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Synthesis and Modification of Alternating Copolymers Based on Vinyl Ethers, Chlorotrifluoroethylene, and Hexafluoropropylene[†]

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ABSTRACT: Fluorinated copolymers bearing ammonium groups were prepared by radical copolymerization of fluorinated olefins (chlorotrifluoroethylene, hexafluoropropylene) with different vinyl ethers (2-chloroethyl, cyclohexyl, *n*-butyl, and ethyl vinyl ethers) followed by the cationization of these copolymers with trimethylamine. Copolymers were obtained in high yield (generally $>85\%$), with molecular weights ranging from 8000 to 25 000 g mol^{-1}. From elemental analysis as well as ^{1}H and ^{19}F NMR spectroscopy, the alternating structure of these polymers was confirmed. The chemical modification of these copolymers consisted of a two-step reaction: (i) the replacement of the chlorine atom by an iodine atom followed by (ii) the substitution of the halogen atom by the trimethylamine into a quaternary ammonium. The resulting copolymers were characterized with the usual techniques to assess their compositions and structures. Their thermal analyses, in dynamic mode, under air, showed decomposition temperatures ($T_{d,10\%}$) higher than 200 °C. Electrochemical properties of some of these polymers were also studied, showing ionic exchange capacities (IEC) ranging from 0.50 to 0.75 mequiv g^{-1} (theoretical IEC up to 3.63 mequiv g^{-1}) and water uptake of 13−25%.

Introduction

Among the different types of fuel cells, solid alkaline fuel cells (SAFCs) appear as an attractive solution to the energy crisis, global warming/green energy, and the development of new sources of energy.[1,2] SAFCs are among the most recent fuel cells technology, combining the best of both alkaline batteries and solid polymer electrolyte membranes for fuel cells (PEMFCs). In contrast to other fuel cells, SAFCs, which use anion-exchange membranes, do not require noble metals (Pt, Ru, ...) as catalysts to function, which is one of the main drawbacks for the commercialization of PEMFCs based on proton-exchange membranes.[1] Nevertheless, SAFCs are still in the early stages of development, especially for membrane−electrodes assembly (MEA). To achieve a good MEA, a binder is required to strengthen the interface between the membrane and the electrodes.

Within this research, our goal is to prepare a polymeric binder endowed with a good conductivity, a high ionic exchange capacity, both water and fuels (such as methanol, ethylene glycol, ...) insolubility, and organic medium solubility (dimethyl sulfoxide, dimethylformamide) for fuel cell implementation reasons.

Fluoropolymers exhibit remarkable properties,[3−7] such as chemical resistance (to acids, bases, organic solvents), low dielectric constants and dissipation factors, hydrophobic and oleophobic properties, excellent weathering, and interesting surface properties. Hence, these high-value-added materials can find applications in many fields of high technology such as aeronautics,[8] microelectronics,[9] optics,[10,11] textile finishing,[12] in the nuclear industry,[13] in paints and coatings,[14] and microlithography.[15]

Chlorotrifluoroethylene (CTFE) was first polymerized in 1934 (its polymerization was patented in 1937).[16] It yields hydrophobic polymers with chemical and thermal resistance along with good mechanical properties. Also, the poly(CTFE) polymers presently marketed by Honeywell, under the Aclar trademark, have remarkable gas-barrier properties.[17]

Since their discovery in 1971 by Tabata and Du Plessis,[18] poly(chlorotrifluoroethylene-*alt*-vinyl ether) copolymers have received much industrial attention in the domain of paints and coatings[19−24] (i.e., Lumiflon marketed by the Asahi Glass Co. Ltd.).[25−29] These applications arise essentially from their excellent resistance to aging and their solubility.[19] Tetrafluoroethylene (TFE) is sometimes preferred to chlorotrifluoroethylene (CTFE) as a precursor of fluorinated materials just like poly(TFE-*alt*-VE) copolymers (Zeffle paints produced by Daikin Co.) mainly because of the presence of a perfluorinated chain instead of a chlorine atom. However, compared to TFE, CTFE can enhance the solubility when introduced as comonomer in alternating copolymers, in contrast to the poly(CTFE) homopolymer which is only soluble in 1,3-dichlorobenzene trifluoride at 150 °C.[30]

As with ethylene[31−39] (Halar from Solvay-Solexis), propylene,[40−43] isobutylene,[41,42,44,45] [1-(fluoromethyl)vinyl]benzene,[46] or vinyl acetate,[47−49] which had led to statistic copolymers of low CTFE content (compared to that of the feed), CTFE can copolymerize with vinyl ethers to form alternated copolymers.[18,19,24,50−52] This particularity arises from the acceptor character of CTFE ($e = 1.56$) opposed to the donor character of the vinyl ethers ($-2.0 < e < -1.5$) which do not homopolymerize under radical polymerization.[53,54] Some studies have described this alternating copolymerization as a propagation by transfer of charges between acceptor and donor complexes.[55,56] However, it is commonly accepted that it results from a traditional mechanism of propagation between free monomers having a different polarity.[50−52,57,58]

