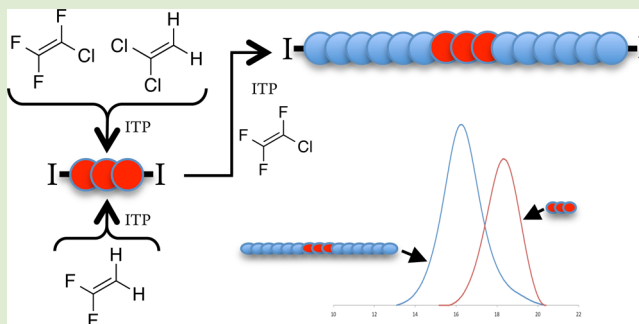


# Synthesis of Chlorotrifluoroethylene-Based Block Copolymers by Iodine Transfer Polymerization

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**ABSTRACT:** Various fluorinated macro-chain transfer agents (CTAs) based on vinylidene fluoride (VDF), chlorotrifluoroethylene (CTFE), or CTFE and vinylidene chloride (VDC), were synthesized by iodine transfer polymerization (ITP). These macro-CTAs were involved in a further ITP reaction that led to the synthesis of original CTFE-based block copolymers exhibiting molecular weight ranging from 2500 to 40000 g/mol and endowed with high thermal stabilities (decomposition temperature at 10% weight loss of ca. 380 °C, under air). ITP of CTFE and VDC as well as ITP of VDF thermally initiated at 100 °C by a catalytic amount of dimanganese decacarbonyl ( $Mn_2(CO)_{10}$ ) are reported for the first time.



Well-architected fluoropolymers prepared by controlled radical polymerization (CRP) are niche macromolecules with low manufacturing volumes.<sup>1</sup> Due to their outstanding properties, these materials are involved in many high-tech fields such as (i) gaskets and O-rings made of thermoplastic elastomers such as Daeil and Tecnoflon, marketed by Daikin Industries Ltd. and Solvay Specialty Polymers, respectively;<sup>2</sup> (ii) fluorinated surfactants based on vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) or perfluoro(methyl vinyl ether) (PMVE) as promising alternatives to bioaccumulative PFOA and PFOS;<sup>3</sup> (iii) fuel-cell<sup>4</sup> and microfiltration<sup>5</sup> membranes; (iv) binders, separators, and electrolytes for Li-ion batteries;<sup>6</sup> (v) protective coatings;<sup>7</sup> and (vi) piezoelectrical devices.<sup>8</sup>

Iodine transfer polymerization (ITP) is an extension of the telomerization reaction.<sup>1,2e,9</sup> Emulsion ITP of VDF and hexafluoropropylene (HFP) initiated by ammonium persulfate (APS) using  $IC_4F_8I$  as the chain transfer agent (CTA) was pioneered by Tatemoto in the late 1970s.<sup>10</sup> Various patents also claim the synthesis of higher molecular weight PVDF by ITP.<sup>11</sup> The kinetics of microemulsion ITP of VDF with HFP involving  $IC_6F_{12}I$  as the CTA was extensively investigated by Apostolo et al.<sup>12</sup> Our group has studied the ITP of VDF in solution with various CTAs, pointing out the crucial role of the CTA structure on the “livingness” character of the reaction,<sup>13</sup> opening to a wide range of fluoroelastomers.<sup>14</sup> In fact, when  $C_6F_{13}I$  and  $C_6F_{13}CH_2CF_2I$  were chosen as CTAs, a controlled behavior was noted, while in the case of  $HCF_2CF_2CH_2I$  used as the CTA, the polymerization was not controlled.<sup>15</sup> Overall, ITP is based on the labile  $CF_2-I$  bond (bond-dissociation energy

(BDE) ca. 200 kJ/mol),<sup>16</sup> which contributes to a faster initiation rate in the initial phase of the polymerization.

