mathrm{Styrene}])/\ln([\mathrm{CTA}]_0/[\mathrm{CTA}]) \quad (6)$$

where $[\mathrm{Styrene}]_0$ and $[\mathrm{CTA}]_0$ stand for the concentrations of the styrene and of the chain transfer agent at initial time, respectively.

When $C_6F_{13}-CH_2CF_2-I$ was used, it was observed that the CTA consumption was the same as that of the styrene consumption. Indeed, as required by this kinetics law, it is essential to consider only low monomer conversion rates to limit any presence of $R_F-[CH_2-CH(C_6H_5)]_n-I$ oligomers (i.e., $[C_6F_{13}CH_2CF_2[CH_2-CH(C_6H_5)]_n-I\ ] \ll [C_6F_{13}CH_2CF_2-I]$), which could undergo other transfer reactions. Different reaction temperatures were used (ranging from 65 to 80 °C) but the C_{tr} values did not change (C_{Tr} was close to 1 at these temperatures for $C_6F_{13}CH_2CF_2I$, while $C_{Tr} = 0$ for $HCF_2CF_2CH_2I$). The values calculated by this method are collected in Table 3.

3. Synthesis of PVDF-*b*-PS Block Copolymers.

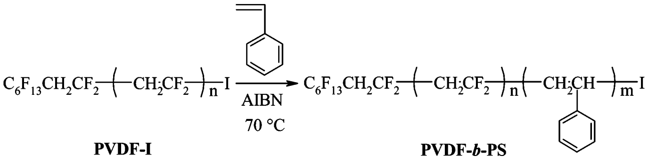
3.1. Synthesis and Characterization of PVDF-*b*-PS Block Copolymers. The synthesis of PVDF-*b*-PS block copolymers requires two steps (Scheme 2).

In the first one, the ITP of VDF was reported in the previous work.[62] In the second step, ITP of styrene was performed at 70

Table 3. Summary of Transfer Constant Values (C_{Tr}) of Different $C_6F_{13}(VDF)_nI$ Oligomers and $HCF_2CF_2CH_2I$ as the Chain Transfer Agents (CTAs) Calculated by O'Brien and Gornick's Method,[71] at Various Temperatures, for the Iodine Transfer Polymerization (ITP) of Styrene with These Fluoroiodinated CTAs

transfer agent	C_{Tr} ($=k_{Tr}/k_p$)	T (°C)
$C_6F_{13}CH_2CF_2I$	0.96	70
	0.98	80
$C_6F_{13}(CH_2CF_2)_9I$	0.95	70
$C_6F_{13}(CH_2CF_2)_{13}I$	0.96	70
$HCF_2CF_2CH_2I$	$\cong 0$	65
	$\cong 0$	70
	$\cong 0$	80

Scheme 2. Synthesis of PVDF-*b*-PS Block Copolymers by ITP of Styrene in the Presence of PVDF−I as the CTA and AIBN as the Initiator



°C, in the presence of PVDF−I, AIBN and acetonitrile as the macromolecular transfer agent, the initiator and the solvent, respectively. The resulting block copolymer was solubilized in THF, precipitated from methanol and then dried under vacuum. The copolymers synthesized from various experimental conditions are listed in Table 4.

The absence of the signal located at −40 ppm assigned to $-CH_2CF_2I$ end group proves that ITP of styrene occurred sucessfully from PVDF−I (Figures 6−8 in the Supporting Information correspond to ^{19}F NMR spectra of $C_6F_{13}CH_2CF_2I$, PVDF−I, and PVDF-*b*-PS block copolymers). This signal underwent a high field shift from −40 ppm to −112 ppm attributed to difluoromethylene group in $-CF_2-CH_2-CH(C_6H_5)-$. Besides, the signal of oligomers bearing $-CF_2-CH_2-I$ end groups remained present, confirming both the poor reactivity of this type of oligomers and the results obtained from $HC_2F_4CH_2I$ (the C_{Tr} value being close to zero).

The ^1H NMR characterization (Figure 6) confirms that the ITP of styrene to produce PVDF-*b*-PS block copolymers occurred. Indeed, signals corresponding to methylene in $-CH_2-CH(C_6H_5)-$ group and to aromatic protons appear from 1.0 to 2.0 ppm and from 6.8 to 7.2 ppm, respectively. As expected, the signal located at about 3.0 ppm is attributed to the protons of PVDF while the incorporation of the styrene unit adjacent to the iodine atom [$-CH(C_6H_5)-I$] is evidenced by a multiplet centered at 4.5 ppm.

However, NMR spectroscopy does not allow us to identify the presence of polystyrene resulting from the direct initiation by AIBN.

