### Synthesis and Characterization of Novel Alternating Fluorinated Copolymers Bearing Oligo(ethylene oxide) Side Chains

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**ABSTRACT:** The synthesis and characterization of novel poly (CTFE-*g*-oligoEO) graft copolymers [chlorotrifluoroethylene (CTFE) and ethylene oxide (EO)] are presented. First, vinyl ether monomers bearing oligo(EO) were prepared by transe-therification of  $\omega$ -hydroxyoligo(EO) with ethyl vinyl ether catalyzed by a palladium complex in 70–84% yields. Two vinyl ethers of different molecular weights (three and 10 EO units) were thus obtained. Then, radical copolymerization of the above vinyl ethers with CTFE led to alternating poly(CTFE-*alt*-VE) copolymers that bore oligo(OE) side chains in satisfactory yields (65%). These original poly(CTFE-*g*-oligoEO) graft copolymers were characterized by <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR spectroscopy. Their molecular weights reached 19,000 g mol<sup>-1</sup>, and their thermal properties were investigated while their

**INTRODUCTION** Fluoropolymers exhibit remarkable properties,<sup>1-5</sup> such as chemical resistance (to acids, bases, and organic solvents), thermostability, low dielectric constants and dissipation factors, hydrophobic and oleophobic properties, excellent weathering, and interesting surface properties. Hence, these high added value materials have found specific applications in many fields of high technology (aerospace, aeronautics, automotive, and electronic industries). Most fluorinated (co)polymers are synthesized by radical (co)polymerization. Actually alternating copolymers are scarce, except E-TFE, E-CTFE, and poly(VDF-alt-HFiB) copolymers [ethylene (E), tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), vinylidene fluoride (VDF), and hexafluoroisobutylene (HFiB)]. To our knowledge, creating hydrophilic fluoropolymers is a challenge,6-8 and it was of interest to synthesize novel fluorinated (co)polymers bearing oligo (ethylene oxide) grafts.

The development of new electrolytes endowed with good thermostability is still a major breakthrough.<sup>9-12</sup> Electrolytes based on poly(ethylene oxide) (PEO) derivatives or analogs<sup>13-19</sup> have good conducting properties for lithium ion

glass transition temperatures ranged between -42 and -36 °C. Their thermogravimetric analyses under air showed decomposition temperatures of 270 °C with 10% weight loss ( $T_{d,10\%}$ ). These novel copolymers are of potential interest as polymer electrolytes in lithium ion batteries, showing room temperature conductivities ranging from 4.49  $\times$  10<sup>-7</sup> to 1.45  $\times$  10<sup>-6</sup> S cm<sup>-1</sup> for unplasticized material. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 977–986

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batteries, especially with plasticizers. PEO is capable of complexing the lithium salts and facilitating the transport of  ${\rm Li}^+$  cations while maintaining an excellent interfacial stability.

Among these polymer electrolytes, fluorinated polymers based on PEO are an attractive option since the fluorinated units introduce properties such as thermostability, chemical stability, and desirable mechanical properties. Several authors have prepared blends of poly(vinylidene fluoride) (PVDF) with PEO<sup>20</sup> or PEO-*b*-PMMA<sup>21</sup> diblock copolymers [poly(methyl methacrylate) (PMMA)] in the presence of dibutyl phthalates in 7/3/10 w/w proportions.

Cui et al.<sup>22</sup> reported blends of PEO with other homopolymers or copolymers based on PEO and poly(propylene oxide) (PPO). (Semi-)Interpenetrated networks prepared by photopolymerization of blends of PVDF with dimethacrylate derivatives containing PEO units have shown promising conductivity values ( $1.5 \times 10^{-3} \text{ S cm}^{-1}$ ).<sup>23,24</sup> Other authors prepared some PVDF-*g*-PEO graft copolymers from PVDF activated by ozone,  $\gamma$ -ray, or <sup>60</sup>Co irradiation.<sup>25</sup> Chen et al.<sup>26</sup> prepared a novel PVDF-*g*-PMMA graft copolymer that was further chemically changed by transesterification with

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PEO-OH leading to PVDF-*g*-PEOM [PEO-methacrylate (PEOM)]. Furthermore, a team from MIT<sup>27</sup> achieved the same graft copolymer by atom transfer polymerization (ATRP) of PEOM ( $M_n = 475 \text{ g mol}^{-1}$ ) using PVDF as the macroinitiator in the presence of CuCl complexed by *N*,*N*,*N'*,*N''*,*N'''*-pentamethyldiethylene triamine. The same approach was reported by a Korean team<sup>28</sup> but from poly(VDF-*co*-CTFE) copolymer (CTFE) using a direct initiation on the C—Cl bonds to yield poly(VDF-*co*-CTFE)-*g*-PEOM graft copolymers. The major drawback of the ATRP method is the difficulty in eliminating all copper ions, which can inhibit the transport of lithium ions resulting in lower battery performances.