In 1955, Haszeldine<sup>17</sup> reported the telomerization of chlorotrifluoroethylene (CTFE) in the presence of  $Cl-CF_2CFCl-I$ . The first successful ITP of CTFE with VDF was achieved by the Daikin company using  $IC_4F_8I$  as the CTA.<sup>2a</sup> This work led to the production of a telechelic I-(VDF-co-CTFE)-I macro-CTA as an elastomeric block ( $T_g = -7$  °C), where the molar percentages of VDF and CTFE were 55 and 45, respectively. This soft  $\alpha,\omega$ -diiodide was able to reinitiate the radical copolymerization of ethylene (E) and CTFE (or E and tetrafluoroethylene (TFE)), leading to original hard–soft–hard triblock thermoplastic elastomers. The melting points of the hard blocks arose from either poly(E-*alt*-CTFE) or poly(E-*alt*-TFE) copolymers and were 247 and 252 °C, respectively. The targeted application dealt with artificial lenses. Nevertheless, the examples of CRP of CTFE by ITP are still scarce in the literature,<sup>18</sup> and we herein report a new contribution in that topic.

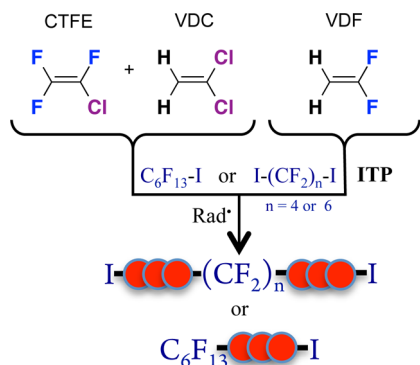
In this study, first various fluorinated macro-CTAs based on VDF or CTFE and vinylidene chloride (VDC) were prepared (Scheme 1). The radical (co)polymerizations were initiated either by *tert*-butylperoxypivalate (TBPPi), by ammonium persulfate (APS,  $(NH_4)_2S_2O_8$ ), or by dimanganese decacarbonyl ( $Mn_2(CO)_{10}$ ), using the conditions supplied in Table 1. After purification (precipitation and drying), the macro-CTAs

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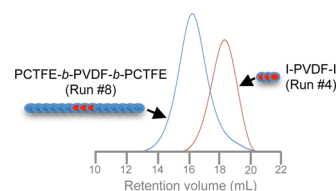
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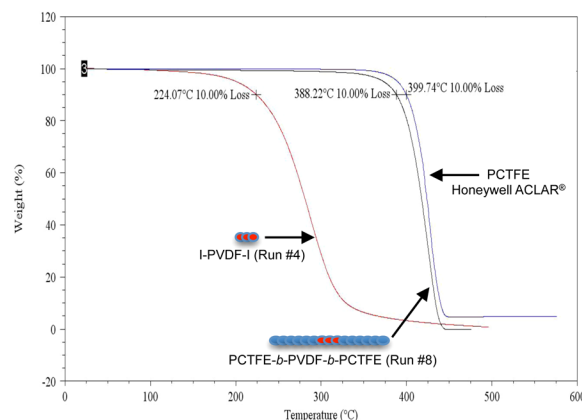
### Scheme 1. Synthesis of Fluorinated Macro-Chain Transfer Agents by Iodine Transfer Polymerization of Various Halogenated Monomers



were characterized by nuclear magnetic resonance (NMR) spectroscopy [Figures S1–S13, Supporting Information (SI)], gel permeation chromatography (GPC; if applicable, i.e., soluble samples, Figure 1), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA, Figure 2). The results are gathered in Table 1. Given that VDF is asymmetrical, both “normal” and “reverse” additions might occur during the polymerization, thus, implying the formation of  $-\text{CF}_2\text{CH}_2-\text{CF}_2\text{CH}_2-$  and  $-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$  dyads, respectively.<sup>15</sup> Moreover, ITP of VDF induces the formation of  $-\text{CH}_2\text{CF}_2-\text{I}$  and  $-\text{CF}_2\text{CH}_2-\text{I}$  chain-ends, which exhibit widely different reactivities.<sup>15,18,19</sup>



**Figure 1.** GPC chromatograms of I-PVDF-I macro-CTA from run #4 and PCTFE-*b*-PVDF-*b*-PCTFE triblock copolymer from run #8 (in DMF using PMMA standards).