The SEC chromatograms (Figure 7) exhibits a shift of the peak that shows an increase of the molecular weights of the produced copolymers. Using a refractive index detector, the PVDF response led to a negative signal whereas the final PVDF-*b*-PS copolymer was identified by a positive signal. This behavior is similar to that observed in previous studies.[11,62] To avoid this change of behavior that may disturb the analysis, a UV detector was employed since it is not sensitive to the presence of the fluorinated block. Indeed, the SEC traces assigned to PVDF and to polystyrene distributions give positive signals such as that in Figure 7 which displays several SEC traces of the reaction mixtures at different times: that of the PVDF−I (macro-CTA) has a higher retention time (or elution volume) than that of the copolymer obtained by ITP. From constant amounts of each aliquot injected to the column system, it was noted that the signal of PVDF decreased while that of the copolymer increased, which is consistent with the formation of PVDF-*b*-PS block copolymers. However, oligomers bearing $-CH_2I$ end groups did not react.

In addition, the C_{Tr} values, assessed for different molecular weights of PVDF−I by O'Brien and Gornick's method,[71] were close to 1 and hence showed that the influence of the molecular weight is negligible.

3.2. Structural Properties. Figure 8 shows the atomic force microscopy (AFM) 2D topological (a) and phase (b) images and 3D topological image (c) of C_6F_{13}-$(VDF)_{20}$-$(Styrene)_{65}-I$ block copolymer (run no. 20), but it also contains unreacted PVDF−I bearing $-CH_2I$ end groups and probably polystyrene resulting from the direct initiation of AIBN. These side products were identified by MALDI−TOF in the model study. The AFM was performed on this copolymer since it exhibits the highest molecular weight. Thus, because of the nanometric scale of this type of microscopy, this copolymer seems to be the most interesting sample to analyze.

The surface roughness, defined as the root-mean-square (RMS) of the height deviations taken from the mean data plane, was 1.37 nm over a 1 μm × 1 μm scan. The AFM image shows a homogeneous surface with white nodules of 30−50 nm. These small nodules represent PVDF crystalline domains.

The mixture of PVDF and PS without any diblock copolymer exhibits a heterogeneous structure[77] with nodules of several

Table 4. Summary of PVDF-*b*-PS Block Copolymers Synthesized from Different Concentrations of Chain Transfer Agents (CTAs), Monomer (M), and Initiator (In)[a]

runs	T (°C)	concentration ratios $[M]_0:[CTA]_0:[In]_0$	targeted M_n (g mol^{-1})	$\alpha_{Styrene}$ (%)	α_{CTA} (%)	$M_{n,theoretical}$ (g mol^{-1})	$M_{n,experimental}$[b] (g mol^{-1})	PDI[b]
			Block 1: M = VDF, CTA = $C_6F_{13}I$, In = TBPPI					
13	75	100.0:10.0:1.0	1090	90	100	1020	1000	1.2
14	75	100.0:4.0:0.4	2050	85	100	1810	1700	1.3
			Block 2: M = Styrene, CTA = PVDF−I, In = AIBN					
15[c]	70	100.0:10.0:1.0	2040	−	−	−	1800	1.9
16[c]	70	100.0:5.0:1.0	3080	−	−	−	2900	1.8
17[d]	70	100.0:12.3:1.0	2550	75	70	2730	2500	1.9
18[d]	70	100.0:6.2:1.0	3780	80	80	3780	3300	2.0
19[d]	70	100.0:3.1:1.0	5880	85	90	5550	5100	1.9
20[d]	70	100.0:1.5:1.0	8630	85	90	8150	6900	2.0

[a] α_M, α_{CTA}, $M_{n,theoretical}$, $M_{n,experimental}$, and PDI represent the monomer and chain transfer agent conversions, the theoretical molecular weights, the experimental molecular weights and the polydispersity indexes, respectively. [b] Determined by SEC analysis by means of a UV detector. [c] Oligomers produced from run no. 13 were used in the ITP of styrene as the $C_6F_{13}(VDF)_{10}I$ (functionality in $-CF_2I = 0.70$). [d] Oligomers produced from run no. 14 were used as the C_6F_{13}-$(VDF)_{20}I$ (functionality in $-CF_2I = 0.33$).