Although there are numerous reports on the synthesis and use of PVDF-*g*-PEO graft copolymers, to the best of our knowledge, there is only one patent that disclosed the preparation of fluorinated copolymers based on CTFE bearing PEO side-chains.<sup>29</sup> Actually, such PCTFE-*g*-PEO graft copolymers are of interest since they exhibit good thermal properties, good chemical inertness, and are stable at low and high electrochemical potentials, thus fulfilling the requirements for Li-ion battery electrolytes.

We chose  $\text{CTFE}^{30}$  as the fluoroolefin because it is an electron-acceptor monomer that is known to yield alternating copolymers with vinyl ethers via an "acceptor-donor" copolymerization.<sup>4,31</sup> This peculiarity arises from the electron-accepting character of the fluorinated olefins (CTFE: e = 1.56<sup>32,33</sup>, and the electron-donating character of the vinyl ether (-2.0 < e < -1.5).<sup>34-36</sup> Furthermore, vinyl ethers do not homopolymerize by radical polymerization.<sup>37,38</sup> The poly(CTFE-alt-VE) copolymers<sup>39–57</sup> exhibit interesting properties arising from the 50 mol % of fluorinated units<sup>3,4</sup> (thermostability, film-forming, hydrophobicity, oleophobicity, chemical inertness, mechanical properties, and electrochemical stability) and the other 50 mol % of the vinyl ether brings the complementary properties (solubility, crosslinking, hydrophilicity, softness, adhesion to metal, and affinity with the lithium anions).<sup>31,35,36,49,50,57</sup> Thus, these are copolymers endowed with good thermal and chemical stability and with excellent mechanical properties.

Several authors have reported the radical copolymerization of vinyl ethers that bear PEO chains  $(H_2C=CH-O-PEO)^{58-61}$  but none of them have been used conjointly with a fluorinated olefin to prepare either oligomers or copolymers having a fluorinated backbone and PEO side chains (especially those of CTFE<sup>31</sup>).

The objective of this work concerns the synthesis of novel fluorinated copolymers obtained by radical copolymerization of commercially available fluoroolefin (CTFE) with vinyl ether macromonomers bearing oligo(EO) side chains. Such vinyl ethers were obtained by transetherification of ethyl vinyl ether with oligo(ethylene glycol) monomethyl ether (n = 3 or 10) catalyzed by a palladium(II) complex. Such macromonomers with different molecular weights (PEO of 300 or 500 g mol<sup>-1</sup>) were prepared leading to copolymers with different morphologies, glass transition temperatures, and melting temperatures.

### EXPERIMENTAL

### Materials

Tert-butylperoxypivalate (TBPPI) was provided by Akzo Nobel (Compiègne, France). CTFE, PCTFE (for Fig. 5), and 1,1,1,3,3-pentafluorobutane  $(C_4F_5H_5)$  were provided by Honeywell and Solvay S.A. (Tavaux, France and Bruxelles, Belgium) and were used as received. Ethyl vinyl ether, palladium acetate, triethylene glycol monomethyl ether, poly (ethylene glycol) monomethyl ether ( $DP_n = 10$ ), 1,10phenanthroline, sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), potassium carbonate  $(K_2CO_3)$ , acetone (analytical grade), dichloromethane (DCM, analytical grade), methanol (analytical grade), and tetrahydrofuran (THF, analytical grade) were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Deuterated solvents for NMR spectroscopy were purchased from Euroiso-top (Grenoble, France) (purity > 99.8%). Lithium trifluoromethanesulfonate (triflate) was purchased from Sigma-Aldrich (Milwaukee).