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The literature does not report any work on the radical copolymerization of hexafluoropropylene (HFP) with vinyl ethers. In addition, to the best of our knowledge, copolymers based on CTFE and vinyl ether have never been reported to be involved in an ionomer membrane, and it was of interest to attempt that challenge. Interestingly, 2-chloroethyl vinyl ether (CEVE) should allow a further introduction of ionic groups on the polymer chain. Originally, using this monomer, poly(CTFE-*alt*-VE) copolymers were used as functional materials.[23] Cyclohexyl vinyl ether (CHVE), butyl vinyl ether (BVE), and ethyl vinyl ether (EVE) have been employed to change the solubility of the resulting polymer and to control the amount of CEVE incorporated and by the means to control the amount of ionic sites. The objectives of this article are, first, to synthesize and to characterize the poly(CTFE-*alt*-VE), poly(HFP-*alt*-VE), and poly[(CTFE-*alt*-VE)-*co*-(HFP-*alt*-VE)] copolymers, to enable their chemical modification into ionomers as original binders for solid alkaline fuel cell (SAFC), and finally to assess their electrochemical and thermal properties.

Experimental Section

Materials. *tert*-Butylperoxypivalate (TBPPi, Trigononx 25-C75, 75 wt % solution in isododecane) and sodium persulfate ($Na_2S_2O_8$, purity >99%) were kindly provided by Akzo Nobel (Compiègne, France). Chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), and 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$) were kindly provided by Solvay S.A. (Tavaux, France & Bruxelles, Belgium) and were used as received. The different vinyl ethers (cylcohexyl vinyl ether (CHVE), 2-chloroethyl vinyl ether (CEVE), ethyl vinyl ether (EVE), and butyl vinyl ether (BVE), all purities >98%), water (HPLC grade), methanol (analytical grade), tetrahydrofuran (THF, analytical grade), potassium carbonate (K_2CO_3, puriss), and trimethylamine (TMA, purum) were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Deuterated solvents for NMR were purchased from Euroiso-top (Grenoble, France) (purity >99.8%).

Radical Copolymerization of Fluoroolefins with Vinyl Ethers. As CTFE and HFP are gases, the reactions were carried in a Hastelloy autoclave Parr system equipped with a manometer, a rupture disk (3000 psi), inlet and outlet valves, and a magnetic stirrer. Prior to reaction, the autoclave was pressurized with 30 bar (i.e., 430 psi) of nitrogen to check for eventual leaks. The autoclave was then conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove any traces of oxygen. The liquid phase was first introduced via a funnel, and then the gases were inserted by double weighing (i.e., the difference of weight before and after filling the autoclave with the gas). Then, the autoclave was placed into an oil bath with a vigorous magnetic stirring. After an initial increase of the internal pressure due to the increasing temperature, the pressure dropped by consumption of the gaseous monomer to produce a polymer in the liquid phase. After the reaction was complete, the product was dried under vacuum (10^{-2} mbar) at 70 °C until constant weight.

*Poly(CTFE-alt-VE) Alternated Copolymers and Terpolymers (**P1**, **P2**, **P4**, **P7**, and **P8** in Tables 1 and 2).* The reaction was carried out in 1,1,1,3,3-pentafluorobutane as the solvent in the presence of *tert*-butylperoxypivalate (TBPPi, 1 mol % vs

Table 1. Experimental Conditions and Compositions of the Poly[(CTFE-*alt*-VE)*co*-(HFP-*alt*-VE] Terpolymers Assessed by Elementary Analysis and ^1H and ^{19}F NMR Spectroscopy

	feed composition (mol %)						terpolymer composition (mol %)								
run no.[a]	CTFE	HFP	CEVE	CHVE	EVE	BVE	CTFE	HFP	CEVE	CHVE	EVE	BVE	t_R (h)	*T* (°C)	yield (%)
P1	50		20	30			50		12	38			15.0	68	83
P2	50			50			50			50			3.5[c]	68	74
P3	10	40		50			15	35		50			0.8[c]	74	44[b]
P4	50		50				50		50				15.0	68	80
P5		50	50					50	50				15.0	68	85
P6	25	25	50				18	32	50				15.0	68	88
P7	50					50	50					50	15.0	67	91
P8	50				50		50				50		15.0	65	85
P9	11	39				50	8	42				50	8.5	67	81
P10	11	39			50		10	40			50		4.0	67	89
P11	50		30		20		50		26		24		15.0	68	91
P12	50		30			20	50		27			23	15.0	68	93