**Figure 2.** TGA thermograms (under air) for macro-CTA from run #4 and triblock copolymer from run #8, compared to that of PCTFE homopolymer (ACLAR).

**Table 1.** Synthesis of Fluorinated Macro-Chain Transfer Agents (Macro-CTAs) by Iodine Transfer Polymerization (ITP) of Vinylidene Fluoride (VDF), Chlorotrifluoroethylene (CTFE), and Vinylidene Chloride (VDC): Experimental Conditions and Results<sup>a</sup>

run #	monomer 1 <sup>b</sup> (mol eq)	monomer 2 <sup>b</sup> (mol eq)	CTA <sup>b</sup> (mol eq)	initiator <sup>b</sup> (mol eq)	T (°C)	solvent	$\alpha_M^c$ (%)	yield (wt %)	$M_n$ (targeted, <sup>d</sup> NMR, <sup>e</sup> GPC/PDI <sup>f</sup> ), $T_g^g$ , $T_m^g$ (°C, °C, °C)	chain-ends ratio <sup>i</sup> %CF <sub>2</sub> -I/%CH <sub>2</sub> -I
1	VDF (100)		C <sub>6</sub> F <sub>13</sub> I (1)	APS (0.1)	80	H <sub>2</sub> O	60	70	4700, 62000, nd/nd nd, 160 and 170, 387	51/49
2	VDF (100)		C <sub>6</sub> F <sub>13</sub> I (1)	Mn <sub>2</sub> (CO) <sub>10</sub> (0.1)	100	DMC	100	65	7000, 8500, 10000:1.44 -34, 160 and 170, 395	0/100
3	CTFE (100)		C <sub>6</sub> F <sub>13</sub> I (1)	Mn <sub>2</sub> (CO) <sub>10</sub> (0.1)	100	DMC	47	14	5600, 4600, nd/nd 40, 162, 377	
4	VDF (9)		IC <sub>4</sub> F <sub>8</sub> I (1)	TBPPi (0.1)	74	C <sub>4</sub> H <sub>9</sub> F <sub>5</sub>	78	46	780, 700, 2100:1.38 nd, 50 and 60, 224	89/11
5	VDF (20)		IC <sub>6</sub> F <sub>12</sub> I (1)	TBPPi (0.1)	74	DMC	65	62	1200, 1100, 1200:1.01 <sup>j</sup> nd, 100 and 120, 305	78/22
6	CTFE (429)	VDC (26)	C <sub>6</sub> F <sub>13</sub> I (9.1)	TBPPi (9.1)	74	C <sub>4</sub> H <sub>9</sub> F <sub>5</sub> /H <sub>2</sub> O 1:1 (v:v)	70	38	6500, 8300, nd/nd 29, 180, 375	
7	CTFE (438)	VDC (26)	IC <sub>4</sub> F <sub>8</sub> I (9.1)	TBPPi (9.1)	74	C <sub>4</sub> H <sub>9</sub> F <sub>5</sub> /H <sub>2</sub> O 1:1 (v:v)	93	38	10200, 10600, nd/nd 29, 178, 382	