### Characterization

### Nuclear Magnetic Resonance

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 400 instrument, using deuterated chloroform,  $d_6$ -N,N-dimethylsulfoxide, and  $d_6$ -acetone as the solvents and tetramethylsilane (TMS) (or CFCl<sub>3</sub>) as the references for <sup>1</sup>H (or <sup>19</sup>F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording <sup>1</sup>H, <sup>13</sup>C, (or <sup>19</sup>F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 512), and a pulse width of 5 µs for <sup>19</sup>F NMR.

### Size Exclusion Chromatography

Size exclusion chromatograms (SEC) were recorded using a GPC 50 from Polymer Labs (Now Varian) with its corresponding software (Cirrus). The system used 2 PL Gel Mixed C columns ( $200 < M_w < 20,000,000 \text{ g mol}^{-1}$ ) with tetrahydrofuran as the eluent with a flow rate of 1.0 mL min<sup>-1</sup> at room temperature. Both RI and UV detectors can be used. Polystyrene standards were used for the calibration. Sample concentration was 1 wt %. Analyses were achieved by injection of 20 µL of 20 µm filtered polymer solution (5 mg mL<sup>-1</sup>).

#### Thermogravimetric analyses

Thermogravimetric analyses (TGA) were performed with a TGA Q50 apparatus from TA Instruments, under air, at a heating rate of 10 °C min<sup>-1</sup> from room temperature up to a maximum of 550 °C. The sample weight varied between 10 and 15 mg.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analyses were carried out with a Netzsch 200F3 DSC apparatus equipped with Proteus software under nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup>. The temperature range was from -100 to +200 °C. The DSC system was first calibrated using indium and *n*-hexane standards. The second run led to the  $T_g$ 

values assessed from the inflection point in the heat capacity jump. The sample weight was about 10 mg.

### **Elemental analyses**

Weight percentages of carbon, fluorine, chlorine, and hydrogen atoms were assessed by elemental analysis (EA) at the CNRS, Service Central d'Analyse (Solaize, France) on a CH elemental analyzer equipped with a  $CO_2/H_2O$  infrared detector. Polymer compositions were calculated using equations:

$$\frac{\%H}{\%C} = \frac{(6+4n)q}{24p+(36+24n)q}$$
$$\frac{\%F}{\%C} = \frac{57p}{24p+(36+24n)q}$$
$$p+q = 1$$

where *p*, *q*, and *n* are the percentages of fluoroolefin, of vinyl ether, and number of ethyleneoxy groups in PEO (n = 3 or 10), respectively.

### Conductivity Assessments

Before conductivity assessment, each polymer was further purified by dialysis versus THF (3 days) followed by dialysis versus dichloromethane (DCM) (3 days) using Spectra/Por regenerated cellulose membranes with a molecular weight cutoff of 1000. Ionic conductivity was measured by electrochemical impedance spectroscopy using a Solartron 1260 impedance analyzer and a custom-built two electrode-cell with platinum electrodes. The temperature of each sample was controlled during analysis by a temperature-regulated oven. Each reported value is the average of five measurements.

Electrolyte samples were prepared by dissolving both the polymer and lithium triflate in acetone. The acetone was then evaporated, and each sample was thoroughly dried by lyophilization. The ratio of lithium triflate to polymer was held constant at 0.235 lithium ions per repeating unit of polymer. An additional sample of poly(CTFE-*alt*-PEOVE10) was prepared to contain the same ratio of oxygen atoms to lithium ions as the sample of poly(CTFE-*alt*-PEOVE3) with 0.235 Li<sup>+</sup> per repeating unit (17.0 O/Li<sup>+</sup>). Control samples consisted of the pure polymer without any lithium triflate.

#### **Synthesis**

### Synthesis of Methoxy-tri(ethylene oxide) Vinyl Ether (PEOVE3)

In a Schlenk flask under inert atmosphere, palladium acetate (380 mg, 1.69 mmol) was dissolved in DCM (10 mL). A solution of 1,10-phenanthroline (458 mg, 2.54 mmol) in DCM (10 mL) was then added into the Schlenk. The reaction medium was further stirred at room temperature for 30 min to generate the palladium catalyst *in situ*. A triethylene glycol monomethyl ether solution (13.90 g, 0.0847 mol) and ethyl vinyl ether (36.66 g, 0.50 mol) were added to the reaction medium, which was then transferred into an autoclave and heated at 60 °C for 24 h. After cooling, the autoclave was opened and both DCM and ethyl vinyl ether were evaporated under vacuum. The remaining product was dissolved in 100 mL of deionized water. The mixture was extracted three

times with 100 mL of dichloromethane. The organic phase was dried with sodium sulfate, filtered, and the dichloromethane evaporated. The final product is a yellow liquid obtained in 84% yield.

