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# SET-LRP of Semifluorinated Acrylates and Methacrylates

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**ABSTRACT.** Single electron transfer-living radical polymerization (SET-LRP) of 1H,1H,2H,2H-perfluorooctyl acrylate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, and 1H,1H,5H-octafluoropentyl methacrylate up to  $[M]_0/[I]_0 = 30$  and 1H,1H,5H-octafluoropentyl acrylate up to 93% monomer conversion targeting  $[M]_0/[I]_0 = 260$  with excellent control of molecular weight and molecular weight distribution was accomplished in 2,2,2-trifluoroethanol (TFE) at 25 °C for the acrylates and 50 °C for the methacrylate. These experiments demonstrated that TFE serves as a very good solvent for SET-LRP of semifluorinated monomers using hydrazine activated Cu(0) wire as catalyst, bis(2-bromopropionyl)ethane and *p*-toluene sulfonyl chloride as initiators, and Me<sub>6</sub>-TREN as ligand. Analysis of the kinetics of polymerization and of the polymer chain ends by a combination of <sup>1</sup>H-NMR, GPC, MALDI-TOF and chain-end functionalization by “thio-bromo” click reaction demonstrated the synthesis of perfect or near-perfect chain-end functional semifluorinated homopolymers.

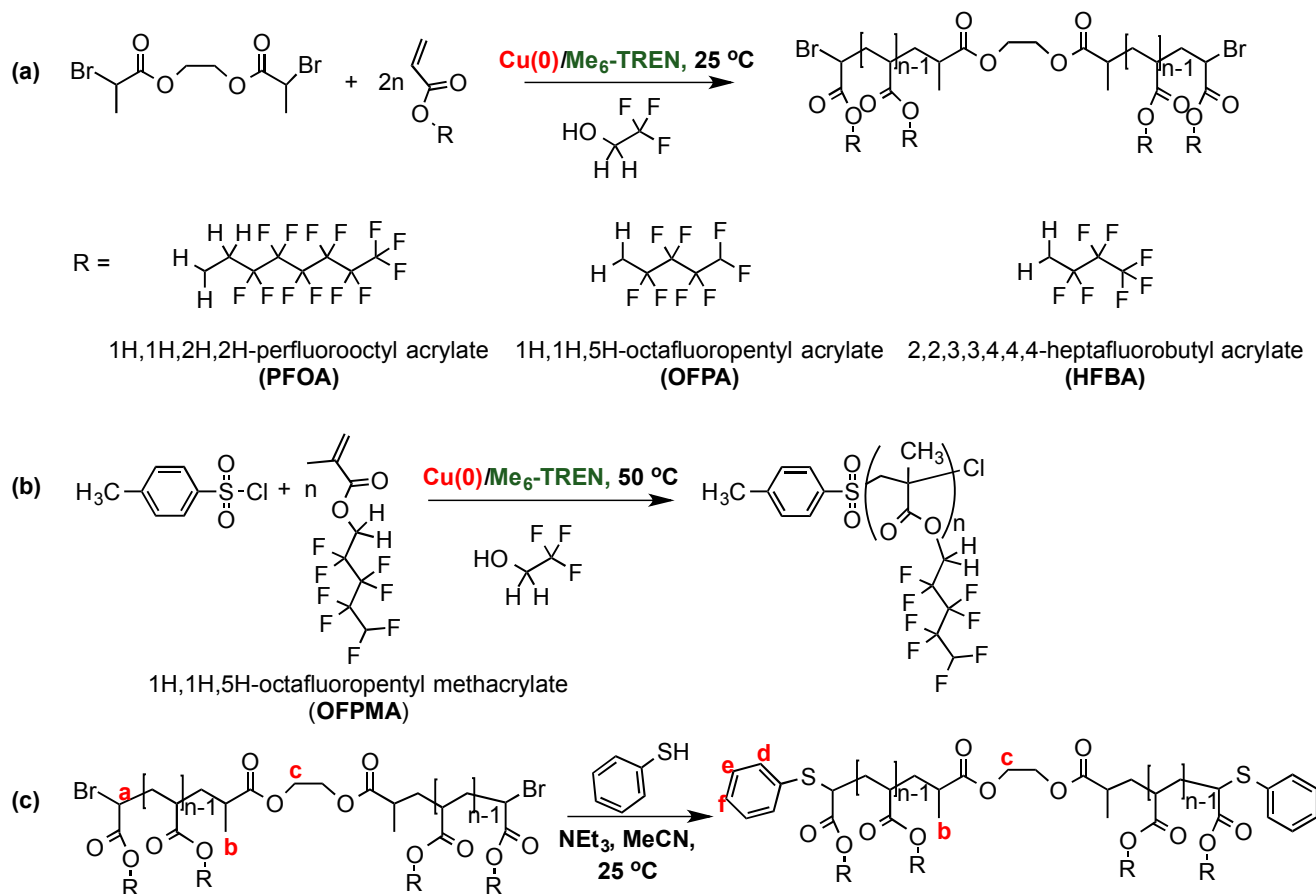
## INTRODUCTION

Fluorinated and semifluorinated polymers have received significant interests since the discovery of the first semifluorinated polymer, poly(chlorotrifluoroethylene), by Fritz Schloffer and Otto Scherer at IG Farben Industry in 1934,<sup>1</sup> and soon after by that of the first perfluorinated polymer, poly(tetrafluoroethylene) (PTFE or Teflon), by Roy Plunkett at DuPont in 1938.<sup>2</sup> Fluorinated and semifluorinated polymers exhibit properties which cannot be achieved by their hydrogenated homologues, namely high thermal and chemical stability, excellent mechanical properties at extreme

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temperatures, good hydrophobicity and lipophobicity, low flammability, refractive index, valuable electric properties, low relative permittivity, high resistance to UV, concentrated mineral acids and bases, low cohesive energy, and surface energy. Therefore, fluorinated polymers have numerous technological applications.<sup>3-7</sup> Examples of highly non-reactive fluorinated polymers include the amorphous copolymer of bis-2,2-trifluoromethyl-4,5-difluoro-1,3-dioxole with tetrafluoroethylene (Teflon-AF),<sup>8,9</sup> poly(vinylidene fluoride)<sup>10-13</sup> and copolymers with other fluorinated monomers. The fluorophobic effect produced by fluorinated and semifluorinated molecules is generated from linear and more complex architectures.<sup>14-18</sup> Fluorinated and semifluorinated polymers can be prepared by various techniques, namely incorporation of fluorine in or along the backbone of the polymer by chemical modification *via* reactions in solution and by surface fluorination.<sup>19,20</sup> In addition, fluorinated and semifluorinated polymers were obtained by polymerization of the corresponding fluorinated monomers by a suitable polymerization process, such as free radical polymerization,<sup>21</sup> polycondensation by Scholl reaction,<sup>22</sup> living cationic,<sup>23-25</sup> living anionic,<sup>26-28</sup> and living radical polymerization (LRP).<sup>29-32</sup> The first living cationic homo- and copolymerization of vinyl ethers bearing a perfluoroalkyl pendant were reported in 1988 by Higashimura laboratory<sup>23</sup> followed by our laboratory in 1992.<sup>24,25</sup> The first SET mediated<sup>33</sup> synthesis of chain ended functional semifluorinated polymers were also reported by our laboratory in 1997 by the Pd(0) catalyzed SET – step polymerization of  $\alpha$ ,  $\omega$ -diiodoperfluoroalkanes with  $\alpha$ ,  $\omega$ -olefins.<sup>33</sup> Research *via* LRP techniques produced various fluorinated architectures mainly by atom transfer radical polymerization (ATRP), in addition to nitroxide-mediated radical polymerization (NMP) and reversible addition–fragmentation chain-transfer (RAFT).<sup>34</sup> However, most often LRP of semifluorinated monomers by these methods in bulk or in solution required copolymerization with non-fluorinated monomers or the use of a non-fluorinated macroinitiator. Interesting results were achieved when supercritical CO<sub>2</sub> was employed as reaction medium or in emulsion systems, such as using a surface-active ATRP initiator.<sup>34</sup> In some cases, it was reported that fluorinated ligands were required to achieve high monomer conversion by