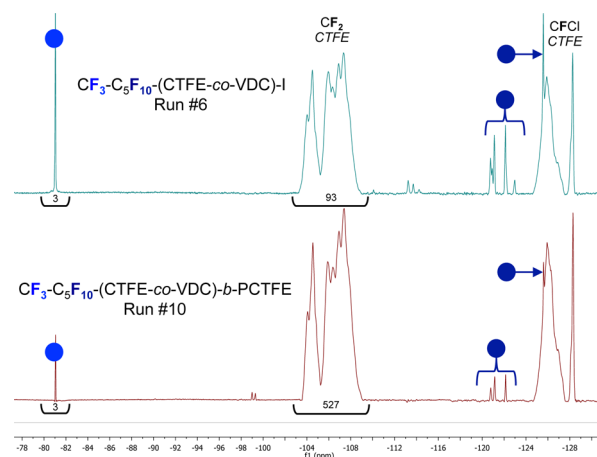
<sup>a</sup>APS, DMC, and TBPPi stand for ammonium persulfate, dimethylcarbonate, and *tert*-butylperoxyvalate, respectively. <sup>b</sup>Molar equivalent. <sup>c</sup> $\alpha_M$  = conversion of monomer(s). <sup>d</sup>Targeted  $M_n$  assessed using the following equation:  $M_n = \alpha_M \times (([F\text{-monomer}]_0 / ([CTA]_0) \times M_{F\text{-monomer}}) + M_{CTA})$  where  $[x]_0$  stands for the initial molar concentration of compound  $x$ ,  $M_x$  represents the molecular weight of compound  $x$ . <sup>e</sup>Determined by <sup>19</sup>F NMR according to the following equation:  $[(Y / \int_{-x} \text{CF}_y(\text{CTA})) \times (\int_{-x} \text{CF}_2(\text{F-monomer}) / 2) \times M_{F\text{-monomer}}] + M_{CTA}$  where  $\int_{-x}$  stands for the integral of the signal centered at  $\delta -x$  ppm assigned either to a CF<sub>3</sub> or to a CF<sub>2</sub> group of the chain transfer agent (CTA), or to the CF<sub>2</sub> groups of a given F-monomer (VDF at  $\delta -92$  ppm or CTFE at  $\delta -108$  ppm).  $Y = 3$  if CTA is C<sub>6</sub>F<sub>13</sub>I while  $Y = 2$  if CTA is IC<sub>4</sub>F<sub>8</sub>I or IC<sub>6</sub>F<sub>12</sub>I.  $M_x$  represents the molecular weight in g/mol of a given compound  $x$ . <sup>f</sup>Assessed by gel permeation chromatography in DMF using PMMA standards. <sup>g</sup>Assessed by DSC. <sup>h</sup>Determined by TGA at 10 °C/min, under air. <sup>i</sup>Determined by <sup>19</sup>F NMR using the following equations: %CH<sub>2</sub>CF<sub>2</sub>-I =  $(\int_{-39}) / (\int_{-39} + \int_{-108})$  and %CF<sub>2</sub>CH<sub>2</sub>-I =  $(\int_{-108}) / (\int_{-39} + \int_{-108})$ . These equations do not take into account the integral of the signal at  $-115$  ppm that corresponds to  $-\text{CF}_2-\text{H}$  dead-ends. <sup>j</sup>This PDI value is unexpectedly low (PDI values for ITP are in general  $1.5 \pm 0.1$ ). This could be explained by a fractionation during the precipitation processes, but this value does not reflect what the polymerization really affords; nd = not determined. All the reactions were carried out in 100 or 600 mL autoclave for ca. 16 h.

