Efficient method to synthesize vinyl ethers (VEs) that bear various halogenated or functional groups and their radical copolymerization with chlorotrifluoroethylene (CTFE) to yield functional poly(VE-alt-CTFE) alternated copolymers

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Experimental part
1. Synthesis of Vinyl ethers

Synthesis of 3-chloro-(2,2-dimethylpropyl) vinyl ether CMPVE (1)

In a 100 mL round-bottom flask, palladium acetate (1.09 g, 4.88 mmol) was dissolved in dichloromethane (25 mL). A solution of 1,10-phenanthroline (1.32 g, 7.43 mmol) in dichloromethane (10 mL) was then added into the round-bottom flask. The reaction medium was stirred at room temperature for 30 minutes to generate the palladium catalyst in situ. A 3-chloro-2,2-dimethyl-1-propanol solution (30.02 g, 0.22 mol) and ethyl vinyl ether (52.93 g, 0.73 mol) were added to the reaction medium that was then transferred into the autoclave and heated at 60 °C for 48 hrs. After cooling, the autoclave was opened and both dichloromethane and ethyl vinyl ether were evaporated under vacuum, while the resulting residue was distilled under vacuum. The final product (b.p = 90 °C/0.001 mmHg) is a colorless liquid obtained in 61% yield characterized by $^1$H (Figure 1) and $^{13}$C (Figure 2) NMR spectroscopy.
Synthesis of 3-chloro-2-chloromethyl-2-methyl-propyl vinyl ether CCMPVE (2)

The experimental procedure and purification are similar as these of vinyl ether (1). Palladium acetate (0.760 g, 3.39 mmol) was dissolved in dichloromethane (5 mL). A solution of 1,10-phenanthroline (0.950 g, 5.27 mmol) in dichloromethane (5 mL) was then added to the palladium. The reaction medium was stirred at room temperature for 15 minutes to generate the palladium catalyst in situ. Meanwhile, 2,2-bis(chloromethyl)propan-1-ol (5.00 g, 3.2 mmol) in dichloromethane (10 mL) and ethyl vinyl ether (16.35 g, 0.227 mol) were inserted into the autoclave. The catalyst solution was then added to the reaction medium, the autoclave was tightly closed and heated at 60 °C for 48 hrs. After cooling, the autoclave was opened and both dichloromethane and ethyl vinyl ether were evaporated, while the resulting residue obtained was distilled under vacuum. The final product (b.p = 100 °C/8 mbar) is a colorless liquid containing 84 % of the desired vinyl ether. The overall yield is 38% yield characterized by ³¹H NMR spectroscopy (Figure S1).

Figure S1: ¹H NMR spectrum of 3-chloro-2-chloromethyl-2-methyl-propyl vinyl ether (2) recorded in acetone d6.
Synthesis of 3-bromo, 2,2-bis(bromomethyl) propyl vinyl ether BBPVE (3)

The experimental procedure and purification are similar as these of vinyl ethers (1) and (2). Palladium acetate (0.69 g, 3.07 mmol), dichloromethane (25 mL), 1,10-phenanthroline (0.83 g, 4.61 mmol), 3-bromo-2,2-bis(bromomethyl)-1-propanol (20.00 g, 0.061 mol) and ethyl vinyl ether (44.39 g, 0.61 mol) were inserted in the autoclave. The reaction was carried out at 60 °C for 48 hrs. After cooling, the autoclave was opened and both dichloromethane and ethyl vinyl ether were evaporated, while the residue obtained was distilled under vacuum. The final product (b.p = 120 °C/0.001 mmHg) is a colorless liquid, obtained in 69% yield and characterized by $^1$H (Figure S2) NMR spectroscopy.

Figure S2: $^1$H NMR spectrum of (3-bromo, 2,2-bis(bromomethyl) propyl vinyl ether (3) recorded in CDCl₃.

Synthesis of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl vinyl ether FFPVE (4)
Palladium acetate (0.738 g, 3.28 mmol), dichloromethane (25 mL), 1,10-phenanthroline (0.88 g, 4.93 mmol), 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-1-pentanol (25.00 g, 0.109 mol) and ethyl vinyl ether (79.00 g, 1.09 mol) were inserted in the autoclave. The reaction was carried out at 60 °C for 48 hrs. After cooling, the autoclave was opened and both dichloromethane and ethyl vinyl ether were evaporated, while the residue obtained was distilled under vacuum. The final product (b.p = 80 °C/0.001 mmHg) is a colorless liquid, obtained in 41% yield and characterized by $^1$H (Figure S3) and $^{19}$F (Figure S4) NMR spectroscopy.