ATRP.<sup>35</sup> Compared to ATRP, the examples of polymerizations of semifluorinated monomers by NMP or RAFT are very few. RAFT polymerization of pentafluorophenyl methacrylate was carried out at 90 °C in dioxane by Eberhardt and Theato yielding homopolymers with narrow molecular weight distribution.<sup>36</sup> Synthesis of poly(hexafluoroisopropyl methacrylate) has also been reported by RAFT polymerization in dioxane at 65 °C.<sup>37</sup> Nevertheless, it remained a challenge to homopolymerize semifluorinated acrylates and methacrylates<sup>14-16</sup> under mild reaction conditions by LRP with good control of molecular weight, molecular weight distribution and complete retention of chain end functionality of the resulting polymer. Here we report homopolymerization of a range of semifluorinated acrylates (**Scheme 1**), 1H,1H,2H,2H-perfluorooctyl acrylate (PFOA), 1H,1H,5H-octafluoropentyl acrylate (OFPA), 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) and 1H,1H,5H-octafluoropentyl methacrylate (OFPMA), using another LRP methodology, single electron transfer-living radical polymerization (SET-LRP). Using an inexpensive organic solvent, 2,2,2-trifluoroethanol (TFE), SET-LRP of these semifluorinated acrylates at 25 °C, and methacrylate at 50 °C resulted in semifluorinated homopolymers with low molecular weight distribution and well defined chain-end functionality. This strategy opens up the opportunity for functionalization of these semifluorinated polymers to synthesize more complex unprecedented architectures.



**Scheme 1.** SET-LRP of semifluorinated acrylates initiated with bis(2-bromopropionyl)ethane (BPE) (a), and semifluorinated methacrylate initiated with *p*-toluene sulfonyl chloride (TsCl) (b) catalyzed with hydrazine-activated  $\text{Cu}(0)$  wire as catalyst and  $\text{Me}_6\text{-TREN}$  as ligand in TFE. Thioetherification of bromine chain-end by thio-bromo "click" reaction (c).

SET-LRP<sup>38-41</sup> is an excellent method for ultrafast synthesis of well-defined and perfectly functional chain-ended polymers<sup>40,42-48</sup> from a large diversity of monomers, including vinyl chloride,<sup>1-3,10,17,18</sup> acrylates,<sup>39,40,44,46,49,50</sup> acrylamides,<sup>51,52</sup> methacrylates,<sup>40,53-58</sup> acrylonitrile,<sup>59,60</sup> and others.<sup>61</sup> SET-LRP is catalyzed by  $\text{Cu}(0)$ ,<sup>39,40,42,62-68</sup> in different forms, wire, powder, nanoparticles etc.<sup>39,40,42,62-68</sup> in the presence of an N-containing ligand, such as tris[(2-dimethylaminoethyl)] amine ( $\text{Me}_6\text{-TREN}$ ) or tris(2-amino)ethyl amine (TREN)<sup>40,42,43,69-71</sup> in a polar solvent, such as  $\text{H}_2\text{O}$ ,<sup>72-77</sup> dimethyl sulfoxide (DMSO),<sup>44,46,56,66,73,78-82</sup> alcohols,<sup>57,78,83-86</sup> and their binary mixture<sup>87</sup> that should preferentially stabilize  $\text{Cu}(\text{II})\text{X}_2$ .<sup>39,40,43,61,63,71,74,78,79,88-91</sup> These solvents result in a self-regulated disproportionation of  $\text{Cu}(\text{I})\text{X}$  to generate *in situ* the extremely active "nascent"  $\text{Cu}(0)$  atomic species and  $\text{Cu}(\text{II})$

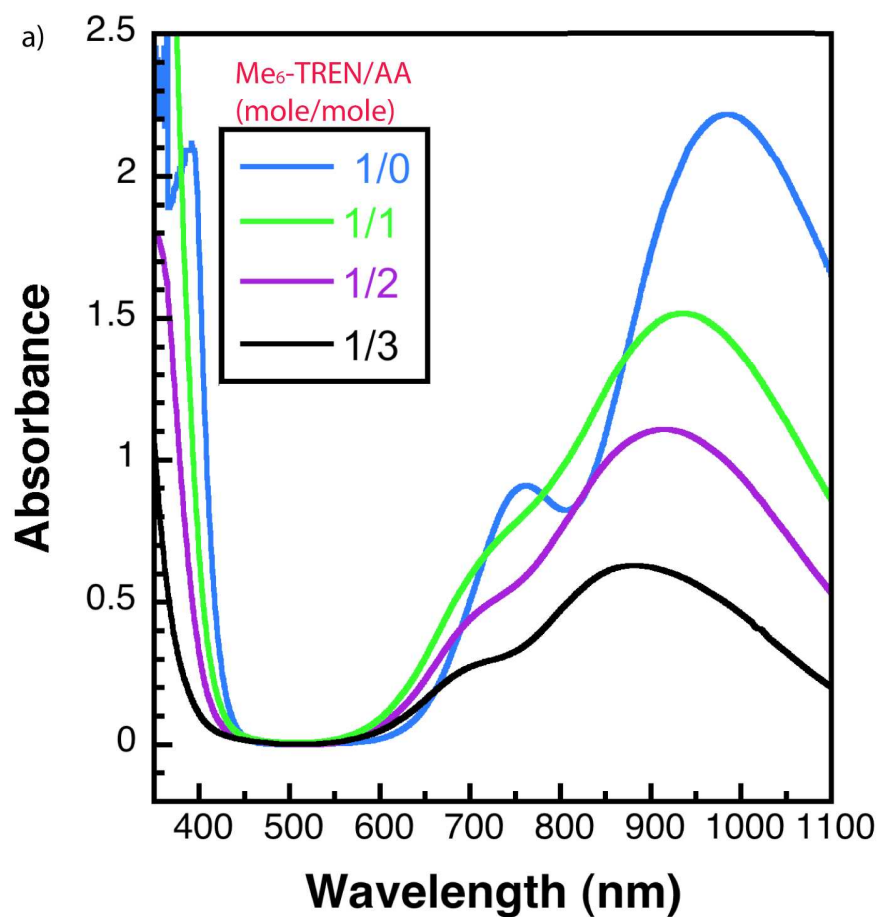
deactivator<sup>39,40,42,43,61,66,69,71,81,88,92-94</sup> resulting in a living polymerization with retention of polymer chain-ended functionality.<sup>40,42-48</sup> The limitations imposed by the requirement of a polar solvent for SET-LRP has recently been overcome by using the fluorinated alcohols, 2,2,2-trifluoroethanol (TFE) and 2,2,3,3-tetrafluoropropanol (TFP) as solvents.<sup>83-86,95</sup> These solvents carry both a fluorinated hydrophobic site, which helps to solubilize hydrophobic monomers, and a hydrophilic site, which helps to mediate the disproportionation of Cu(I), result in a LRP for both polar and non-polar acrylates.<sup>73-76,85</sup> Hence, SET-LRP of the semifluorinated monomers was carried out using TFE as solvent in the presence of Me<sub>6</sub>-TREN as ligand. However, due to electron withdrawing fluorinated side chain separated by only one methylene unit from the ester functionality of the acrylate or methacrylate, HFBA, OFPA and OFPMA undergo base-catalyzed transesterification *in situ* where Me<sub>6</sub>-TREN acts as base and TFE as the nucleophile. Hence, to overcome this side reaction, SET-LRP of these monomers was carried out in the presence of acetic acid (AA) at a Me<sub>6</sub>-TREN/AA = 1/2 mole/mole ratio. In a previous report from our laboratory, it was demonstrated that the presence of AA has no significant effect on SET-LRP of methyl methacrylate (MMA) in methanol, and it was also demonstrated that CuCl/Me<sub>6</sub>-TREN undergoes disproportionation in AA.<sup>55</sup> Herein, we report SET-LRP as an excellent methodology under mild reaction conditions for homopolymerization of semifluorinated acrylates and methacrylates using TFE as solvent, hydrazine activated Cu(0) wire as catalyst, Me<sub>6</sub>-TREN as ligand for PFOA, in the presence of two equivalents of AA for HFBA, OFPA and OFPMA.