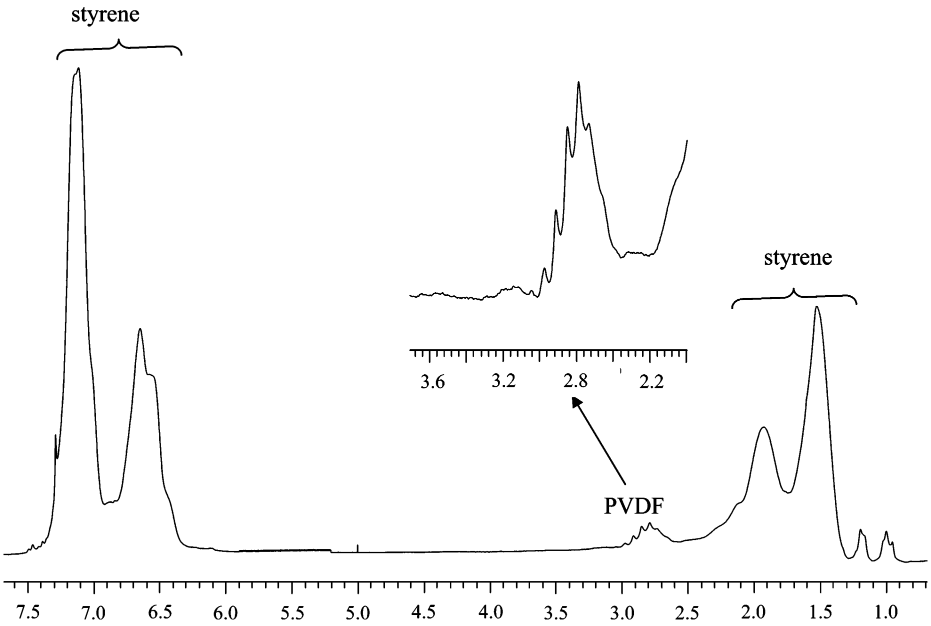


Figure 6. ^{1}H NMR spectrum of C_6F_{13}-$(CH_2-CF_2)_{20}$-PS-I oligomers obtained by iodine transfer polymerization (ITP) of styrene with C_6F_{13}-$(CH_2-CF_2)_{20}$-I as the macro-CTA (400 MHz, deuterated DMF) (run no. 20, Table 4). Experimental Conditions: Iodine transfer polymerization (ITP) of styrene performed in the presence of C_6F_{13}-$(CH_2-CF_2)_{20}$-I at 70 °C in acetonitrile; molar ratio $[Styrene]_0$:$[C_6F_{13}$-$(CH_2-CF_2)_{20}-I]_0$:$[AIBN]_0$ = 100.0:1.5:1.0.

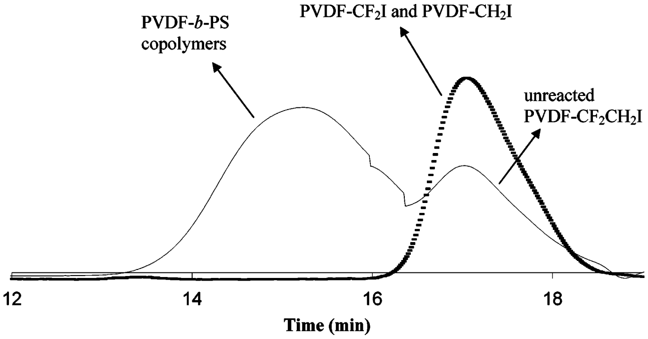


Figure 7. SEC chromatograms of $C_6F_{13}(VDF)_{20}$-I polymer (run no. 14, Table 4) (dotted line) and total product mixture $C_6F_{13}(VDF)_{20}$-$(styrene)_{50}$I copolymer (run no. 20, Table 4) (full line) (UV detector). Experimental conditions: iodine transfer polymerization (ITP) of styrene performed in the presence of C_6F_{13}-$(CH_2-CF_2)_{20}$-I at 70 °C in acetonitrile; molar ratio $[Styrene]_0$:$[C_6F_{13}$-$(CH_2-CF_2)_{20}-I]_0$:$[AIBN]_0$ = 100.0:1.5:1.0.

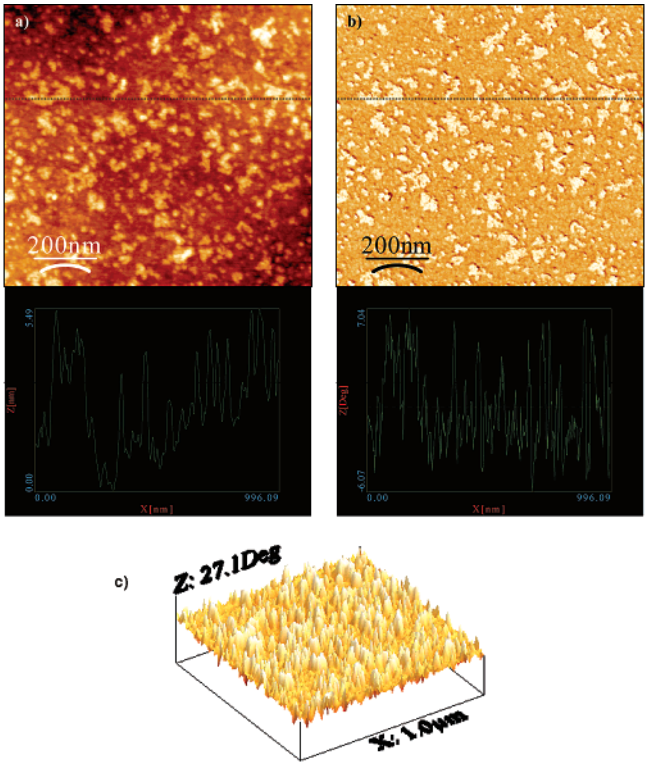


Figure 8. AFM images of run no. 20 (blend of $C_6F_{13}(VDF)_{20}$-$(Styrene)_{65}$-I copolymers, PVDF-CH_2I end groups, and directly initiated PS). Topological or height 2D image (a), amplitude or phase 2D image (b), and height 3D image (c).

micrometers (from 2 to 10 μm). The presence of smaller nodules demonstrates the presence of block copolymers and a certain compatibilization.