Indeed, the  $-\text{CF}_2\text{CH}_2\text{-I}$  halide end-group is about  $25\times$  less reactive than its isomeric counterpart under radical conditions.<sup>15</sup> As a consequence, chain-end functionality remains a critical parameter for the synthesis of fluorinated block copolymers. Interestingly, Asandei et al.<sup>18</sup> have recently reported the  $\text{Mn}_2(\text{CO})_{10}$ -photomediated synthesis of VDF-based well-defined block copolymers, through a complete activation of not only the  $-\text{CH}_2\text{CF}_2\text{-I}$  chain-ends but also that of the less reactive  $-\text{CF}_2\text{CH}_2\text{-I}$  ones. The same authors have also pointed out that VDF polymerizations were especially successful in dimethylcarbonate (DMC). The present work confirms this finding since DMC was used in runs #2, #3, and #5 (Table 1) with no great change compared to those achieved in the presence of 1,1,1,3,3-pentafluorobutane (run #4, Table 1) that is a much more expensive solvent. The successful ITP of VDF and CTFE through the thermal initiation by a catalytic amount of  $\text{Mn}_2(\text{CO})_{10}$  is described in this present work for the first time (runs #2 and #3, Table 1). ITP of VDF using  $\text{C}_6\text{F}_{13}\text{I}$  as the CTA (run #2) led to the corresponding macro-CTA in a good yield and with a quantitative conversion of VDF. As expected from a high-conversion ITP of VDF,<sup>18,19</sup>  $-\text{CH}_2\text{CF}_2\text{-I}$  end-groups that resonate at  $-39$  ppm (Figures S6 and S8, SI) were not observed in the  $^{19}\text{F}$  NMR spectrum of product from run #2 (Figure S3, SI), while the signal attributed to  $-\text{CF}_2\text{CH}_2\text{-I}$  end-groups was clearly detected at  $-108$  ppm.<sup>15</sup> In fact, the concentration of reactive  $-\text{CH}_2\text{CF}_2\text{-I}$  end-groups decreases, while unreactive  $-\text{CF}_2\text{CH}_2\text{-I}$  end-groups accumulate with conversion, thus, contributing to PDI broadening.<sup>18,19</sup> Furthermore, ITP of CTFE thermally initiated by  $\text{Mn}_2(\text{CO})_{10}$  was also studied (run #3, Table 1). In that case, both the CTFE conversion and the yield were modest (47 and 14%, respectively), probably due to the lack of solubility of CTFE in DMC. The presence of  $\text{CF}_2\text{-CFCl-I}$  end-groups observed at  $-57$  ppm<sup>20</sup> in the  $^{19}\text{F}$  NMR spectrum of product from run #3 (Figure S5, SI) confirms the catalytic activation by  $\text{Mn}_2(\text{CO})_{10}$ .

Poly(vinylidene chloride) (PVDC) is known to possess a resistance to a wide variety of solvents as well as an extremely low permeability to water and to oxygen, because of its high degree of crystallinity.<sup>21</sup> As PCTFE is an expensive material, it was worth synthesizing poly(CTFE-*co*-VDC) macro-CTAs with the objective to get a synergetic effect from both comonomers units (runs #6 and #7, Table 1). Although the conventional radical copolymerization of CTFE with VDC was pioneered in 1959,<sup>22</sup> the successful ITP of CTFE and VDC is described here for the first time. The NMR data for the obtained poly(CTFE-*co*-VDC) macro-CTAs are supplied in Figures S10–S13 (SI) and the  $^{19}\text{F}$  NMR spectrum corresponding to run #6 is displayed in Figure 3 (top spectrum). All the expected signals for PCTFE microblocks and dyads<sup>23</sup> were observed.

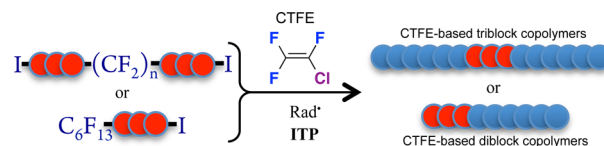
The synthesis of CTFE-based triblock copolymers was first achieved using the I-PVDF-I macro-CTA (obtained at run #4) that exhibits 89% of  $-\text{CH}_2\text{CF}_2\text{-I}$  end-groups (Scheme 2, runs #8 and #9, Table 2).