# Synthesis of Methoxypoly(ethylene oxide) Vinyl Ether (PEOVE10)

The experimental procedure and purification were similar as that of methoxy-tri(ethylene oxide) vinyl ether PEOVE3. Palladium acetate (448 mg, 2.0 mmol), dichloromethane (25 mL), 1,10-phenanthroline (540 mg, 3.0 mmol), poly(ethylene glycol) monomethyl ether, (20.00 g, 0.04 mol), and ethyl vinyl ether (17.3 g, 0.24 mol) were introduced in the autoclave. The reaction was carried out at 60 °C for 24 h. The purification procedure was similar to that used above for PEOVE3. The final product was a yellow liquid obtained in 71% yield.

## Radical Copolymerization of Chlorotrifluoroethylene with Vinyl Ethers

The radical copolymerizations were performed in a 160-mL Hastelloy Parr autoclave system (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves. An electronic device regulated and controlled both the stirring and heating of the autoclave. Before reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then conditioned for the reaction with vacuum  $(10^{-2} \text{ mbar})$  for 40 min to remove any trace of oxygen. The liquids and dissolved solids were introduced via a funnel and then the gas (CTFE) was introduced by double weighing (i.e., the difference of weight before and after filling the autoclave with the gas).

### Copolymerization of PEOVE3 with chlorotrifluoroethylene

To prevent any homopolymerization of the vinyl ether by acid catalysis (i.e., cationic initiation) and the formation of the acetal from the vinyl ether, potassium carbonate (161 mg, 1.16 mmol) was introduced in the reaction prior to conditioning. PEOVE3 (7.30 g, 0.0338 mol), tert-butyl peroxypivalate (TBPPi; 1.80 g, 7.76 mmol), and 50 mL of 1,1,1,3,3pentafluorobutane were inserted via a tight funnel. CTFE (13.5 g, 0.116 mol) was then introduced by double weighing. The copolymerization was carried out at 74 °C for 15 h. First, an increase of pressure was noted due to the exothermicity of this reaction. Then, a pressure drop was observed correlated to the consumption of the CTFE during the polymerization. After the polymerization, the reactor was cooled in an ice bath for 30 min and then degassed. No gas was released meaning a high gas conversion (though CTFE has a good solubility in the 1,1,1,3,3-pentafluorobutane). The reaction mixture was dissolved in acetone and then precipitated from pentane to eliminate any residual solvent, monomer, potassium carbonate, initiator, and oligomers. The product was dried under vacuum at 50 °C until constant weight yielding 12.6 g of a red gum (5) (yield = 61%).

### *Copolymerization of PEOVE10 with Chlorotrifluoroethylene* The experimental procedure was similar as that of the radical copolymerization of CTFE with vinyl ether **PEOVE3**.





**SCHEME 1** Preparation of vinyl ethers bearing oligo(ethylene oxide) (PEO) chains (PEOVE (n = 3 or 10) and their radical copolymerization with chlorotrifluoroethylene (CTFE).

Potassium carbonate (138 mg, 1 mmol), **PEOVE10** (20.41 g, 0.0388 mol), TBPPi (1.80 g, 7.76 mmol), 50 mL of 1,1,1,3,3pentafluorobutane, and CTFE (13.5 g, 0.116 mol) were introduced in the autoclave. The copolymerization was carried out at 74 °C for 15 h. Similar increase and drop of pressure were observed. Similar postcopolymerization procedure, work-up, and purification were also carried out. The copolymerization yielded 15.1 g of a red gum after precipitation (**6**) (yield = 68%).

#### **RESULTS AND DISCUSSION**

The synthesis of the PEO-bearing vinyl ether (PEOVEn, where n corresponds to the number of ethylene oxide units in the PEO chain) and their radical copolymerization with CTFE were carried out according to Scheme 1.