## RESULTS AND DISCUSSION

### Disproportionation of Cu(I)Br/ Me<sub>6</sub>-TREN in TFE in the Presence of Acetic Acid

Previously, the influence of acidity on the SET-LRP of MMA in protic solvents, methanol and ethanol, and dipolar aprotic solvents, dimethyl sulfoxide was investigated in our laboratory.<sup>55</sup> It was demonstrated that SET-LRP tolerates a high concentration of AA and yet preserves a good control

over the polymerization process. Even in acetic acid, the polymerization exhibits features of a living process.<sup>55</sup> The disproportionation of Cu(I)Cl/Me<sub>6</sub>-TREN in deoxygenated AA was examined by UV-*vis* spectroscopy and demonstrated a pronounced absorption with a maximum at 680 nm corresponding to Cu(II)Cl<sub>2</sub>/Me<sub>6</sub>-TREN complex. This indicated that AA itself is a disproportionating solvent.<sup>55</sup> On the other hand disproportionation of Cu(I)Br/Me<sub>6</sub>-TREN and the stability of the resulting Cu(II)Br<sub>2</sub>/Me<sub>6</sub>-TREN complex in TFE was demonstrated previously at CuBr/Me<sub>6</sub>-TREN = 1/1 (CuBr = 16.5 mM).<sup>83</sup> In the present work the disproportionation of Cu(I)Br/Me<sub>6</sub>-TREN was carried out in TFE in the presence of different concentrations of AA (**Figure 1**). The absorbance of CuBr<sub>2</sub>/Me<sub>6</sub>-TREN complex from the UV-*vis* spectrum<sup>40,92</sup> of the disproportionation mixture (**Figure 1a**) validates the formation of the CuBr<sub>2</sub>/N-ligand complex. It was observed that the  $\lambda_{\max}$  for Cu(II)Br<sub>2</sub>/Me<sub>6</sub>-TREN complex in the presence of AA gradually shifts to a lower wavelength probably due to binding of AA to Me<sub>6</sub>-TREN. However, even at Me<sub>6</sub>-TREN/AA = 1/3 a prominent absorption band for CuBr<sub>2</sub>/Me<sub>6</sub>-TREN complex was observed indicating the disproportionation of Cu(I)Br/Me<sub>6</sub>-TREN under these conditions. In addition, the *nascent* Cu(0) formed by disproportionation of CuBr/Me<sub>6</sub>-TREN immediately aggregates and precipitates resulting in Cu(0) nanoparticles at the bottom of the UV-*vis* cuvette cell (**Figure 1b, c**).



Me<sub>6</sub>-TREN/AA (mole/mole) = 1/1

Me<sub>6</sub>-TREN/AA (mole/mole) = 1/2

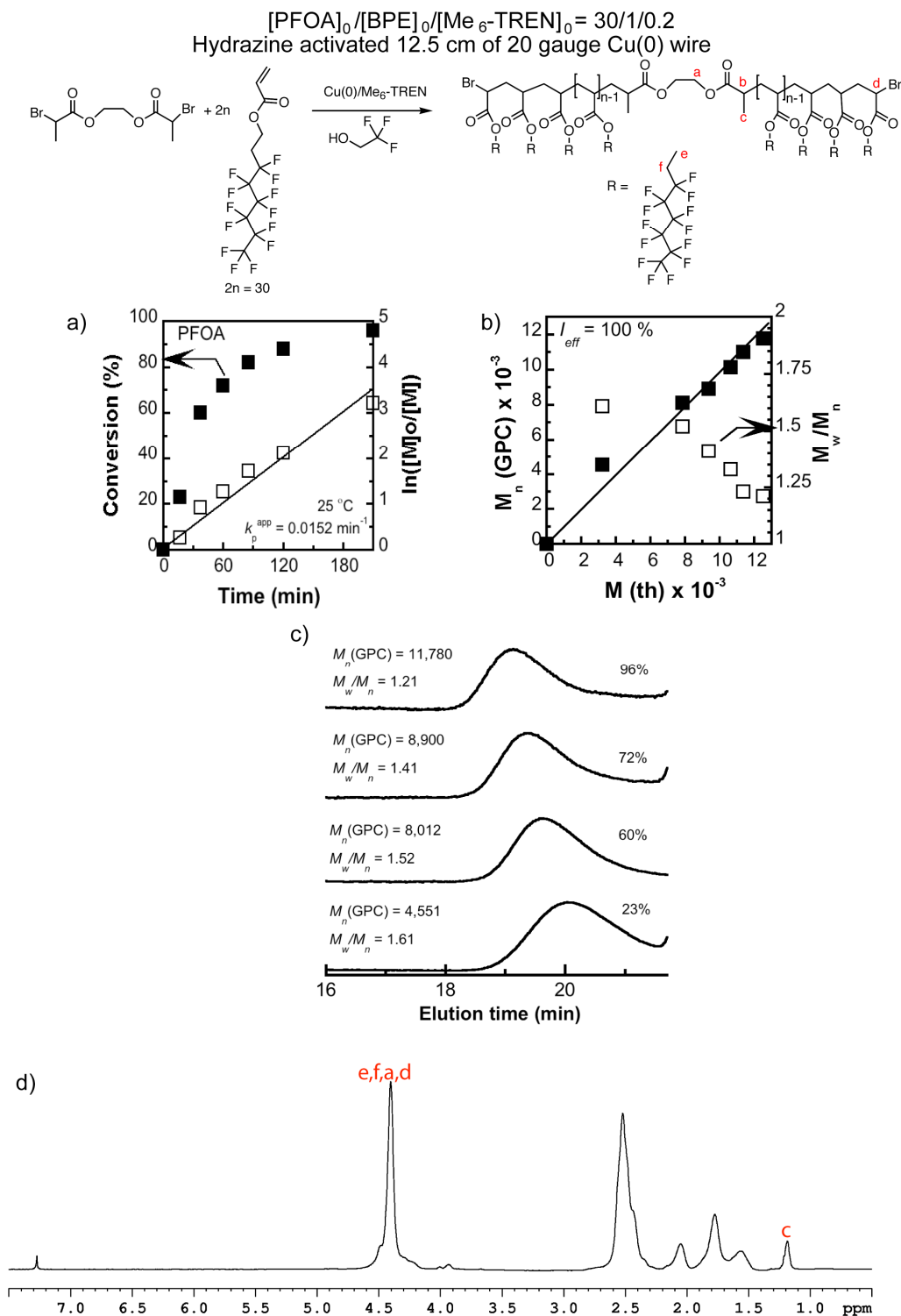


**Figure 1.** UV-*vis* spectra (a) and visual observation (b and c) of disproportionation of Cu(I)Br in TFE in the presence of various amounts of acetic acid recorded after 60 min of mixing reagents at 25 °C. Conditions: [Cu(I)Br]<sub>0</sub> = 16.5 mM, TFE = 1.8 mL, [Cu(I)Br]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub> = 1/1.