3.3. Thermal Properties. Differential scanning calorimetry (DSC) was used to investigate their thermal properties and phase separation. The thermograms of PVDF and of the corresponding PVDF-*b*-PS block copolymers are given in the Supporting Information (Figures 9−12). The DSC thermograms of PVDF-I show an endothermal melting point at 150 °C, slightly lower than the expected value[78] (PVDF is claimed to exhibit a melting point ranging from 160 to 178 °C), because of the low molecular weight of the sample. Indeed, the resulting block copolymers consist of crystalline sequences and amorphous segments. The thermograms of the PVDF-*b*-PS block copolymer shows a melting point (T_m = 149 °C) and a new transition, which appears at 90 °C assigned to the glass transition temperature (T_g) of the PS block. Moreover, the enthalpy of melting depends on the molecular weight of the PVDF block since a decrease of its melting point is observed when the molecular weight decreases. In fact, the presence of PS block disturbs the organization of the crystalline domains. In addition, the enthalpy of melting of PVDF segment decreases with an increase of the molecular weight of the PS block (See Table 2 in Supporting Information). It is noted that enthalpy values are close to 13, 30, and 58 J g^{-1} for molecular weights of PS of 6900, 3300, and 2500 g mol^{-1}, respectively.

The thermal stabilities of all the samples were studied by thermogravimetric analysis (TGA), under air, from 30 to 600

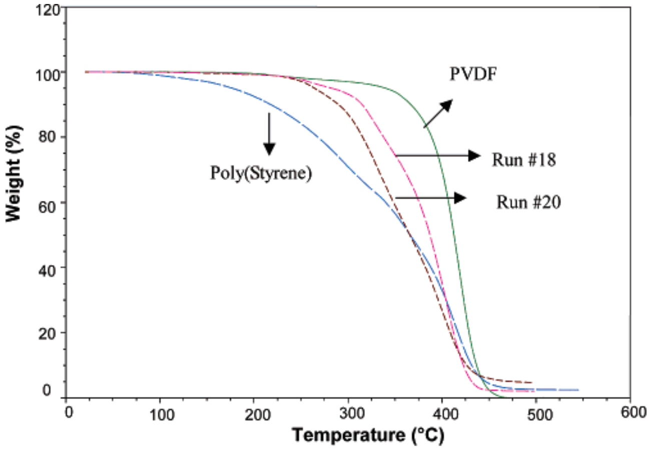


Figure 9. TGA thermograms, recorded under air, of different oligomers: PVDF−I, run no. 14, $M_{n,SEC} = 1700$ g mol^{-1}; poly(Styrene), run no. 2, $M_{n,SEC} = 2100$ g mol^{-1}; $C_6F_{13}(VDF)_{20}(Styrene)_{15}-I$, run no. 18, $M_{n,SEC} = 3300$ g mol^{-1}; $C_6F_{13}(VDF)_{20}(Styrene)_{65}-I$), run no. 20, $M_{n,SEC} = 6900$ g mol^{-1}).

°C. Figure 9 represents the comparison of the thermal stabilities of (i) a PVDF−I (containing 20 VDF units, run no. 14), (ii) a PS−I (containing 27 styrene units, run no. 2), and (iii) two PVDF-*b*-PS block copolymers (named runs nos. 18 and 20 for $C_6F_{13}(VDF)_{20}(Styrene)_{15}I$ and $C_6F_{13}(VDF)_{20}(Styrene)_{65}I$, respectively) all prepared by ITP. As expected, these TGA thermograms show that PVDF is more thermostable than PS: the decomposition of the former polymer is observed from 350 °C while the latter one starts to decompose from 250 °C. Besides, both PVDF-*b*-PS copolymers (containing 20 VDF units) exhibit a better thermal stability than that of PS. In addition, for the same content of VDF, the higher the styrene amount in the block copolymer, the lower its thermal stability. However, the thermal degradation of that polystyrene block occurs very quickly toward the decomposition of high PS usually decomposition reported in the literature.[79] This difference can be explained by the low molecular weight of our PS sample (2100 g mol^{-1}, run no. 2), synthesized by ITP, from $C_6F_{13}CH_2CF_2I$ as CTA. Finally, the thermogram shows that the decomposition-rate of PS is more slowly in contrast to those of PVDF and of PVDF-*b*-PS block copolymers.