### **Preparation of the Macromonomer**

Our goal was to prepare liquid vinyl ether monomers bearing PEO chain from poly(ethylene glycol) monomethyl ether (PEGMe) (Scheme 1). Four main synthetic pathways have been reported for the chemical modification of an alcohol with a functional vinyl ether: addition onto acetylene,62 phase transfer catalysis based on a Williamson reaction (between an alcoholate and 2-chloroethyl vinyl ether),<sup>63-65</sup> the modification of vinyl acetate in the presence of an iridium complex,<sup>66</sup> and transetherification.<sup>63,67-72</sup> This latter strategy has been extensively studied in the presence of either mercuric acetate or palladium acetate, especially by Watanabe and Conlon,<sup>67</sup> Mc Keon,<sup>73</sup> and Boutevin and Youssef.<sup>63</sup> This last study even compared the transetherification with the Williamson reaction. More recently, Pichavant<sup>74</sup> reported the synthesis of a vinyl ether by transetherification catalyzed by a palladium (II) complex in the presence of ethyl vinyl ether in dichloromethane.

Recently, we synthesized novel vinyl ethers bearing lateral chloromethyl<sup>49</sup> or carbonate groups<sup>50,57</sup> by transetherification catalyzed by a palladium (II) complex generated *in situ*. Reactions were carried out in dichloromethane in the presence of 2% of palladium (II) acetate catalyst and 1,10

phenanthroline (as the ligand) at 60 °C. Using these optimized parameters,  $^{49,50}$  PEOVE3 and PEOVE10 monomers were prepared by transetherification of ethyl vinyl ether and PEOMe (Scheme 1). The reaction was carried out in the presence of dichloromethane at 60 °C in an autoclave yielding both macromonomers in 84 and 71 mol % yield, respectively.

PEOVEn (n = 3 or 10) macromonomers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Both <sup>1</sup>H NMR spectra (Fig. 1) in CDCl<sub>3</sub> at 20 °C displays the two nonequivalent protons CH<sub>a</sub>H<sub>b</sub> of the vinyl group as two doublets of doublets at 4.11 and 3.93 ppm for PEOVE3 and PEOVE10. The doublet of doublets assigned to the terminal methyne proton (=CH–) of the vinyl ether is located at 6.41 ppm. The same observation can be noted for the methylene group of the PEO ( $\delta$  = 3.70 ppm). The singlet assigned to the methoxy group of PEOMe is located at 3.30 ppm for PEOVE3 and PEOVE10.

## Radical Copolymerization of PEOVEn with Chlorotrifluoroethylene

The radical copolymerizations were carried out in an autoclave, in the presence of *tert*-butylperoxypivalate (TBPPi 5 mol % compared to monomers) and 1,1,1,3,3-pentafluorobutane at 74 °C, as the initiator and solvent, respectively (Scheme 1). The amount of initiator (5 mol %) may be considered high compared to the usual conditions (< 1 mol %), but for the intended use (polymer electrolyte for lithium batteries) low-molecular-weight polymers are highly desirable, and thus a high quantity of initiator was required.

A small amount of potassium carbonate ( $K_2CO_3$ ) was added into the polymerization media to prevent from both the cationic homopolymerization and the formation of acetal from vinyl ether.<sup>75</sup> CTFE was used in slight excess to enable the complete consumption of the vinyl ether.

The radical copolymerization of CTFE with vinyl ether is an exothermic reaction, and a rapid increase of pressure in the autoclave was observed (12 bar), followed by a sharp drop of pressure (3 bar). Such a copolymerization is called "acceptor-donor copolymerization" and yields alternating



FIGURE 1 <sup>1</sup>H NMR spectra of PEOVE3 (lower spectrum) and PEOVE10 (upper spectrum) recorded in CDCl<sub>3</sub> at room temperature.

copolymers. Poly(CTFE-*alt*-PEOVEn) copolymers were obtained and their characteristics are listed in Table 1.

When using *t*-butylperoxypivalate (5 mol % with respect to monomers) as the initiator at 75 °C, the yield of polymerization after precipitation ranged between 61 and 68%. This is a satisfactory value compared to those of the literature for the radical copolymerization of CTFE with VE in solution that ranges between 47 and 88%.<sup>31,35,36</sup> The obtained copolymers were isolated by precipitation from pentane yielding red to brown very viscous liquids soluble in polar solvents (acetone, DMF, DMSO, and THF), while PCTFE was not soluble in such solvents. Both copolymers were characterized by <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR spectroscopy, size exclusion chromatography (SEC) and elemental analysis. SEC showed that the molar masses of the poly(CTFE-*alt*-PEOVE) copolymers ranged from 13,700 to 19,000 g mol<sup>-1</sup> (compared to PS standards) and present typical polydispersity