## SET-LRP of PFOA

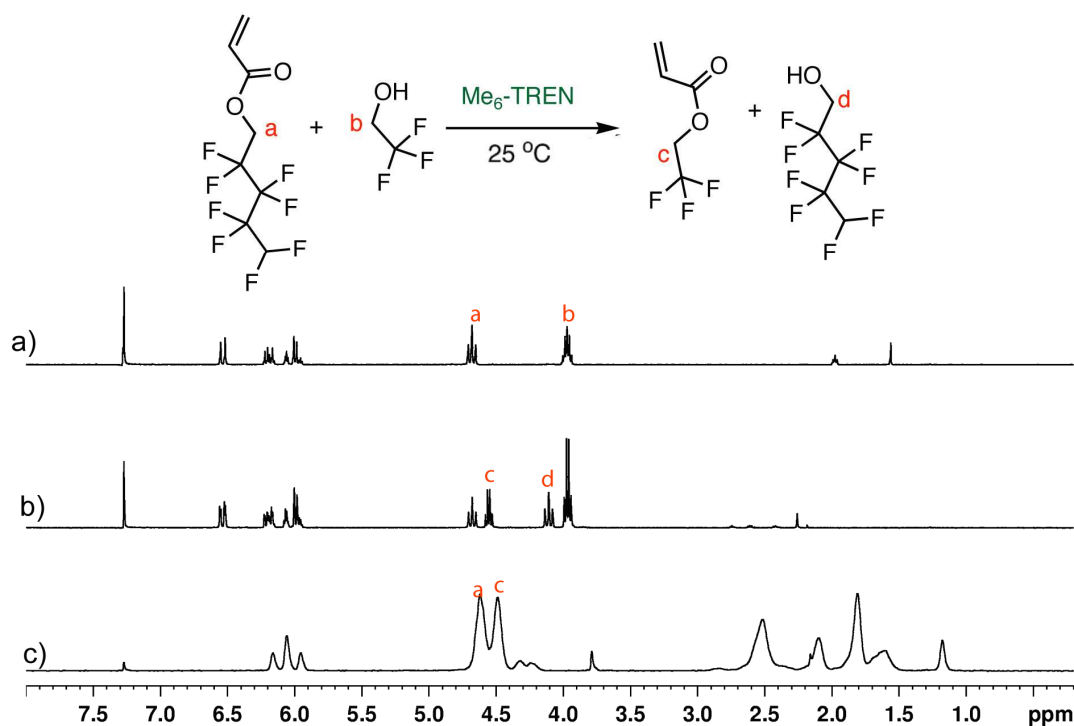
In the case of PFOA, the ester moiety is separated from the electron withdrawing fluorinated side chain by two methylenic groups that decrease the inductive effect and make this monomer stable towards transesterification during SET-LRP in the presence of Me<sub>6</sub>-TREN and TFE. Hence, SET-LRP of PFOA initiated with BPE, and catalyzed with hydrazine activated Cu(0) wire and Me<sub>6</sub>-TREN ligand was performed in TFE without the addition of AA. The kinetic experiments for [PFOA]<sub>0</sub>/[BPE]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub> = 30/1/0.2 are shown in **Figure 2a,b**. Ln[M]<sub>0</sub>/[M] showed a linear dependence with time, where [M] is the monomer concentration at time *t*, and [M]<sub>0</sub> is the initial monomer concentration at time zero, demonstrating first order rate of polymerization on monomer concentration. The relative number-average molecular weight (*M<sub>n</sub>*) and the molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) were determined by gel permeation chromatography (GPC) in THF with PMMA as standard. The experimental values of the apparent rate constant of propagation (*k<sub>p</sub><sup>app</sup>*) and initiator efficiency (*I<sub>eff</sub>*) measured from *M<sub>th</sub>* vs *M<sub>n</sub>* are shown in the kinetic plots (**Figure 2a,b**). Under the reaction conditions, from **Figure 2** it can be seen that *M<sub>n</sub>* (relative to PMMA standards by GPC) increases linearly with monomer conversion and exhibits linear dependence on the theoretical molecular weight. Narrow *M<sub>w</sub>*/*M<sub>n</sub>* was obtained regardless of conversion up to almost complete monomer conversion. The <sup>1</sup>H NMR spectra of the poly(PFOA) was recorded in CDCl<sub>3</sub>/Freon 113 (2/1 v/v) at 96% monomer conversion (**Figure 2c**). However, the limited solubility of purified poly(PFOA) in common organic solvents prevented the nucleophilic substitution of bromine chain-end by thio-bromo “click” reaction.<sup>96,97</sup> Moreover, in <sup>1</sup>H NMR spectrum of the poly(PFOA) the signal from H<sub>d</sub>, corresponding to the proton from the α-position of the bromine chain-end, is buried under the signal from H<sub>e</sub>, H<sub>f</sub>, and H<sub>a</sub> (**Figure 2c**). This prevented the analysis of the chain-end functionality by the integration of the signals from H<sub>a</sub>.



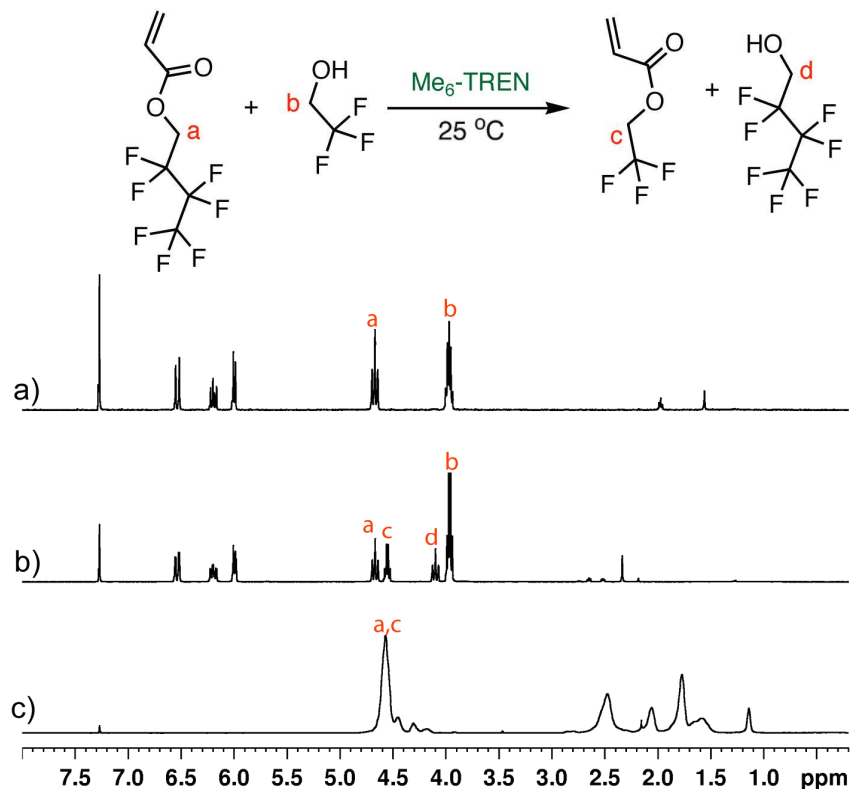
**Figure 2.** Kinetic plot (a) and  $M_n$  and  $M_w/M_n$  vs theoretical  $M_{th}$  (b), GPC traces of poly(PFOA) at various monomer conversions (c) for SET-LRP of PFOA performed in TFE, and <sup>1</sup>H NMR spectrum of the poly(PFOA) in CDCl<sub>3</sub>/Freon 113 (2/1 v/v) at 96% monomer conversion (d). Conditions: PFOA= 0.5 mL, TFE = 0.5 mL, and [PFOA]<sub>0</sub>/[BPE]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub> = 30/1/0.2, hydrazine activated 12.5 cm Cu(0) wire, 25 °C.

## SET-LRP of OFPA and HFBA

Unlike PFOA, where the ester moiety is separated from the electron withdrawing fluorinated side chain by two methylenic units, in the case of OFPA and HFBA the ester moiety is separated from the fluorinated side chain by only one methylenic unit. Therefore, due to the stronger inductive effect the ester group is activated and transesterification takes place in TFE in the presence of Me<sub>6</sub>-TREN. <sup>1</sup>H NMR spectra of the transesterification are shown in **Figure 3a,b** for OFPA, and in **Figure 4a,b** for HFBA in the presence of TFE and a catalytic amount of Me<sub>6</sub>-TREN. Transesterification reactions were carried out at room temperature. After 4 h, OFPA and HFBA resulted in 55% and 43% transesterification, respectively. When SET-LRP of these monomers were carried out in TFE at [monomer]<sub>0</sub>/[BPE]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub> = 30/1/0.2 the resulting polymers contained 45% and 20% (by <sup>1</sup>H NMR) transesterified polymer product for OFPA and HFBA, respectively (**Figure 3c and 4c**).



**Figure 3.** <sup>1</sup>H NMR spectra of: OFPA/ TFE = 1/ 2.54 (mole/mole) recorded in CDCl<sub>3</sub> (a), OFPA/ TFE /Me<sub>6</sub>-TREN = 1/2.54/0.008 (mole/mole) recorded in CDCl<sub>3</sub> after 4 h of mixing the reagents (b), and the polymer product obtained from SET-LRP of OFPA performed in trifluoroethanol (TFE) under conditions: [OFPA]<sub>0</sub>/[BPE]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub> = 30/1/0.2, OFPA = 0.5 mL, TFE = 0.5 mL, and hydrazine activated 12.5 cm Cu(0) wire, 25 °C recorded in CDCl<sub>3</sub>/Freon 113 (2/1 v/v) at 95% monomer conversion (c).