Conclusion

PVDF-*b*-PS block copolymers were synthesized by sequential iodine transfer copolymerization (ITP) of vinylidene fluoride and styrene in the presence of 1-iodofluoroalkanes as chain transfer agents (CTAs). First, model reactions of ITP of styrene in the presence of two CTAs containing the possible extremities of PVDF−I oligomers ($C_6F_{13}-CH_2CF_2I$ and $HC_2F_4CH_2I$) were required to check the feasibility of such a copolymerization. In particular, it was of interest to check if that involving PVDF−I oligomers as the macromolecular CTA was able to control the radical polymerization of styrene. Both CTAs exhibited opposite behaviors. On one hand, ITP of styrene with $C_6F_{13}-CH_2CF_2-I$ as the CTA was successfully achieved. Indeed, ^{1}H and ^{19}F NMR spectroscopies, MALDI−TOF mass spectrometry, and SEC chromatography showed that ITP of styrene occurred sucessfully. Moreover, a good control of the molecular weight of these polymers endowed with low polydispersity indexes could be evidenced. On the other hand, from similar experimental conditions, the radical polymerization of styrene involving $HC_2F_4CH_2I$ failed, since the obtained polystyrene, which exhibit higher molecular weights than the targeted ones, were shown to stem from the direct initiation of azobis(isobutyronitrile) onto styrene. Thus, from O’Brien and Gornick’s method, the transfer constant (C_{Tr}) of $C_6F_{13}(CH_2CF_2)_nI$ involved in ITP of styrene was assessed (0.95), whatever the degree of polymerization of PVDF−I oligomers. Then, PVDF-*b*-PS block copolymers of various molecular weights were synthesized in the presence of different concentrations in monomer and CTA. They were characterized and monitored by ^{1}H and ^{19}F NMRs and by SEC chromatography. Then, structural properties were observed by AFM microscopy, showing a homogeneous block copolymer, despite of usual immiscibility of both PVDF and PS homopolymers. This analysis, associated with thermal characterizations, confirmed the structures of the copolymers. These block copolymers are potential emulsifiers for PVDF/PS blends, under study. In addition, another investigation in synthesizing PVDF-*b*-PS block copolymers could consist in using functional monomers derived from styrene. Further investigations dealing with PVDF-based amphiphiles are under progress.

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Supporting Information Available: (i) Text and reaction schemes for the mechanism of ITP, (ii) figures showing theoretical curves of molecular weight (M_n) and PDI vs C_{tr} and C_{ex}, respectively, (iii) SEC chromatograms, (iv) styrene and CTA conversions vs time, ln[Styrene]$_0$/[Styrene] vs time, (v) ^{19}F NMR spectra of $C_6F_{13}-CH_2-CF_2-I$, $C_6F_{13}(CH_2-CF_2)_n-I$ and $C_6F_{13}(CH_2-CF_2)_n-PS$, (vi) evolution of molar masses and polydispersity indexes vs monomer conversions, and (vii) DSC thermograms of $C_6F_{13}(CH_2-CF_2)_{20}-I$, $C_6F_{13}(CH_2-CF_2)_{20}(Styrene)_{25}-I$ and $C_6F_{13}(CH_2-CF_2)_{20}(Styrene)_{50}-I$, and tables of reaction conditions and thermal properties. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Feiring, A. E. In Organofluorine Chemistry; Plenum: New York, 1994; pp 339−372. Scheirs, J., Ed. *Modern Fluoropolymers*; Wiley: New York, 1997. Hougham, G.; Cassidy, P. E.; Johns, K.; Davidson, T.. Eds.; *Fluoropolymers 2: Properties*; Kluwer/Plenum: New York, 1999.

(2) Ameduri, B.; Boutevin, B. *Well-Architectured Fluoropolymers: Synthesis, Properties and Applications*; Elsevier: Amsterdam, 2004.

(3) Thomas, W. M.; O’Shaughnessy, M. T. *J. Polym. Sci.* **1953**, *11*, 455−470.

(4) Court, F.; Leibler, L.; Mourran, A.; Navarro, C.; Royackkers, V. WO 9929772 (Elf Atochem S.A.), 1999.

(5) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5830−5835. Sawamoto, M.; Inayama, T.; Murata, S.; Konishi, S. JP 2002220427 (Kyowa Hakko Kogyo Co., Ltd.) (*Chem. Abstr.* **2002**, 591973), 2002. Sawamoto, M.; Ando, T.; Kamigaito, M. *Nippon Gomu Kyokaishi* **2003**, *76*, 285−288 (*Chem. Abstr.* **2003**, 812371).

(6) Ameduri, B.; Boutevin, B.; Gramain, P. *Adv. Polym. Sci.* **1997**, *127*, 87−142.

(7) Oki, H.; Okamoto, Y.; Sawamoto, M.; Kano, Y.; Kitahata, S.; Yamada, K.; Okano, Y.; Nishimura, M.; Terada, K.; Ida, H. JP 2000264937 (Zaidan Hojin Kagaku Gijitsu Senryakusuishin Kiko) (*Chem. Abstr.* **2000**, 674119), 2000. Kwon, T. S.; Takagi, K.; Kunisada, H.; Yuki, Y. *J. Macromol. Sci. Chem.* **2002**, *A39*, 991−1006. Otsu, T.; Kuriyama, A. *Polym. J.* **2002**, *34*, 124−131. Chen, H.; Wang, G. *Gaofenzi Tongbao* **2003**, 79−84 (*Chem. Abstr.* **2004**, 1065668); Matyjaszewski, K. *Macromol. Rapid Commun.* **2005**, *26*, 135−142. Ishizu, K.; Katsuhara, H.; Kawauchi, S.; Furo, M. *J. Appl. Polym. Sci.* **2005**, *95*, 413−418. Ishizu, K.; Katsuhara, H.; Itoya, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 230−233. Kwon, I. K.; Matsuda, T. *Biomaterials* **2006**, *27*, 986−995.