indices for such a copolymerization ( $1.70 < M_w/M_n < 2.48$ ). <sup>1</sup>H NMR spectra (Fig. 2) of poly(CTFE-*alt*-PEOVEx) exhibit the absence of signals centered at 6.41 ppm characteristic of unreacted VE vinylic protons. However, their polymerized equivalent  $-CH_2-CH(PEOMe)$  can be found between 2.5 and 3.0 ppm, and between 4.5 and 5.0 ppm for the methylene and methyne protons, respectively. Both signals are complete and spread due to the presence of two types of asymmetric carbons leading to two diastereoisomers, which makes these protons nonequivalent (anisochronous). Methylenic protons of the PEO chain ( $-OCH_2-$ ) are similar in both polymers and are located at 3.65 ppm, while the protons adjacent to the oxygen from the vinyl ether are located at 3.93 ppm. However, the methoxy protons can be found at about 3.30 ppm.

Furthermore, the <sup>19</sup>F NMR spectra of the poly(CTFE-*alt*-PEOVE) copolymers (Fig. 3) do not exhibit the characteristic signal at

TABLE 1 Radical Copolymerization of PEOVE3 and	I PEOVE10 with	Chlorotrifluoroethylene	e (CTFE
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	Monomer Feed Ratio (%) <sup>a</sup>		Copolymer Composition (%) <sup>b</sup>			M C	
Entries	CTFE	PEOVE	Yield (%)	CTFE	PEOVE	(g mol <sup>-1</sup> )	$M_{\rm w}/M_{\rm n}^{\rm c}$
1	65	PEOVE3 (35)	61	53	47	13,700	2.4
2	65	PEOVE10 (35)	68	49	51	19,000	1.7

<sup>a</sup> Polymerization conditions: *t*-butylperoxypivalate (5 mol %), Solvent: 1,1,1,3,3-pentafluorobutane, potassium carbonate (3 mol %), T = 74 °C for 14 h. Products characterized after precipitation in pentane.

<sup>b</sup> Copolymer composition was assessed from elemental analyses. <sup>c</sup> Molar masses and polydispersity assessed from SEC calibrated with polystyrene standards.





**FIGURE 2** <sup>1</sup>H NMR spectra of poly(CTFE-*alt*-PEOVE3) (lower spectrum) and poly(CTFE-*alt*-PEOVE10) (upper spectrum) recorded in acetone- $d_6$  at room temperature.

-127 ppm of the CTFE-CTFE dyads, that is, the central CFCl in  $-CF_2CFCl-CF_2CFCl-.^{52,57,76}$  This is evidence that these copolymers have an alternating - [CF<sub>2</sub>CFCl-CH<sub>2</sub>CH(O-PEGMe)]<sub>n</sub>-structure. However, these spectra showed that the chemical shifts assigned to the CTFE units are independent of the PEOMe chain length. Signals ranging between -107.0 and -123.1 ppm,<sup>53</sup> and the signal centered at -124.4 ppm were assigned

to the  $-CF_2$ - and -CFCl- of both A and B diastereoisomers, respectively, as depicted in Figure 3.

Unlike other poly(fluoroalkene-*co*-vinyl ether) copolymers,<sup>31</sup> these new poly(CTFE-*alt*-PEOVE) copolymers were also characterized by DEPT <sup>13</sup>C NMR spectroscopy (Fig. 4). The spectra show that all the signals assigned to the carbons



**FIGURE 3**<sup>19</sup>F NMR spectrum of poly(CTFE-*alt*-PEOVE3) recorded in acetone-*d*<sub>6</sub> at room temperature.



**FIGURE 4** <sup>13</sup>C NMR spectra of poly(CTFE-*alt*-PEOVE3) (lower spectrum) and poly(CTFE-*alt*-PEOVE10) (upper spectrum) recorded in acetone- $d_6$  at room temperature.