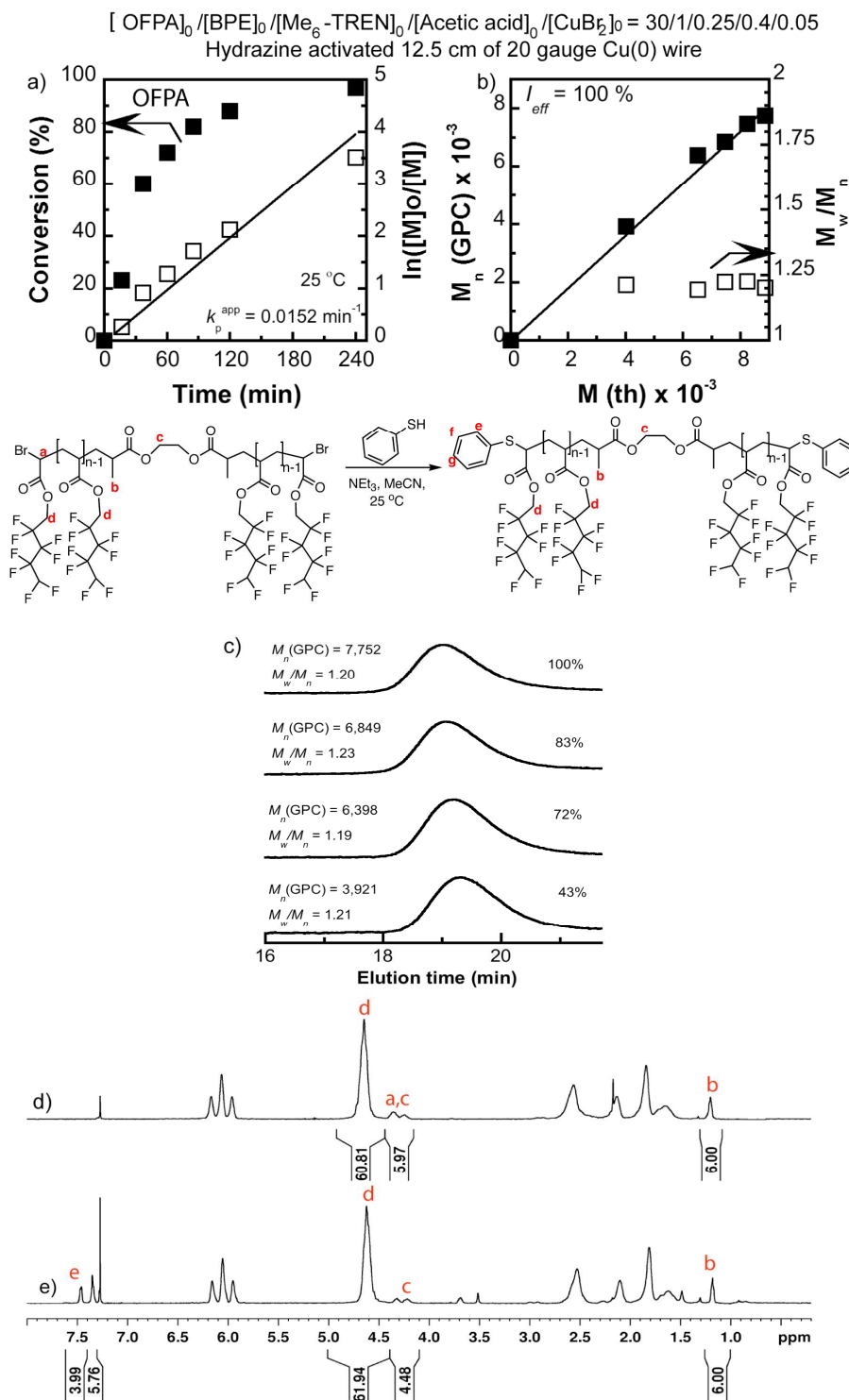
**Figure 4.**  $^1\text{H}$  NMR spectra of: HFBA/ TFE = 1/ 2.37 (mole/mole) recorded in  $\text{CDCl}_3$  (a) HFBA/ TFE / $\text{Me}_6\text{-TREN}$  = 1/2.37/0.008 (mole/mole) recorded in  $\text{CDCl}_3$  after 4 h of mixing the reagents (b), and the polymer product obtained from SET-LRP reactions of OFPA performed in trifluoroethanol (TFE) under conditions:  $[\text{HFBA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0 = 30/1/0.2$ , HFBA = 0.5 mL, TFE = 0.5 mL, and hydrazine activated 12.5 cm of 20 gauge Cu(0) wire, 25 °C recorded in  $\text{CDCl}_3/\text{Freon 113}$  (2/1 v/v) at 98% monomer conversion (c).

The undesirable transesterification of OFPA and HFBA during SET-LRP in TFE was overcome by adding 2 equivalents of AA with respect to  $\text{Me}_6\text{-TREN}$ . In the presence of 2 equivalents of AA, at  $[\text{M}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{AA}] = 30/1/0.2/0.4$ , 12.5 cm of 20 gauge activated Cu(0) wire, monomer/TFE = 1/1 (v/v) at 25 °C the transesterification was completely eliminated for both OFPA and HFBA, but the resulting polymer exhibited broader polydispersity ( $M_w/M_n=1.5$ ) and a shoulder due to low molecular weight polymer. This can be attributed to the fact that, due to the presence of AA the slow disproportionation at the beginning of the polymerization resulted in an insufficient amount of Cu(II) deactivator which led to a small extent of termination of the propagating radicals. Hence, a small amount of  $\text{Cu(II)Br}_2$  (0.05 equivalent per monomer) was added in the reaction mixture and a perfect SET-LRP was obtained at  $[\text{monomer}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{AA}]/[\text{Cu(II)Br}_2] =$