(8) Oki, Y.; Okamoto, Y. *Polym. J.* **2002**, *34*, 736−741.

(9) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(10) Zhang, Z.; Ying, S.; Shi, Z. *Polymer* **1998**, *40*, 1341−1345.

(11) Destarac, M.; Matyjaszewski, K.; Silverman, E.; Ameduri, B.; Boutevin, B. *Macromolecules* **2000**, *33*, 4613−4615.

(12) Percec, V.; Guliashvili, T.; Popov, A. V. US 2005131186, 2005.

(13) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromol. Symp.* **2000**, *157*, 193−200. Sawamoto, M.; Kamigaito, M. *Polym. News* **2000**, *25*, 149−155. Fuji, Y.; Watanabe, K.; Baek, K.-Y.; Ando, T.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2055−2065. Onishi, I.; Baek, K.-Y.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2033−2043. Nishimura, M.; Sawamoto, M.; Kamigaito, M.; Okamoto, Y.; Okano, Y.; Terada, K.; Otake, T.; Nagata, N.; Nagae, Y. JP 2002146001 (Daicel Chemical Industries, Ltd.; Kuraray Co. Ltd.; Unitika Ltd.) (*Chem. Abstr.* **2002**, 381330), 2002.

(14) Jin, Y.-Z.; Hahn, Y. B.; Nahm, K. S.; Lee, Y.-S. *Polymer* **2005**, *46*, 11294−11300. Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5643−5651. Kubo, K.; Goto, A.; Sato, K.; Kwak, Y.; Fukuda, T. *Polymer* **2005**, *46*, 9762−9768. Eberhardt, M.; Theato, P. *Macromol. Rapid Commun.* **2005**, *26*, 1488−1493. Albertin, L.; Stenzel, M. H.; Barner-Kowollik, C.; Foster, L. J. R.; Davis, T. P. *Macromolecules* **2005**, *38*, 9075−9084. Mori, H.; Nakano, S.; Endo, T. *Macromolecules* **2005**, *38*, 8192−8201. Bussels, R.; Bergman-Goettgens, C.; Meuldijk, J.; Koning, C. *Polymer* **2005**, *46*, 8546−8554. Mertoglu, M.; Garnier, S.; Laschewsky, A.; Skrabania, K.; Storsberg, J. *Polymer* **2005**, *46*, 7726−7740.

(15) Tatemoto, H. *Int. Polym. Sci. Technol.* **1985**, *12*, 85−91.

(16) Tatemoto, H. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Chapter 5, pp 3847−3862.

(17) David, G.; Boyer, C.; Tonnar, J. F.; Ameduri, B.; Lacroix-Desmazes, P.; Boutevin, B. *Chem. Rev.* **2006**, *106*, 3936−3962.

(18) Boyer, C.; Lacroix-Desmazes, P.; Robin, J.-J.; Boutevin, B. *Macromolecules* **2006**, *39*, 4044−4053.

(19) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2−166.

(20) Hadjichristidis, N. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*; John Wiley & Sons: Chichester, U.K., 2002. Lacroix-Desmazes, P.; Ameduri, B.; Boutevin, B. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1383−1415. Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204*, 265−273.

(21) Tatemoto, M.; Suzuki, T.; Tomoda, M.; Furukawa, Y.; Ueta, Y. DE 2815187 (Daikin Kogyo Co., Ltd., Japan), 1978. Tatemoto, M.; Nakagawa, T. DE 2729671 (Daikin Kogyo Co., Ltd., Japan), 1978.

(22) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745.

(23) Tatemoto, M.; Tomoda, M.; Ueta, Y. DE 2940135 (Daikin Kogyo Co., Ltd., Japan), 1980.

(24) Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23−32. Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001. Destarac, M.; Bzducha, W.; Taton, D.; Gauthier-Gillaizeau, I.; Zard, S. Z. *Macromol. Rapid Commun.* **2002**, *23*, 1049−1054.

(25) Yagi, T.; Tsuda, N.; Noguchi, T.; Sakaguchi, K.; Tanaka, Y.; Tatemoto, M. EP 422644 (Daikin Industries, Ltd.), 1991. Arcella, V.; Brinati, G.; Albano, M.; Tortelli, V. EP 661312 (Ausimont S.P.A.), 1995. Gayer, U.; Schuh, T.; Arcella, V.; Albano, M. EP 885928 (Ausimont S.P.A.), 1998.

(26) Hung, M. H. US 5231154 (du Pont de Nemours, E. I., Co.), 1993.

(27) Shi, Z.; Holdcroft, S. *Macromolecules* **2004**, *37*, 2084−2089.

(28) Shi, Z.; Holdcroft, S. *Macromolecules* **2005**, *38*, 4193−4201.

(29) Jo, S.-M.; Lee, W.-S.; Ahn, B.-S.; Park, K.-Y.; Kim, K.-A.; Paeng, I.-S. R. *Polym. Bull. (Berlin)* **2000**, *44*, 1−8.