[a] The "P" prefix in the sample name stands for polymer. Standard deviation on the determination of the copolymer composition by NMR: ± 2%. [b] Copolymerization interrupted after 45 min due to mechanical stirrer problem. [c] Copolymerization in emulsion; the others were carried out in solution. Solution copolymerization: solvent = $C_4F_5H_5$, initiator = *tert*-butylperoxypivalate (1 mol % with respect to all monomers), potassium carbonate (3 mol % vs all vinyl ethers) Emulsion copolymerization: solvent = deionized water + $C_4F_5H_5$ (3 wt %), initiator = sodium persulfate (1 mol % with respect to all monomers), potassium carbonate (3 mol % vs all vinyl ethers).

Table 2. Properties and Elemental Analysis of the Poly[(CTFE-*alt*-VE)-*co*-(HFP-*alt*-VE)] Terpolymers

	% C		% H				$T_{g,calculated}$ (°C)				
run no.	calcd[a]	measd[b]	calcd[a]	measd[b]	M_n (g mol^{-1})[c]	PDI[c]	ref 80	ref 81	ref 82	$T_{g,exp}$ (°C)[d]	$T_{d,10\%}$ (°C)[e]
P1	45.63	43.86	5.22	4.98	14 800	2.4	53	53	53	52	338
P2	49.50	48.78	5.81	6.74	42 200	2.6	66	66	66	43	331
P3	48.28	47.86	5.30	7.34	19 600	2.1	104	36	46	55	327
P4	32.31	32.84	3.16	5.44	20 600	2.4	13	13	13	26	203
P5	32.76	35.66	2.75	4.19	7 800	1.8	61	−14	−3	−9	217
P6	32.61	34.26	2.89	3.33	12 600	2.7	43	−6	2	3	
P7	44.36	44.57	5.59	6.46	23 800	4.4	−8	−8	−8	−8	313
P8	38.22	38.24	4.27	5.44	25 500	5.4	8	8	8	14	303
P9	43.38	42.90	4.95	5.24	3 300	1.9	30	−27	−18	−20	291
P10	37.92	38.57	3.75	4.68	5 300	3.6	52	−16	−6	6	288
P11	34.87	34.80	3.65	4.80	25 400	3.7	11	11	11	23	
P12	37.71	37.67	4.25	7.76	18 600	5.9	3	3	3	11	

[a] Amount calculated from the polymer compositions assessed by ^1H and ^{19}F NMR. [b] Assessed by elemental analysis. [c] Determined by SEC analysis in THF as the solvent. [d] Determined by DSC. [e] Determined TGA analysis.

monomers) as the initiator and potassium carbonate (3 mol % vs CHVE) to prevent the cationic homopolymerization of CHVE and the formation of the acetal from the vinyl ether.[59] The reaction was allowed to proceed at 68 °C for 12 h, showing a drop of pressure as CTFE was reacting. After the reaction, the autoclave was cooled in an ice bath, vented from the unreacted gases, and opened. After the distillation of the solvent, the product was precipitated from methanol to remove any remaining solvents, monomers, potassium carbonate, initiators, and oligomers. The polymer, obtained as a white powder, was then dried in a vacuum (10^{-2} mbar) oven at 50 °C until constant weight. For the **P2** copolymer, the reaction was carried out in deionized water instead, in the presence of 1,1,1,3,3-pentafluorobutane (3 wt %) to favor the dispersion of the fluorinated monomer in the aqueous phase. The copolymerization was initiated by $Na_2S_2O_8$ (1 mol %), and K_2CO_3 was also used.

Example: *Synthesis of **P4***. CEVE (18.1 g, 0.17 mol), TBPPi (0.79 g, 3.4×10^{-3} mol), K_2CO_3 (0.68 g, 5×10^{-3} mol), and 1,1,1,3,3-pentafluorobutane (80 mL) were introduced in the autoclave. Then CTFE (20 g, 0.17 mol) was added. The autoclave was heated at 68 °C for 15 h. After reacting, the crude product was degassed and precipitated in methanol and then dried, the yield was assessed (80%), and the copolymer was characterized (SEC indicated a M_n of 20 600 g mol^{-1} and a PDI of 2.4, and the alternating structure was demonstrated by NMR and elemental analysis).