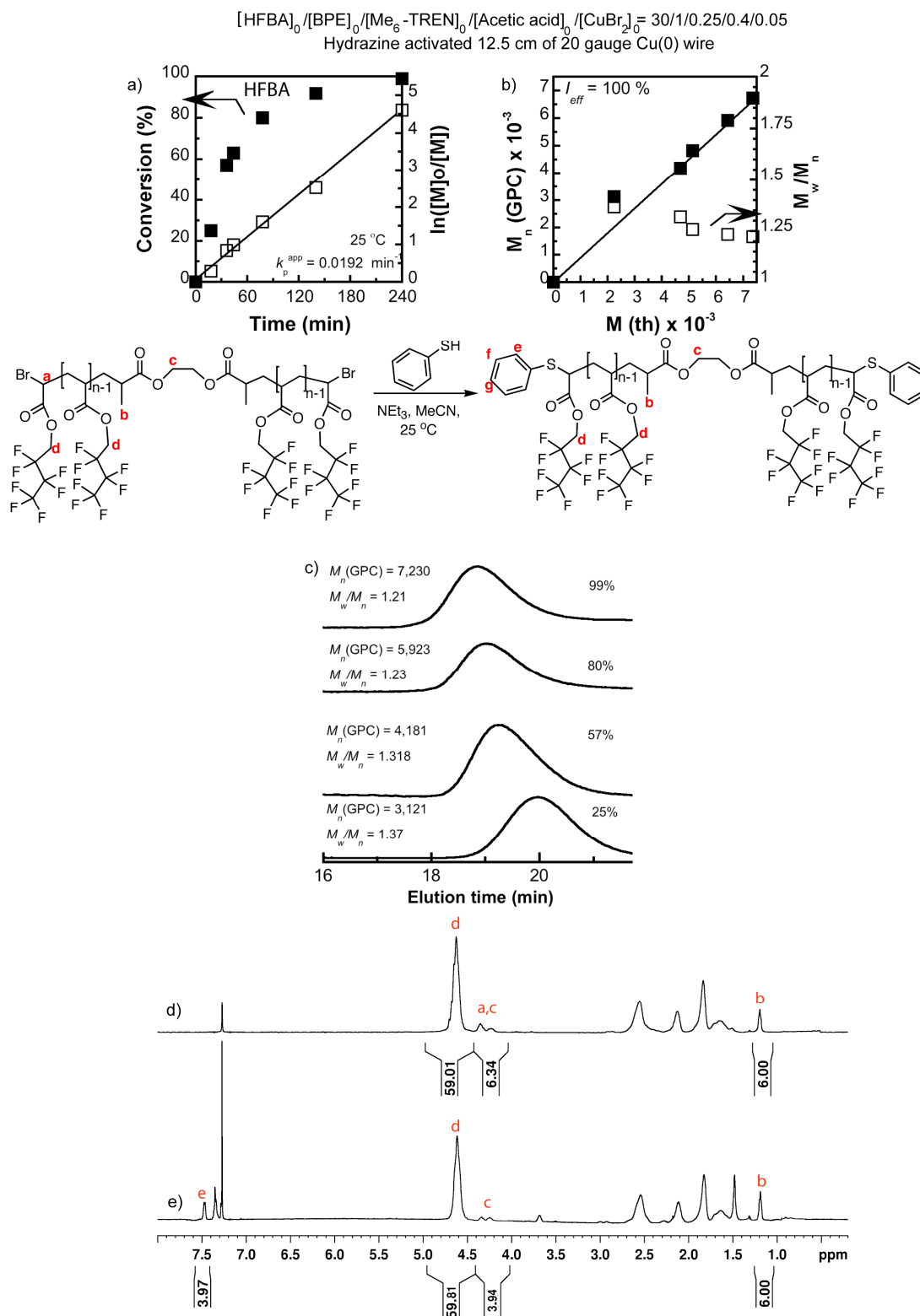
30/1/0.25/0.4/0.05 for both OFPA and HFBA. Under these conditions a linear dependence of  $\ln[M]_0/[M]$  on time was observed (**Figure 5a** and **6a**), and in both cases, linear correlations of  $M_n$  (relative to PMMA standards by GPC) with the theoretical molecular weight and narrow  $M_w/M_n$  were obtained up to complete or near complete monomer conversion (**Figure 5b,c**, and **6b,c**). Comparison of the integrals of  $H_b$ , corresponding to the initiator  $\text{CH}_3\text{-CH}$  group, and  $H_a$ , corresponding to the proton from the  $\alpha$ -position of the bromine chain-end (**Figure 5d** and **6d**) gives the fraction of chains initiated that are still functionalized with a bromine atom. Further thio-bromo “click” reaction was carried out with thiophenol with the poly(OFPA) and poly(HFBA) at almost complete monomer conversion and the thioetherified polymers were analyzed by  $^1\text{H}$  NMR spectroscopy to evaluate the bromine chain end functionality. The  $^1\text{H}$  NMR spectra of the polymer before “click” reaction (**Figure 5d** and **Figure 6d**) indicates presence of total six protons at 4.1-4.4 ppm, consisting of two protons from  $H_a$  and four protons from  $H_c$  of the bifunctional BPE initiator. Further, upon nucleophilic substitution of the bromine chain end with thiophenol, signals for four protons correspond to  $H_c$  (7.5 ppm) from the thiophenol moiety appear in the aromatic region (**Figure 5e** and **Figure 6e**). Thus,  $^1\text{H}$  NMR spectra from before and after thio-bromo “click” reaction indicates retention of near quantitative bromine chain ends (two protons) for the bifunctional poly(OFPA) and poly(HFBA).

The chain end structure of poly(OFPA) was further analyzed by MALDI-TOF spectrometry at 40% and 82% monomer conversion (**Figure 7a,b**). The MALDI-TOF spectra for  $[M]_0/[I]_0 = 40$  exhibits only one distribution of signals of 286 mass unit correspond to OFPA repeat unit (**Figure 7a**). However, the MALDI-TOF spectra for  $[M]_0/[I]_0 = 82$  shows an additional signal distribution 130 mass unit below the distribution of OFPA. These secondary signals correspond to the transesterified polymer product resulted during SET-LRP of OFPA in TFE (**Figure 7b**). Since MALDI-TOF spectrometry is dependent on the structure of the compound, a more accurate quantification of transesterified product in the resulting polymer can be carried out by analysis of the polymer structure by  $^{19}\text{F}$  NMR spectroscopy. The  $^{19}\text{F}$  NMR spectra revealed the presence of <1% transesterified

polymer (**Figure 7c**). In the case of  $[M]_0/[I]_0 = 40$  no signal, and for  $[M]_0/[I]_0 = 82$  less than 2% signal corresponding to polymer resulted from termination of bromine chain end was observed (**Figure 7a, b**). Therefore, MALDI-TOF spectra demonstrated the retention of near quantitative bromine chain end functionality of poly(OFPA) prepared by SET-LRP in TFE mediated by activated Cu(0) wire in the presence of Me<sub>6</sub>-TREN ligand.



**Figure 5.** Kinetic plot (a) and  $M_n$  and  $M_w/M_n$  vs theoretical  $M_{th}$  (b) for SET-LRP of OFPA performed in trifluoroethanol, GPC traces of poly(OFPA) at various monomer conversions (c), <sup>1</sup>H NMR spectra of the poly(OFPA) in CDCl<sub>3</sub>/Freon 113 (2/1 v/v) at 98% monomer conversion before (d), and after (e) thio-bromo “click” reaction. Conditions: OFPA = 0.5 mL, TFE = 0.5 mL, and [OFPA]<sub>0</sub>/[BPE]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub>/[acetic acid]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub> = 30/1/0.25/0.4/0.05, hydrazine activated 12.5 cm Cu(0) wire, 25 °C.

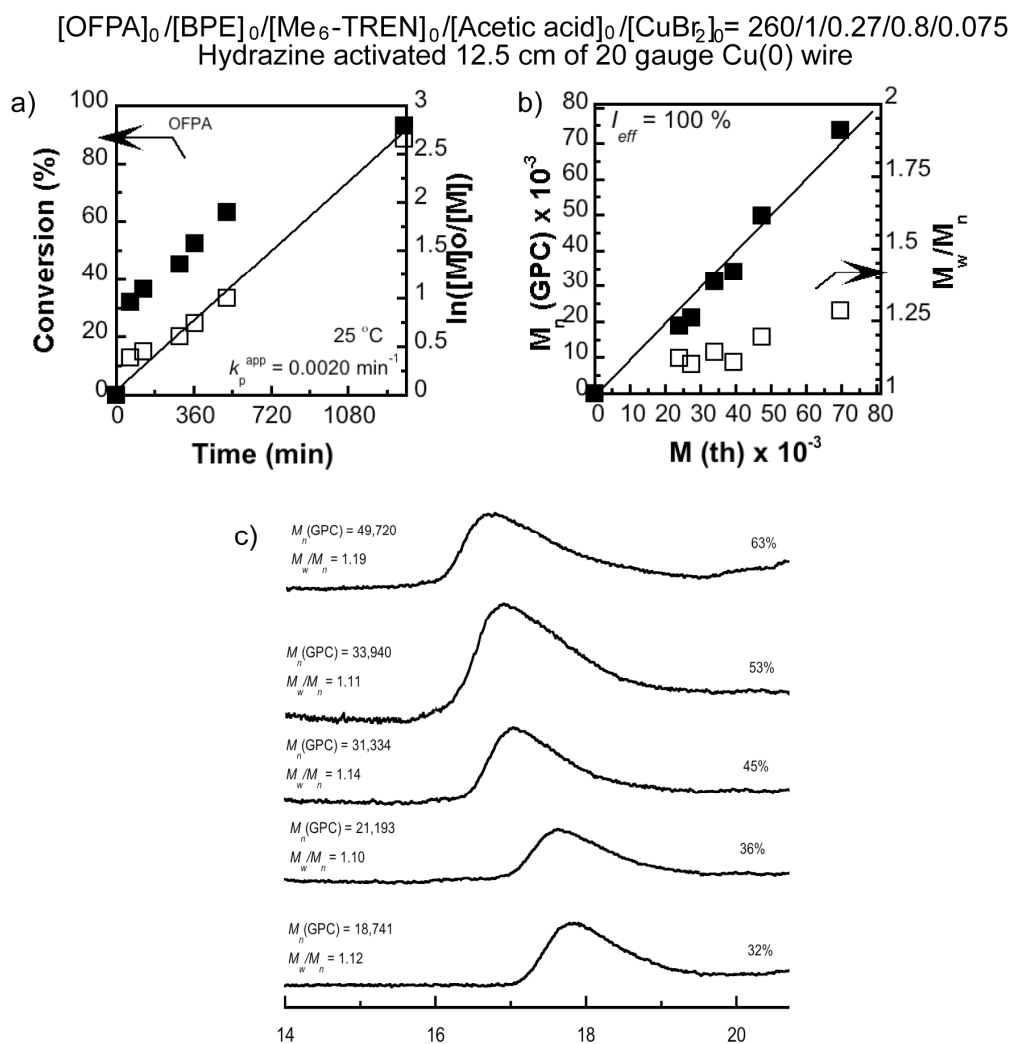


**Figure 6.** Kinetic plot (a) and  $M_n$  and  $M_w/M_n$  vs theoretical  $M_{th}$  (b) for SET-LRP of HFBA performed in trifluoroethanol (TFE), GPC traces of poly(HFBA) at various monomer conversion (c), <sup>1</sup>H NMR spectra of the poly(HFBA) in CDCl<sub>3</sub>/Freon 113 (2/1 v/v) at 99% monomer conversion before (d), and after (e) thio-bromo "click" reaction. Conditions: HFBA = 0.5 mL, TFE = 0.5 mL, and [HFBA]<sub>0</sub>/[BPE]<sub>0</sub>/[Me<sub>6</sub>-TREN]<sub>0</sub>/[acetic acid]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub> = 30/1/0.25/0.4/0.05, hydrazine activated 12.5 cm of 20 gauge Cu(0) wire, 25 °C.