Figure S3: $^1$H NMR spectrum of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl vinyl ether FFPVE (4) in CDCl$_3$. 
Figure S4: $^{19}$F NMR spectrum of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl vinyl ether FFPVE (4) in CDCl$_3$.

**Synthesis of 3-dimethylamino-(2,2-dimethylpropyl) vinyl ether MMPVE (5)**

The protocol and purification were similar to those of vinyl ether (2). Palladium acetate (0.171 g, 0.762 mmol), dichloromethane (10 mL), 1,10-phenanthroline (0.206 g, 1.14 mmol), 3-dimethylamino-2,2-dimethylpropan-1-ol (10.00 g, 76.2 mmol) and ethyl vinyl ether (54.9 g, 0.762 mol) were inserted into the autoclave. The reaction was carried out at 60 °C for 48 hrs. The purification was similar as that used above for vinyl ethers (1-2). The final product (b.p = 40°C/10 mbar) is a colorless liquid containing 92 % of the desired vinyl ether, with an overall yield of 62 %, characterized by $^1$H (Figure S5) NMR spectroscopy.
**Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (GCVE) (6)**

Palladium acetate (760 mg, 3.38 mmol), dichloromethane (40 mL), 1,10-phenanthroline (916 mg, 5.08 mmol), glycerol carbonate (20.00 g, 0.169 mol) and ethyl vinyl ether (73.33 g, 1.01 mol) were introduced in the autoclave. The reaction was carried out at 60 °C for 48 hrs. After cooling, the autoclave was opened and both dichloromethane and ethyl vinyl ether were evaporated under vacuum. The remaining product was dissolved in 200 mL of deionized water. The mixture was extracted three times with 200 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 45% yield, and characterized by $^1$H (Figure S6) NMR spectroscopy.
**Synthesis of methoxy-tri(ethylene oxide) vinyl ether (PEOVE3) (7)**

Palladium acetate (380 mg, 1.69 mmol), 1,10-phenanthroline (458 mg, 2.54 mmol), dichloromethane (40 mL), triethylene glycol monomethyl ether (13.90 g, 0.0847 mol) and ethyl vinyl ether (36.66 g, 0.50 mol) were inserted into the autoclave. The reaction was carried out at 60 °C for 48 hrs. After cooling, the autoclave was opened and both dichloromethane and ethyl vinyl ether were evaporated under vacuum. The remaining product was dissolved in 100 mL of deionized water. The mixture is 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, and characterized by $^1$H (Figure S7) NMR spectroscopy.
Synthesis of methoxydeca(ethylene oxide) vinyl ether (PEOVE10) (8)

Palladium acetate (448 mg, 2.0 mmol), dichloromethane (25 mL), 1, 10-phenanthroline (540 mg, 3.0 mmol), deca(ethylene glycol) monomethyl ether, (20.00 g, 0.04 mol) and ethyl vinyl ether (17.3 g, 0.24 mol) were inserted into the autoclave. The reaction was carried out at 60 °C for 48 hrs. The purification procedure was similar as that used above for PEOVE3. The final product was a yellow liquid obtained in 71% yield, characterized by $^1$H (Figure S7) NMR spectroscopy.

Figure S7: $^1$H NMR spectra of PEOVE3 (7) (lower spectrum) and PEOVE10 (8) (upper spectrum) recorded in CDCl$_3$. 
Synthesis of oligo(fluoroether) vinyl ether (9)

Palladium acetate (0.48 g, 1.79 mmol), dichloromethane (25 mL), 1,10-phenanthroline (0.485 g, 2.69 mmol), PolyFox™ PF-7002 (30 g, 0.017 mol) and ethyl vinyl ether (25.9 g, 0.35 mol) were inserted in the autoclave. The reaction was carried out at 60 °C for 48 hrs. The purification was similar as that used above for vinyl ethers (1-8). The final product was a yellow liquid obtained in 55% yield, characterized by ¹H (Figure S8) and ¹⁹F (Figure S9) NMR spectroscopy.