from either CTFE or the vinyl ether and are not much affected by the PEOMe chain length (3 or 10 units). Several signals assigned to the CTFE units were observed at 121.05, 118.57, 115.94, 113.81, 111.80, and 109.97 ppm (n = 3) or, 121.04, 118.31, 115.42, 113.60, 111.40, and 109.40 (x =10). The signals assigned to the methylene in the -CH<sub>2</sub>-CH(PEOMe)- group of the vinyl ether units are located at 38.93 (n = 3) or 39.18 ppm (n = 10). The two signals either at 78.73 and 75.75 ppm (n = 3) or 78.56 and 75.75 (n = 10) resulting from both diastereoisomers were assigned to the asymmetric carbon atom in -CH<sub>2</sub>-C\*H(PEGMe)-. These tertiary carbon atoms induced negative signals in DEPT <sup>13</sup>C NMR spectra. The -O-CH<sub>2</sub>adjacent to the backbone and the methoxy carbon  $(-OCH_3)$ are located at 72.41 and 58.79 ppm, or 72.81 and 58.94 ppm for copolymers having n = 3 and 10, respectively. The carbon atoms of the PEOMe chains are located between 70.41 and 74.07, or 69.90 and 73.62 ppm for n = 3 and 10, respectively.

Thermal properties of these copolymers were assessed by TGA and DSC. Figure 5 represents the TGA thermograms for both poly(CTFE-*alt*-PEOVE3) and poly(CTFE-*alt*-PEOVE10) copolymers, and PCTFE under air. Only one main degradation was observed and the decomposition temperatures at 5 and 10 percent weight loss were different in both copoly-

mers: poly(CTFE-alt-PEOVE3) degradation initiated at about 215 °C while that of poly(CTFE-alt-PEOVE10) copolymer started from at 267 °C and lasted up to 540 °C in both cases. This difference was attributed to the increased thermostability with increasing PEO chain length. Though PCTFE displays a very high thermostability, that of both these copolymers can be regarded as fair to satisfactory as explained by the good chemical and thermal stability of the CTFE units (the degradation of which begins at about 300 °C) compensating for the poor thermal stability of the VE units (that usually occurs as soon as 150 °C).77,78 A more detailed analysis of the TGA thermograms provides evidence of two main decompositions: Although the TGA experiments did not clearly evaluate the durability of these polymers at a given temperature, we can consider that in the operating temperature range for the lithium-ion batteries (-30 to +150 °C), these polymers should not degrade.

Such a huge difference with the thermostability of PCTFE may also confirm the alternated character of these copolymers. DSC analyses (Table 2) of the poly(CTFE-*alt*-PEOVEx) copolymers demonstrate both the decrease of the glass transition temperature with increasing PEO content (i.e., chain length) and the absence of melting temperature due to the amorphous character of these copolymers.<sup>79,80</sup> Actually, the presence of the ether groups in PEO induces lower  $T_{\rm g}$ . The





**FIGURE 5** TGA thermograms obtained under air at 10 °C min<sup>-1</sup> for both poly(CTFE-*alt*-PEOVEx) copolymers (n = 3 and 10) and PCTFE (dotted line).

thermal properties of these copolymers contrast with the high  $T_{\rm g}$  (ca. 55–70 °C) and melting point ( $T_{\rm m} = 214-220$  °C) of PCTFE,<sup>30</sup> which is a semicrystalline homopolymer. These alternating poly(CTFE-*al*-VE) copolymers do not contain any oligo(CTFE) sequences that would allow any crystallization.<sup>30</sup>

These fluorinated elastomers have remarkable properties (good thermostability, low glass transition temperature, and amorphous character) fulfilling the requirements for polymer electrolytes in lithium-ion batteries.

### **Conductivities of these Copolymers**

Electrolyte samples were prepared using each of the copolymers by dissolving them in acetone along with lithium triflate. The amount of lithium in each sample was held constant at a ratio of 0.235 lithium ions per repeating unit (r.u.) of polymer. Ionic conductivity was measured as a function of temperature by electrochemical impedance analysis. Even at 30 °C, both copolymers are more than 60 °C above their  $T_{g}$ , and therefore, the electrolytes exhibit Arrhenius-type behavior (Fig. 6) in the temperature range studied (from 30 to 110 °C). The electrolyte prepared from poly(CTFE-*alt*-PEOVE3) copolymer showed the best room temperature conductivity of  $1.45 \times 10^{-6}$  S cm<sup>-1</sup>, while the electrolyte prepared from poly(CTFE-*alt*-PEOVE10) cooligomer had a slightly lower room temperature conductivity of  $8.92 \times 10^{-7}$  S cm<sup>-1</sup>. These conductivities are similar to the room temperature.