In addition to  $[M]_0/[I]_0 = 30$ , SET-LRP of OFPA targeting  $[M]_0/[I]_0 = 260$  at  $[M]_0/[BPE]_0/[Me_6-TREN]_0/[AA]/[Cu(II)Br_2] = 260/1/0.27/0.8/0.075$  was also carried out under the similar reaction conditions (**Figure 8a, b**). A linear dependence of  $\ln[M]_0/[M]$  with time was obtained up to 93% monomer conversion. The  $M_n$  (relative to PMMA standards by GPC) increased monotonically and linearly with theoretical molecular weight resulting in poly(OFPA) with narrow  $M_w/M_n$  (**Figure 8c**) up to 64% monomer conversion. A slight broadening of the molecular weight distribution ( $M_w/M_n = 1.29$ ) was observed at 93% monomer conversion with a shoulder due to a higher molecular weight.



**Figure 8.** Kinetic plot (a) and  $M_n$  and  $M_w/M_n$  vs theoretical  $M_{th}$  (b) for SET-LRP of OFPA performed in TFE, and GPC traces of poly(OFPA) at various monomer conversions (c). Conditions: OFPA= 0.5

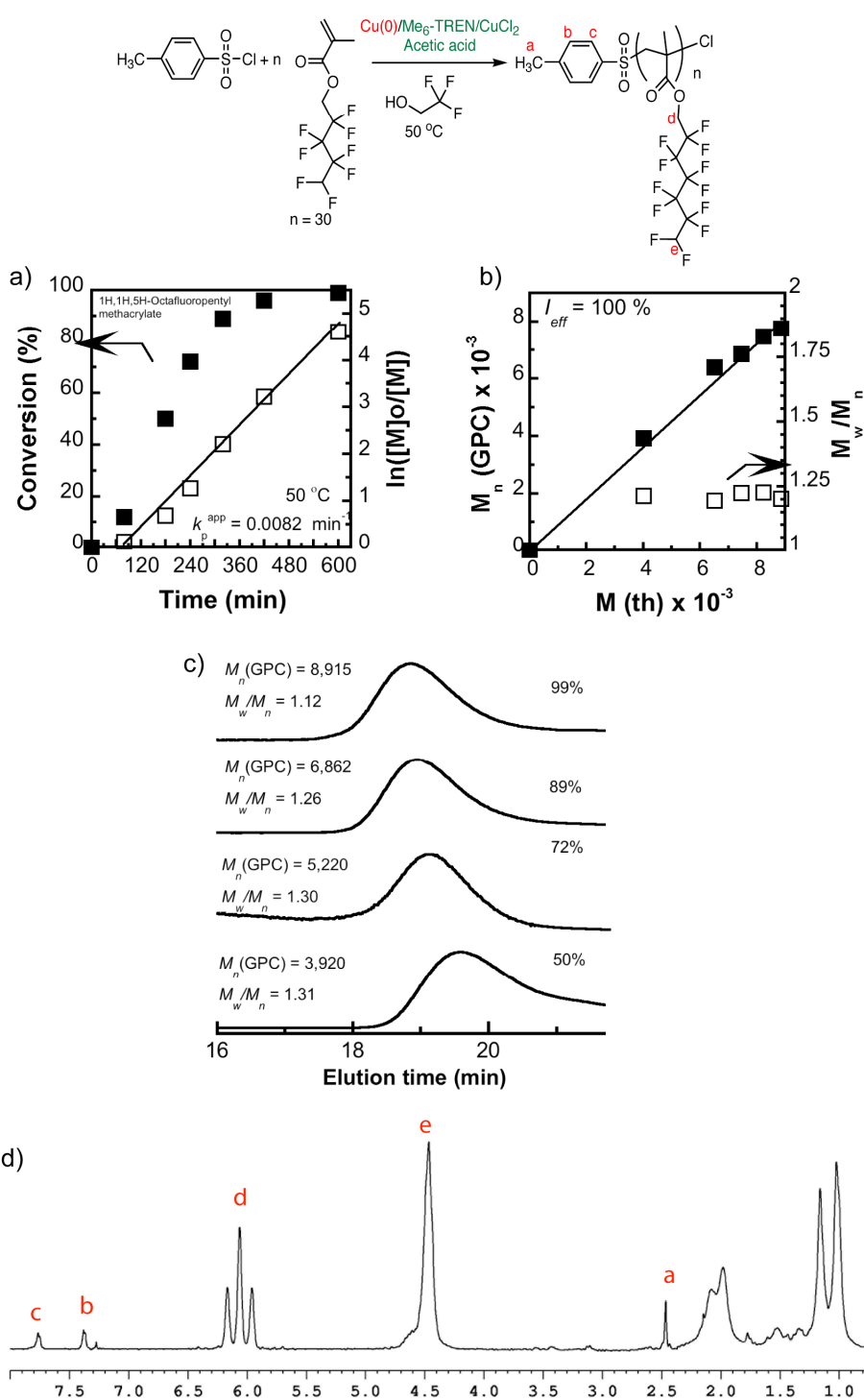
mL, TFE = 0.5 mL, and  $[\text{OFPA}]_0/[\text{BPE}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{acetic acid}]/[\text{CuBr}_2]_0 = 260/1/0.27/0.8/0.075$ , hydrazine activated 12.5 cm of 20 gauge Cu(0) wire, 25 °C.

### SET-LRP of OFPMA

Encouraged by the successful SET-LRP of OFPA in TFE, SET-LRP of OFPMA was also carried out in the same solvent using TsCl as initiator under conditions:  $[\text{OFPMA}]_0/[\text{TsCl}]_0/[\text{Me}_6\text{-TREN}]_0/[\text{AA}]/[\text{CuCl}_2]_0 = 30/1/0.125/0.2/0.025$ . Remarkably, in the case of OFPMA also a linear dependence of  $\ln[M]_0/[M]$  with time was obtained up to almost complete monomer conversion (**Figure 9a**). Theoretical and  $M_n$  (relative to PMMA standards by GPC) showed linear correlation and narrow  $M_w/M_n$  (**Figure 9b,c**).

$[115\text{-OFPMA}]_0/[TsCl]_0/[Me_6\text{-TREN}]_0/[Acetic\ acid]_0/[CuCl_2]_0 = 30/1/0.125/0.3/0.025$

Hydrazine activated 12.5 cm of 20 gauge Cu(0) wire



**Figure 9.** Kinetic plot (a) and  $M_n$  and  $M_w/M_n$  vs theoretical  $M_{th}$  (b) for SET-LRP of OFPMA performed in trifluoroethanol (TFE), GPC traces of poly(OFPMA) at various monomer conversions (c),  $^1H$  NMR spectrum of the poly(OFPMA) in acetone-d<sub>6</sub> at 99% monomer conversion (d). Conditions: OFPMA = 0.5 mL, TFE = 0.25 mL, and  $[OFPMA]_0/[TsCl]_0/[Me_6\text{-TREN}]_0/[acetic\ acid]_0/[CuCl_2]_0 = 30/1/0.125/0.25/0.025$ , hydrazine activated 12.5 cm Cu(0) wire, 50 °C.