(30) Kageishi, K.; Yasuda, S.; Kishi, N. JP 62230811 (Atom Chemical Paint Co., Ltd., Japan) (*Chem. Abstr.* **1988**, 152228), 1987.

(31) Kassis, C. M.; Steehler, J. K.; Betts, D. E.; Guan, Z.; Romack, T. J.; DeSimone, J. M.; Linton, R. W. *Macromolecules* **1996**, *29*, 3247−3254. Guan, Z.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 5527−5532.

(32) Arnold, M. E.; Nagai, K.; Spontak, R. J.; Freeman, B. D.; Leroux, D.; Betts, D. E.; DeSimone, J. M.; DiGiano, F. A.; Stebbins, C. K.; Linton, R. W. *Macromolecules* **2002**, *35*, 3697−3707.

(33) Roussel, J.; Boutevin, B. *J. Fluorine Chem.* **2001**, *108*, 37−45.

(34) Arcella, V.; Brinati, G.; Albano, M.; Tortelli, V. EP 683186 (Ausimont S.P.A.), 1995.

(35) Hikita, M.; Takizuka, N.; Tanaka, K.; Takahara, A.; Kajiyama, T. *Trans. Mater. Res. Soc. Jpn.* **2004**, *29*, 225−228.

(36) Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. *Macromolecules* **2005**, *38*, 3263−3270.

(37) Borkar, S.; Jankova, K.; Siesler, H. W.; Hvilsted, S. *Macromolecules* **2004**, *37*, 788−794.

(38) Li, K.; Guo, J.; Li, X.; Wu, P.; Han, Z. *Gaofenzi Xuebao* **2002**, 235−241 (*Chem. Abstr.* 2002: 348383).

(39) Rixens, B.; Severac, R.; Boutevin, B.; Lacroix-Desmazes, P. *Polymer* **2005**, *46*, 3579−3587.

(40) Andruzzi, L.; Chiellini, E.; Galli, G.; Li, X.; Kang, S. H.; Ober, C. K. *J. Mater. Chem.* **2002**, *12*, 1684−1692.

(41) Lacroix-Desmazes, P.; Andre, P.; Desimone, J. M.; Ruzette, A.-V.; Boutevin, B. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3537−3552.

(42) Gelin, M.-P.; Ameduri, B. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *41*, 160−171.

(43) Moggi, G.; Marchionni, G. EP 320005 (Ausimont, S.r.l.), 1989.

(44) Moggi, G.; Modena, S.; Marchionni, G. *J. Fluorine Chem.* **1990**, *49*, 141−146.

(45) Yang, Y.; Shi, Z.; Holdcroft, S. *Eur. Polym. J.* **2004**, *40*, 531−541.

(46) Percec, V.; Lee, M. *J. Macromol. Sci., Chem.* **1992**, *A29*, 723−740.

(47) Matsumoto, K.; Kubota, M.; Matsuoka, H.; Yamaoka, H. *Macromolecules* **1999**, *32*, 7122−7127. Matsumoto, K.; Mazaki, H.; Nishimura, R.; Matsuoka, H.; Yamaoka, H. *Macromolecules* **2000**, *33*, 8295−8300. Matsumoto, K.; Mazaki, H.; Matsuoka, H. *Macromolecules* **2004**, *37*, 2256−2267.

(48) Clark, M. R.; Kendall, J. L.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 6011−6014.

(49) Storozhakova, N. A.; Efanova, E. Y.; Rakhimov, A. I. *Russ. J. Appl. Chem.* **2002**, *75*, 1715−1717.

(50) Sugiyama, K.; Izhizone, T.; Hirao, A.; Nakahama, S. *Acta Polym.* **1995**, *46*, 424−431.

(51) Genzer, J.; Sivaniah, E.; Kramer, E. J.; Wang, J.; Koerner, H.; Char, K.; Ober, C. K.; DeKoven, B. M.; Bubeck, R. A.; Fischer, D. A.; Sambasivan, S. *Langmuir* **2000**, *16*, 1993−1997.

(52) Hems, W. P.; Yong, T.-M.; van Nunen, J. L. M.; Cooper, A. I.; Holmes, A. B.; Griffin, D. A. *J. Mater. Chem.* **1999**, *9*, 1403−1407. Imae, T.; Tabuchi, H.; Funayama, K.; Sato, A.; Nakamura, T.; Amaya, N. *Colloids Surf., A Physicochem. Eng. Asp.* **2000**, *167*, 73−81. Ito, H.; Imae, T.; Nakamura, T.; Sugiura, M.; Oshibe, Y. *J. Colloid Interface Sci.* **2004**, *276*, 290−298.

(53) Antonietti, M.; Forster, S.; Micha, M. A.; Oestreich, S. *Acta Polym.* **1997**, *48*, 262−268. Ren, Y.; Lodge, T. P.; Hillmyer, M. A. *Macromolecules* **2001**, *34*, 4780−4787.