Figure S8: ¹H NMR spectrum of oligo(fluoroether) vinyl ether (9) recorded in CDCl₃.
Synthesis of (p-methylchlorobenzyl) vinyl ether MCBVE (10)

Palladium acetate (0.35 g, 1.59 mmol), dichloromethane (25 mL), 1,10-phenanthroline (0.43 g, 2.39 mmol), 4-(chloromethyl) benzyl (5.00 g, 0.031 mol) and ethyl vinyl ether (23.02 g, 0.31 mol) were inserted into the autoclave. The reaction was carried out at 60 °C for 48 hrs. The purification is similar as that used above for vinyl ether (1-9). The final product (b.p = 105 °C, 0.001 mmHg) is a yellow liquid obtained in 81% yield, characterized by $^1$H (Figure S10) NMR spectroscopy.
Figure S10: $^1$H NMR spectrum of ($p$-methylchlorobenzyl) vinyl ether (10) recorded in CDCl$_3$.

Radical copolymerization of chlorotrifluoroethylene (CTFE) with Vinyl ethers (VEs)

Radical copolymerization of 3-chloro-(2,2-dimethylpropyl) vinyl ether (1) with chlorotrifluoroethylene

To prevent any cationic homopolymerization of the vinyl ether by acid catalysis and the formation of the acetal from the vinyl ether, potassium carbonate K$_2$CO$_3$ (0.228 mg, 1.65 mmol) was inserted in the reaction vessel prior conditioning. Vinyl ether (1) (8.19 g, 0.055 mol), tert-butylperoxypivalate (TBPPi) (0.213 g, 1.22 mmol), and 50 mL of 1,1,1,3,3-pentafluorobutane were introduced via a tight funnel. Chlorotrifluoroethylene (15 g, 0.128 mol) was then transferred by double weighing. The copolymerization was carried out at 74 °C for 8 hrs. First a pressure increase was noted due to the increasing temperature and exothermicity of this reaction, followed by a pressure drop correlated to the consumption of the CTFE during the polymerization. After the copolymerization, the reactor was cooled in an ice bath for 30 min and then degased. No gas was vented off meaning a quantitative gas conversion (though CTFE has a good solubility in the 1,1,1,3,3-pentafluorobutane). The reaction mixture was dissolved in acetone and precipitated from methanol to eliminate any residual solvent,
monomer, potassium carbonate, and initiator. The product was dried under vacuum at 50 °C until constant weight yielding 15 g of white powder (Yield = 66%), characterized by $^1$H (Figure 3), $^{19}$F (Figure S11) and $^{13}$C NMR (Figure S12) spectroscopy.

![Chemical structure](image)

Figure S11: $^{19}$F NMR spectrum of poly(CTFE-alt-VE1) (P1) copolymer (CDCl$_3$ at 20 °C, 400 MHz).
Figure S12: APT $^{13}$C NMR spectrum of poly(CTFE-alt-VE1) (P1) copolymer (CDCl$_3$ at 20 °C, 400 MHz).

Radical copolymerization 3-bromo-2,2-bis(bromomethyl)-propyl vinyl ether (3) with chlorotrifluoroethylene

The experimental procedure was similar to that of the radical copolymerization of CTFE with vinyl ethers (1) and (2). Potassium carbonate (177 mg, 1.28 mmol), vinyl ether (3) (15.06 g, 0.042 mol), tert-butylperoxypivalate (TBPPi) (0.59 g, 3.43 mmol), 50 mL of 1,1,1,3,3-pentafluorobutane, and CTFE (15 g, 0.128 mol) were transferred into the autoclave. The copolymerization was carried out at 74 °C for 8 hrs. Similar increase and drop of pressure were observed. Similar post-copolymerization purification was also carried out. The copolymerization yielded 19.8 g of a brown powder after precipitation and drying (yield = 66%), characterized by $^1$H (Figure S13), and $^{19}$F (Figure S14) NMR spectroscopy.
Figure S13: $^1$H NMR spectrum of poly(CTFE-alt-VE3) (P2) copolymer (CDCl$_3$ at 20 °C, 400 MHz).