## Conclusions

SET-LRP of semifluorinated acrylates and methacrylates was demonstrated in TFE. Remarkably, in all cases an excellent control of molecular weight and polydispersity at ambient temperature was obtained. Previously TFE was demonstrated to be a very good solvent for SET-LRP of both hydrophobic and hydrophilic monomers<sup>73-76,85</sup> and consequently was ranked as a “universal solvent”. Here we report that TFE is an excellent solvent for homopolymerization of various semifluorinated acrylates and methacrylates under very mild reaction conditions. It was also demonstrated that SET-LRP provides a robust and versatile LRP methodology for the synthesis of highly hydrophobic semifluorinated homopolymers. SET-LRP of semifluorinated monomers with more complex architectures is under investigation.<sup>14-16</sup>

## EXPERIMENTAL

### Materials

Cu wire (20 gauge or 0.812 mm diameter, from Fisher), TFE (SynQuest Laboratories), and hydrazine hydrate (100%, hydrazine 64%, Acros) used for the activation of Cu wire were used as received. Tosyl chloride (99%, Aldrich) was recrystallized twice from hexane. The semifluorinated monomers, 1H,1H,2H,2H-perfluorooctyl acrylate (SynQuest Laboratories), 1H,1H,5H-octafluoropentyl methacrylate (SynQuest Laboratories), 1H,1H,5H-octafluoropentyl acrylate (SynQuest Laboratories), and 2,2,3,3,4,4,4-heptafluorobutyl acrylate (Acros), were used for polymerization without removal of the radical inhibitor.<sup>98</sup> Hexamethylated *tris*(2-aminoethyl)amine (Me<sub>6</sub>-TREN) was synthesized as described in the literature.<sup>99</sup> Copper (0) wire (20 gauge wire, 0.812 mm diameter from Fischer) was activated with hydrazine hydrate according to a procedure elaborated in our laboratory.<sup>62</sup>

## Techniques

500 MHz  $^1\text{H}$ -NMR spectra were recorded on a Bruker DRX500 NMR instrument at 20 °C in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard. Gel Permeation Chromatography (GPC) analysis was performed on a Perkin-Elmer Series 10 high-performance liquid chromatograph, equipped with an LC-100 column oven maintained at 30°C, a Nelson Analytical 900 Series integration data station, a Perkin-Elmer 785 UV-vis detector (254 nm) and two AM gel columns (500 Å, 5  $\mu\text{m}$ ; and 1000 Å, 5  $\mu\text{m}$ ). HPLC grade THF (Fisher) was used as eluent at a flow rate of 1 mL/min. The relative number-average molecular weight,  $M_n$  (relative to PMMA standards by GPC) and molecular weight distribution ( $M_w/M_n$ ) were determined with poly(methyl methacrylate) (PMMA) standards purchased from American Polymer Standards. Prior to GPC analysis, the polymer product was purified by dissolving it in THF and passing through a short column of basic alumina to remove any residual  $\text{CuBr}_2$  deactivator.

## Typical Procedure for the Disproportionation Experiments

Disproportionation experiments were performed in a 3.5 mL volume Starna UV-vis quartz cuvette with airtight screw cap fitting. The glovebox was an Innovative Technology Inc. model operating under a nitrogen atmosphere, deoxygenated with a copper catalyst and with moisture level ideally maintained below 25 ppm. Photographs were taken with a digital camera using a white background. UV-vis spectra were recorded on a Shimadzu 1601 spectrometer with Shimadzu UV-Probe software. A microsyringe was kept in the glovebox to handle the ligand.  $\text{CuBr}$  (4.3 mg, 0.03 mmol) was measured into a UV cuvette and carefully transferred into the glovebox. Ligand  $\text{Me}_6\text{-TREN}$ , acetic acid, TFE were deoxygenated by three freeze pump thaw cycles and transferred into the glovebox. Inside the glovebox, 1.8 mL of solvent was delivered into the cuvette containing  $\text{CuBr}$  using a disposable 3 mL plastic syringe, followed by the addition of the required amount of acetic acid for  $\text{Me}_6\text{-TREN}$  /acetic acid = 1/1 to 1/3 ratios. Subsequently, 8  $\mu\text{L}$  of  $\text{Me}_6\text{-TREN}$  (6.8 mg, 0.03 mmol)

was added to the cuvette to achieve  $[\text{CuBr}] = [\text{Me}_6\text{-TREN}] = 16.5 \text{ mM}$ . The cuvette was sealed with an airtight screw cap, shaken and removed from the glovebox for further studies.

### Typical Procedure for Polymerization Kinetics

A stock solution of  $\text{CuBr}_2$  in MeOH was prepared by dissolving 16.84 mg (0.075 mmol) of  $\text{CuBr}_2$  in 0.2 mL of MeOH. In a 25 mL Schlenk tube 5.77  $\mu\text{L}$  of  $\text{Me}_6\text{-TREN}$ , 11.40  $\mu\text{L}$  of  $\text{CuBr}_2$  stock solution, and 2.96  $\mu\text{L}$  of acetic acid was added. Subsequently, the monomer (OFPA, 0.5 mL, 2.59 mmol), 0.5 mL of BPE (28.55 mg, 0.086 mmol), and solvent (0.50 mL TFE) were added to the Schlenk tube. The reaction mixture was thereafter degassed by 6 freeze-pump-thaw cycles. After the 6<sup>th</sup> cycle, hydrazine-activated Cu(0) catalyst (12.5 cm of gauge 20 wire, wrapped around a Teflon-coated stirrer bar) was dropped into the Schlenk tube under positive pressure of Ar and the Schlenk tube was placed in an oil bath thermostated at the desired temperature (25°C) with stirring. The side arm of the tube was purged with nitrogen before it was opened for samples to be removed at predetermined times, with an airtight syringe. Samples were dissolved in acetone- $d_6$ , and the conversion was measured by  $^1\text{H}$  NMR spectroscopy. This solution was then passed through a small basic  $\text{Al}_2\text{O}_3$  chromatographic column to remove any residual nascent Cu(0) catalyst and Cu(II) deactivator before it was analyzed by GPC with a Perkin-Elmer 785 UV-vis detector (254 nm) for  $M_n$  and  $M_w/M_n$  determination.

### Functionalization of poly(OFPA) via Thio-Bromo “Click” Reaction

In a 6 mL vial, thiophenol (16.62  $\mu\text{L}$ , 0.16 mmol) and distilled triethylamine ( $\text{NEt}_3$ ) (21.60  $\mu\text{L}$ , 0.16 mmol) were added to a solution of poly(OFPA) with  $M_n$  (relative to PMMA standards by GPC) = 7,752,  $M_w/M_n = 1.20$  (0.223 g, 0.029 mmol) in 3 mL MeCN. The reaction mixture was stirred at 25 °C for 3 h, and the polymer was precipitated several times (two to four times) in 10 mL cold methanol with 5% for complete removal of residual thiophenol. After decantation of methanol, the final polymer was transferred to a pre-weighed vial and dried under high vacuum to constant weight.

### MALDI-TOF Analysis of Poly(OFPA)

MALDI-TOF analysis of poly(OFPA) was performed on a Voyager DE (Applied Biosystems) instrument with a 337 nm nitrogen laser (3 ns pulse width). For all polymers, the accelerating potential was 25 kV, the grid was 92.5, the laser power was 1950, and a positive ionization mode was used. The sample analysis was performed with 2-(4-hydroxyphenylazo)benzoic acid as the matrix. Solutions of the matrix (25 mg/mL in THF), NaCl (2 mg/mL in deionized H<sub>2</sub>O), and polymer (10 mg/mL) were prepared separately. The solution for MALDI-TOF analysis was obtained by mixing the matrix, polymer, and salt solutions in a 5/1/1 volumetric ratio. Then, 0.5  $\mu$ L portions of the mixture were deposited onto three wells of sample plate and dried in air at room temperature before subjected to MALDI-TOF analysis.

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For the first time SET-LRP of 1H,1H,2H,2H-perfluorooctyl acrylate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, 1H,1H,5H-octafluoropentyl acrylate and 1H,1H,5H-octafluoropentyl methacrylate by SET-LRP in 2,2,2-trifluoroethanol as solvent at 25 °C for acrylates and at 50 °C for methacrylate was accomplished.

### Graphical Abstract