(54) Busse, K.; Kressler, J.; van Eck, D.; Hoering, S. *Macromolecules* **2002**, *35*, 178−184.

(55) Ren, Y.; Lodge, T. P.; Hillmyer, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 6830−6831.

(56) McLain, S. J.; Sauer, B. B.; Firment, L. E. *Macromolecules* **1996**, *29*, 8211−8219.

(57) Krupers, M. J.; Cabelo, F. M. E.; Moeller, M. *Macromol. Symp.* **1996**, *102*, 99−106. Krupers, M. J.; Moeller, M. *J. Fluorine Chem.* **1997**, *82*, 119−124. Krupers, M. J.; Sheiko, S. S.; Moeller, M. *Polym. Bull. (Berlin)* **1998**, *40*, 211−217. Feast, W. J.; Khosravi, E. *J. Fluorine Chem.* **1999**, *100*, 117−125. Khosravi, E. *NATO Sci. Ser., II: Math., Phys. Chem.* **2002**, *56*, 133−141.

(58) Yang, S.; Wang, J.; Ogino, K.; Valiyaveettil, S.; Ober, C. K. *Chem. Mater.* **2000**, *12*, 33−40.

(59) Bratton, D.; Brown, M.; Howdle, S. M. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6573−6585.

(60) Boeker, A.; Reihs, K.; Wang, J.; Stadler, R.; Ober, C. K. *Macromolecules* **2000**, *33*, 1310−1320. Cacialli, F.; Feast, W. J.; Friend, R. H.; de Jong, M.; Lovenich, P. W.; Salaneck, W. R. *Polymer* **2002**, *43*, 3555−3561.

(61) Chapman, T. M.; Benrashid, R.; Gribbin, K. L.; Keener, J. P. *Macromolecules* **1995**, *28*, 331−335; Chapman, T. M.; Marra, K. G. *Macromolecules* **1995**, *28*, 2081−2085.

(62) Boyer, C.; Valade, D.; Sauguet, L.; Ameduri, B.; Boutevin, B. *Macromolecules* **2005**, *38*, 10353−10362.

(63) Boyer, C.; Valade, D.; Lacroix-Desmazes, P.; Ameduri, B.; Boutevin, B. *J. Polym. Sci., Part A, Polym. Chem.* **2006**, *44*, 5763−5777.

(64) Balague, J.; Ameduri, B.; Boutevin, B.; Caporiccio, G. *J. Fluorine Chem.* **2000**, *102*, 253−268.

(65) Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J.-P.; Pirri, R. *Macromolecules* **1999**, *32*, 7354−7360.

(66) Gaynor, S. G.; Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 8051−8056.

(67) Jackson, A. T.; Yates, H. T.; Scrivens, J. H. *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 1206. Borman, C. D.; Jackson, A. T.; Bunn, A.; Cutter, A. L.; Irvine, D. J. *Polymer* **2000**, *41*, 6015−6020.

(68) Bamford, C. H.; Tipper, C. F. H. *Comprehensive Chemical Kinetics, Vol. 14A: Free Radical Polymerization*; Pergamon: Oxford, 1976.

(69) Kowalczuk-Bleja, A.; Trzebicka, B.; Komber, H.; Voit, B.; Dworak, A. *Polymer* **2004**, *45*, 9−18.

(70) Bauduin, G.; Boutevin, B.; Mistral, J. P.; Sarraf, L. *Makromol. Chem.* **1985**, *186*, 1445−1455.

(71) O'Brien, J. L.; Gornick, F. *J. Am. Chem. Soc.* **1955**, *77*, 4757−4765.

(72) Mueller, A. H. E.; Yan, D.; Litvinenko, G.; Zhuang, R.; Dong, H. *Macromolecules* **1995**, *28*, 7335−7338. Litvinenko, G.; Mueller, A. H. E. *Macromolecules* **1997**, *30*, 1253−1266.

(73) Fukuda, T.; Goto, A.; Ohno, K. *Macromol. Rapid Commun.* **2000**, *21*, 151−165. Fukuda, T.; Goto, A. *ACS Symp. Ser.* **2000**, *768*, 27−38. Fukuda, T.; Yoshikawa, C.; Kwak, Y.; Goto, A.; Tsujii, Y. *ACS Symp. Ser.* **2003**, *854*, 24−39.

(74) Bechkok, A.; Belbachir, M.; Guyot, B.; Boutevin, B. *Eur. Polym. J.* **1998**, *35*, 413−421. Boyer, C.; Boutevin, G.; Robin, J. J.; Boutevin, B. *Polymer* **2004**, *45*, 7863−7876.

(75) Teodorescu, M. *Eur. Polym. J.* **2001**, *37*, 1417−1422.

(76) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.

(77) Herrero, C. R.; Morales, E.; Acosta, J. L. *J. Appl. Polym. Sci.* **1994**, *51*, 1189−1197.

(78) Seiler, D. A. In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley: New York, 1997; Chapter 25, pp 487−505.

(79) Vovelle, C.; Mellottee, H. *Eur. Polym. J.* **1983**, *19*, 387−390.

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