Figure S14: $^{19}$F NMR spectrum of poly(CTFE-alt-VE3) (P2) copolymer (CDCl$_3$ at 20 °C, 400 MHz).
Radical copolymerization 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl vinyl ether FFPVE (4) with chlorotrifluoroethylene

Potassium carbonate (98 mg, 0.71 mmol), 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl vinyl ether FFPVE (4) (6.04 g, 0.023 mol), tert-butyl peroxyacetate (TBPPi) (0.275 g, 1.58 mmol), 50 mL of 1,1,1,3,3-pentafluorobutane, and CTFE (11 g, 0.095 mol) were inserted into the autoclave. The copolymerization was carried out at 74 °C for 8 hrs. Similar increase and drop of pressure were observed. Similar post-copolymerization procedure, work-up, and purification were also carried out. The copolymerization yielded 11 g of a red gum after precipitation (yield = 68%), characterized by $^1$H (Figure S15), $^{19}$F (Figure 4) and $^{13}$C (Figure 5) NMR spectroscopy.

![NMR spectrum of poly(CTFE-alt-VE4) (P3) copolymer (THF-$d_8$ at 20 °C, 400 MHz).](image-url)
Radical copolymerization of 3-dimethylamino-(2,2-dimethylpropyl) vinyl ether MMPVE (5) with chlorotrifluoroethylene

Potassium carbonate $\text{K}_2\text{CO}_3$ (263 mg, 1.91 mmol), vinyl ether MMPVE (5) (10 g, 0.0636 mol), tert-butylperoxypivalate (TBPPi) (0.278 g, 1.59 mmol), chlorotrifluoroethylene (11.1 g, 95.4 mmol) and 60 mL of 1,1,1,3,3-pentafluorobutane were transferred in the autoclave. The copolymerization was carried out at 74 °C for 15 hrs. Similar increase and drop of pressure were observed. Similar post-copolymerization purification was also carried out. The copolymerization yielded 9.5 g of a viscous orange oil after precipitation and drying (yield = 55 %), characterized by $^1\text{H}$ (Figure S16) and $^{19}\text{F}$ (Figure S17) NMR spectroscopy.

Figure S16: $^1\text{H}$ NMR spectrum of poly(CTFE-alt-VE5) copolymer (P4) (CDCl$_3$ at 20 °C, 400 MHz).
Radical Copolymerization of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (GCVE) (6) with chlorotrifluoroethylene (CTFE)

Potassium carbonate $\text{K}_2\text{CO}_3$ (161 mg, 1.16 mmol), vinyl ether GCVE (6) (5.6 g, 0.0338 mol), tert-butylperoxypivalate (TBPPi) (1.80 g, 7.76 mmol), and 50 mL of 1,1,1,3,3-pentafluorobutane and chlorotrifluoroethylene (13.5 g, 0.116 mol) were introduced in the autoclave. The copolymerization was carried out at 74 °C for 15 hrs. Similar increase and drop of pressure were observed. Similar post-copolymerization purification was also carried out. The copolymerization yielded 17.14 g of powder after precipitation and drying (yield = 79%), characterized by $^1\text{H}$ (Figure S18), $^{19}\text{F}$ (Figure S19) and $^{13}\text{C}$ (Figure S20) NMR spectroscopy.
Figure S18: $^1$H NMR spectrum of poly(CTFE-alt-VE6) (P5) copolymer (CDCl$_3$ at 20 °C, 400 MHz).

Figure S19: $^{19}$F NMR spectrum of poly(CTFE-alt-VE6) copolymer (P5) (CDCl$_3$ at 20 °C, 400 MHz).
Copolymerization of methoxy-tri(ethylene oxide) vinyl ether (PEOVE3) (7) with chlorotrifluoroethylene

Potassium carbonate (161 mg, 1.16 mmol), methoxy-tri(ethylene oxide) vinyl ether (PEOVE3) (7) (7.30 g, 0.0338 mol), tert-butyl peroxypivalate (TBPPi) (1.80 g, 7.76 mmol), 50 mL of 1,1,1,3,3-pentafluorobutane and chlorotrifluoroethylene (13.5 g, 0.116 mol) were inserted into the autoclave. The copolymerization was carried out at 74 °C for 8 hrs. Similar increase and drop of pressure were observed. Similar post-copolymerization purification was also carried out. The copolymerization led to 12.6 g of a red gum (yield = 61%), characterized by $^1$H (Figure S21), $^{19}$F (Figure S22) and $^{13}$C NMR (Figure S23) spectroscopy.
Copolymerization of methoxyoligo(ethylene oxide) vinyl ether (PEOVE10) (8) with chlorotrifluoroethylene