Such a VDF-based macro-CTA possessing a low  $M_n$  was employed with the objective of breaking the hard crystalline arrangements inherent in PCTFE ( $T_m = 220$  °C),<sup>23b</sup> thus, improving the solubility of the resulting triblock copolymers in organic solvents such as DMF. As a result, GPC and NMR analyses were successfully carried out. Monomodal GPC traces and a clear shift with respect to the macro-CTA were observed,



**Figure 3.**  $^{19}\text{F}$  NMR spectra for macro-CTA from run #6 (top spectrum  $\text{C}_6\text{F}_{13}\text{-(CTFE-}co\text{-VDC)-I}$ ) and for diblock copolymer from run #10 (bottom spectrum  $\text{C}_6\text{F}_{13}\text{-(CTFE-}co\text{-VDC)-}b\text{-PCTFE}$ ), recorded in toluene- $d_8$  at 90 °C using a 600 MHz spectrometer.

### Scheme 2. Synthesis of CTFE-Based Diblock or Triblock Copolymers by Iodine Transfer Polymerization



indicating the successful chain extension and thus formation of block copolymer (Figures 1 and S16, SI).

Nevertheless, as a broad PDI was observed at run #8, the obtained triblock copolymer must contain a small amount of I- $\text{CH}_2\text{-CF}_2\text{-PVDF-}b\text{-PCTFE}$  diblock copolymer arising from I- $\text{CH}_2\text{-CF}_2\text{-PVDF-CH}_2\text{-CF}_2\text{-I}$  macro-CTA.<sup>24</sup> Actually,  $-\text{CF}_2\text{CH}_2\text{-I}$  end-groups are known to be only activated by a stoichiometric amount of  $\text{Mn}_2(\text{CO})_{10}$ .<sup>18</sup> PCTFE homopolymer may also be present in the case of run #9 (in contrast to a peroxide initiator,  $\text{Mn}_2(\text{CO})_{10}$  is not supposed to induce any F-olefin homopolymerization<sup>18</sup>). I- $\text{CH}_2\text{-CF}_2\text{-PVDF-CH}_2\text{-CF}_2\text{-I}$  macro-CTA and PVDF bearing  $\text{CF}_2\text{-H}$  dead-ends must have been removed during the precipitation process in acetone. The  $^{19}\text{F}$  NMR spectra (Figures S14 and S17, SI) clearly show the presence of the characteristic signals belonging to both PVDF ( $\text{CF}_2$  at  $-92$  ppm)<sup>15</sup> and PCTFE ( $\text{CF}_2$  at  $-110$  ppm and  $\text{CFCl}$  at  $-128$  ppm),<sup>23</sup> with a greater integral value for the signal at  $-110$  ppm.  $\text{CFCl-I}$  chain end-groups were also observed at  $-57$  ppm.<sup>20</sup> In addition, the thermogravimetric analyses clearly exhibit an improvement of the thermal behavior for the obtained block copolymers compared to that of the corresponding macro-CTA (Figure 2).

The synthesis of CTFE-based block copolymers was then carried out using poly(CTFE-*co*-VDC)-based macro-CTAs (Scheme 2, runs #10 and #11, Table 2). Although molecular weights were not assessed by GPC due to the lack of solubility of the obtained polymers in commonly used organic solvents, NMR spectra were successfully recorded in toluene- $d_8$  at 90 °C (Figures S20 and S21, SI). The  $\int_{\text{CF}_2(\text{CTFE})} / \int_{\text{CTA}}$  integral ratio is much greater in the  $^{19}\text{F}$  NMR spectra of the expected block copolymers than in those of the corresponding macro-CTAs (Figures S10 and S12, SI), thus, implying a larger amount of CTFE in the first case (Figure 3). Nevertheless, a standardized method of diffusion ordered  $^{19}\text{F}$  NMR spectroscopy (DOSY)<sup>25</sup>