**TABLE 2** Glass Transition ( $T_g$ ) and DecompositionTemperatures ( $T_d$ ) of Poly(CTFE-*alt*-PEOVEn) CopolymersObtained by DSC and TGA under Air, Respectively

(Co)polymers	$T_{g}$ (°C)	<i>T</i> <sub>d,5%</sub> (°C)	<i>T</i> <sub>d,10%</sub> (°C)
poly(CTFE- <i>alt</i> -PEOVE3)	-36	160	215
poly(CTFE-alt-PEOVE10)	-42	247	269
PCTFE	55–70	420	435

ature conductivity of PEO homopolymer,  $1.3 \times 10^{-6}$  S cm<sup>-1</sup>, measured at an optimized lithium content of one lithium ion per 24 r.u.<sup>81</sup> The room temperature (30 °C) results are summarized in Table 3. When the electrolytes are compared using equal ratios of Li<sup>+</sup> per repeating unit, one might expect the electrolyte containing the longer PEO chains to have a higher conductivity. However, the conductivity is actually lower because the concentration of lithium ions is lower due to the added volume of the longer PEO chains.

An additional electrolyte sample containing the same ratio of oxygen atoms to  $Li^+$  as the previous electrolyte based on poly(CTFE-*alt*-PEOVE3) (17.0 O/Li<sup>+</sup>) was prepared from poly(CTFE-*alt*-PEOVE10). When the conductivity of the



**FIGURE 6** Arrhenius plots of the conductivity of poly(CTFE-*alt*-PEOVEn) copolymers-based electrolytes. Circles mark the electrolyte containing an equal Li<sup>+</sup>/repeating unit (r.u.) ratio, whereas triangles represent the electrolyte containing an equal O/Li<sup>+</sup> ratio. Each point represents the average of five measurements. All points have an error of less than 1.5%.

**TABLE 3** Conductivity Values of Poly(CTFE-*alt*-PEOVEn) Copolymer Electrolytes at 30 °C

Copolymers	Pure Polymer (S cm <sup>-1</sup> )	0.235 Li <sup>+</sup> /r.u. (S cm <sup>-1</sup> )	17.0 O/Li <sup>+</sup> (S cm <sup>-1</sup> )
poly(CTFE- <i>alt</i> - PEOVE3)	а	$1.45\times10^{-6}$	$1.45 \times 10^{-6}$
poly(CTFE- <i>alt</i> - PEOVE10)	$6.44 \times 10^{-7}$	$8.92\times10^{-7}$	$4.49\times10^{-7}$

<sup>a</sup> No conductivity could be detected for the pure polymer (r.u. stands for repeating unit).

electrolytes is compared in this way, the electrolyte with longer PEO chains is still less conductive. This lower conductivity is likely due to the greater number of transient crosslinks generated by interchain associations to Li<sup>+</sup>, which decrease the free volume of the electrolyte and thus hinder ion transport, or to the beginning of crystallite formation due to the packing of the longer PEO chains. Because of the relatively low conductivity of the unplasticized electrolytes, a suitably thermostable solvent should be chosen as plasticizer to produce gel-electrolytes, for actual device fabrication.

### CONCLUSIONS

Novel fluorinated copolymers were prepared by radical copolymerization of CTFE with vinyl ether macromonomers bearing oligo(EO) chains of various lengths. These oligo(EO) bearing vinyl ethers were prepared by transetherification of ethyl vinyl ether with  $\alpha$ -hydroxylated oligo(EO) catalyzed by a palladium complex. PEOVE3 and PEOVE10 macromonomers were obtained in good yield (70-84 mol %) and characterized by NMR. Acceptor-donor copolymerization of these PEOVEn (where *n* represents the number of EO units, n = 3or 10) with CTFE yielded alternating copolymers in 61-68% yields. Poly(CTFE-alt-PEOVE) copolymers were characterized by <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR, SEC, and their thermal properties were investigated (good thermostability, low  $T_{\rm g}$  and amorphous character). Electrolytes based on the fluoropolymers have room temperature ionic conductivities ranging from  $4.49\,\times\,10^{-7}$  to  $1.45\,\times\,10^{-6}$  S  $cm^{-1}$  due to the coordination of Li<sup>+</sup> by the PEO units. Such copolymers could be used in conjunction with a suitable plasticizer as polymer-gel electrolytes for lithium ion batteries intended for devices in which thermal stability is a concern.

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