Potassium carbonate (138 mg, 1 mmol), methoxyoligo(ethylene oxide) vinyl ether (8) (20.41 g, 0.0388 mol), tert-butyl peroxyvalerate (TBPPi) (1.80 g, 7.76 mmol), 50 mL of 1,1,1,3,3-pentafluorobutane, and CTFE (13.5 g, 0.116 mol) were inserted into the autoclave. The copolymerization was carried out at 74 °C for 8 hrs. Similar increase and drop of pressure were observed. Similar post-copolymerization procedure, work-up, and purification were also carried out. The copolymerization led to 23 g of a red gum after precipitation (yield = 68%), characterized by $^1$H (Figure S21), $^{19}$F (Figure S22) and $^{13}$C (Figure S23) NMR spectroscopy.
Figure S21: $^1$H NMR spectra of poly(CTFE-alt-PEOVE3) (P6) copolymer (lower spectrum) and poly(CTFE-alt-PEOVE10) (P7) copolymer (upper spectrum) recorded in acetone-d6.

Figure S22: $^{19}$F NMR spectrum of poly(CTFE-alt-PEOVE3) copolymer (P6) recorded in acetone-d6 at room temperature.
Figure S23: $^{13}$C NMR spectrum of poly(CTFE-alt-PEOVE3) copolymer (P6) (lower spectrum) and poly(CTFE-alt-PEOVE10) copolymer (P7) (upper spectrum) recorded in acetone-d6 at room temperature.

Radical copolymerization of oligo(fluoroether) vinyl ether (9) with chlorotrifluoroethylene

$$
\text{O-Rf} + F_2C=CFCl \xrightarrow{\text{tert-Butyl peroxypivalate}} \text{CF}_2\text{CF}_2\text{CH}_2\text{OCH}_2\text{C}_2\text{H}_5\text{F}_5, 75 ^\circ \text{C}
$$

Oligo(fluoroether)

$$x+y = 4-5$$
Potassium carbonate (59 mg, 4.29 mmol), oligo(fluoroether) vinyl ether (10) (24.27 g, 0.014 mol), tert-butyl peroxypivalate (TBPPi) (1.65 g, 9.48 mmol), 50 mL of 1,1,1,3,3-pentafluorobutane, and CTFE (15 g, 0.128 mol) were introduced in the autoclave. The copolymerization was carried out at 74 °C for 15 hr. Similar increase and drop of pressure were observed. Similar post-copolymerization procedure, work-up, and purification were also carried out. The copolymerization yielded 25.35 g of a red gum after precipitation (yield = 65%). This product is insoluble in THF, acetone, DMF, DMSO, and CHCl₃.

Radical copolymerization of (p-methylchlorobenzyl) vinyl ether (10) with chlorotrifluoroethylene

The experimental procedure is similar to that of the radical copolymerization of CTFE with vinyl ether (1-9). Potassium carbonate (228 mg, 1.65 mmol), vinyl ether (10) (10.08 g, 0.055 mol), tert-butylperoxypivalate (TBPPi) (2.13 g, 9.19 mmol), 50 mL of 1,1,1,3,3-pentafluorobutane, and CTFE (15 g, 0.128 mol) were inserted in the autoclave. The copolymerization was carried out at 74 °C for 15 hr. Similar increase and drop of pressure were observed. Similar post-copolymerization purification was also carried out. The copolymerization yielded 11 g of brown powder after precipitation and drying (yield = 68%), characterized by $^1$H (Figure S24) and $^{19}$F NMR spectroscopy.
Figure S24: $^1$H NMR spectrum of poly(CTFE-alt-VE10) (P9) copolymer (CDCl$_3$ at 20 °C, 400 MHz).
Figure S25: TGA thermograms of poly(CTFE-alt-VE) copolymers (P1-3, 5-8, 10) recorded under air at 10 °C.min⁻¹.