**Table 2. Synthesis of Chlorotrifluoroethylene-Based Block Copolymers by Iodine Transfer Polymerization: Experimental Conditions and Results**

run #	monomer <sup>a</sup> (mol eq)	macro-CTA <sup>a</sup> from run # (mol eq)	initiator <sup>a</sup> (mol eq)	T (°C)	solvent	$\alpha_M^b$ (%)	yield (wt %)	$M_n$ (targeted, <sup>c</sup> NMR, <sup>d</sup> GPC/PDI <sup>e</sup> ) $T_d^{100f}$
8	CTFE (100)	I-PVDF-I from run #4 (1)	Mn <sub>2</sub> (CO) <sub>10</sub> (0.1)	100	DMC	60	32	7500, 6800, 7200:2.05 nd, 180, 388
9	CTFE (20)	I-PVDF-I from run #4 (1)	TBPPi (0.1)	74	DMC	65	32	3200, 2500, 4200:1.06 <sup>h</sup> nd, 175, 378
10	CTFE (200)	C <sub>6</sub> F <sub>13</sub> -(CTFE-co-VDC)-I from run #6 (1)	TBPPi (8)	74	C <sub>4</sub> H <sub>5</sub> F <sub>3</sub> /H <sub>2</sub> O 1:1 (v/v)	71	45	23500, 39000, nd/nd nd, 160, 370
11	CTFE (300)	I-(CTFE-co-VDC)-I from run #7 (1)	TBPPi (5)	74	C <sub>4</sub> H <sub>5</sub> F <sub>3</sub> /H <sub>2</sub> O 1:1 (v/v)	78	44	33000, 28000, nd/nd nd, 170, 375

<sup>a</sup>Molar equivalent. <sup>b</sup> $\alpha_M$  = conversion of CTFE. <sup>c</sup>Targeted  $M_n$  assessed using the following equation:  $M_n = \alpha_M \times (([CTFE]_0 / ([macroCTA]_0) \times M_{CTFE}) + M_{macroCTA})$ , where  $[x]_0$  stands for the initial molar concentration of compound  $x$ ,  $M_x$  represents the molecular weight of compound  $x$ . <sup>d</sup>Determined by <sup>19</sup>F NMR according to the following equation:  $[(\int_{-108} CF_2(CTFE) / \int_{-92} CF_2(VDF)) \times \#VDF \text{ units in macroCTA} \times M_{CTFE}] + M_{macroCTA}$ . <sup>e</sup>Assessed by gel permeation chromatography in DMF using PMMA standards. <sup>f</sup>Determined by TGA at 10 °C/min under air. <sup>g</sup>Assessed by DSC. <sup>h</sup>This PDI value is unexpectedly low (PDI values for ITP are in general 1.3 ± 0.1). This could be explained by a fractionation during the precipitation processes but this value does not reflect what the polymerization really affords; nd = not determined. All the reactions were carried out in 100 or 600 mL Autoclave for ca. 16 h.

would be of great interest to unambiguously prove that the desired block copolymers are the only macromolecules present in solution.

To summarize, various original fluorinated macro-CTA based on VDF, CTFE, or CTFE and VDC, were successfully synthesized by iodine transfer polymerization (ITP). ITP of CTFE and VDC as well as ITP of VDF thermally initiated at 100 °C by a catalytic amount of dimanganese decacarbonyl (Mn<sub>2</sub>(CO)<sub>10</sub>) were reported for the first time. Syntheses of PCTFE-*b*-PVDF-*b*-PCTFE triblock copolymers endowed with high thermal stabilities ( $T_d^{100\%}$  of ca. 380 °C, under air) were carried out from a low molecular weight VDF-based macro-CTA. Further work on the characterization of the polymers by diffusion ordered <sup>19</sup>F NMR spectroscopy (DOSY) is under progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

Representative procedures for polymerization in autoclave and characterization data of the polymers (<sup>1</sup>H and <sup>19</sup>F NMR spectra, TGA thermograms, GPC chromatograms). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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