*Poly(HFP-alt-VE) Copolymers (**P5**) and Poly[(CTFE-alt-VE)-co-(HFP-alt-VE)] Terpolymers (**P3**, **P6**, **P9**, **P10**, **P11**, and **P12** in Tables 1 and 2)*. As above, the polymerization was achieved in an autoclave in the presence of *tert*-butyl peroxypivalate (TBPPi, 1% vs monomers) and 1,1,1,3,3-pentafluorobutane as the initiator and the solvent, respectively. K_2CO_3 was also introduced (3 mol % vs VE) prior to reaction. Fluorinated monomers were introduced in slight excess to favor the complete consumption of the vinyl ether. In the case of **P3**, the reaction was carried out in the same conditions as for **P2**, i.e., in deionized water with 3 wt % of $C_4F_5H_5$, initiated by $Na_2S_2O_8$ (1 mol % vs monomers) in the presence of K_2CO_3 (3 mol % vs vinyl ethers). The polymerization was allowed to occur at 68 °C for 15 h. The same procedure as above was used for the purification of poly[(CTFE-*alt*-VE)-*co*-(HFP-*alt*-VE)] terpolymers.

Modifications of Copolymers. *Iodination Reaction (Table 3)*. The copolymer was dissolved in acetone in a single-neck round-bottom flask equipped with a magnetic stirrer and a condenser. Then, 3 equiv of sodium iodide were introduced in the flask, and the reaction was allowed to reflux for 7 days. After the reaction and upon cooling to room temperature, the produced salts (sodium chloride and sodium iodide) were filtered. Then, the polymer was precipitated in methanol and dried under vacuum at 50 °C for 4 h to produce a white powder. The product was obtained in high yield (> 81%).

Amination Reaction. The copolymer was first dissolved in acetone in a single-neck round-bottom flask equipped with a magnetic stirrer and a condenser. Then, 3 equiv (vs iodine sites) of trimethylamine (TMA) were introduced in the flask, and the reaction was allowed to pursue at 40 °C for 48 h. The copolymer which changed solubility (from nonpolar toward polar solvents) was then dried by evaporation of the amine and acetone, resulting in a crystalline powder. The yield was quantitative.

Table 3. Substitution of the Chlorine Atoms by Iodine Atoms from CEVE in the Different Poly(CTFE-*alt*-VE) Copolymers after Various Reaction Times[a]

sample	P1i1	P1i2	P4i	P5i	P6i	P11i	P12i
t_R (days)	2	7	7	7	7	7	7
yield (%)	55	85	64	77	87	81	90

[a] The "i" in the sample name stands for iodinated copolymer. Iodination carried out at reflux of acetone in the presence of 3 equiv of NaI.

Counterion Exchange. To replace the iodide counteranions by hydroxides, the polymer was immersed in a 1 M solution of sodium hydroxide for 24 h under a vigorous stirring. The procedure was repeated another time to reach complete conversion, and the polymer was then rinsed several times with water (HPLC quality) and dried under vacuum at 50 °C for 3 h.

Preparation of Membranes. The membranes were cast from a polymer solution in DMSO (ca. 1 g of polymer for 2 g of DMSO) onto a glass substrate followed by a vacuum drying at 50 °C for 24 h. The membranes were then removed from the substrate by immersion in water. Most products exhibited good casting properties (homogeneous surface after drying and immersion). These membranes were soft but shrank, and several of them became brittle when drying.

Characterizations. *SEC*. Size exclusion chromatography (SEC) measurements were conducted on a Spectra-Physics apparatus equipped with two 5 μm Mixed-C PL-gels columns (Polymer Laboratories), a SP8430 Spectra-Physics refractive index detector using THF as the eluent at room temperature, and a flow rate of 0.6 mL/min. Monodisperse polystyrene standards were used for the calibration.

NMR. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 400 instrument, using deuterated chloroform, acetone, or dimethyl sulfoxide as the solvent and tetramethylsilane (TMS) (or $CFCl_3$) as the references for ^1H (or ^{19}F) nuclei. The experimental conditions for recording ^1H (or ^{19}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 ^{19}F NMR.

The microstructures of the copolymers of the polymers were assessed by ^1H and ^{19}F NMR spectroscopy. The absence of signals at −100 ppm[60] and −127 ppm[61] on the ^{19}F NMR spectra indicates the absence of CTFE−CTFE diads, which is considered as an evidence of the alternating structure of the CTFE with vinyl ethers. Vinyl ethers do not homopolymerize by radical polymerization, and thus no VE−VE diads could be observed. The measured chemical shifts assigned to vinyl ethers were in good agreement with previous works demonstrating the alternating structure of poly(CTFE-*alt*-VE) copolymers.[51,52] In addition, NMR spectroscopy did not enable us to make the difference between poly[(CTFE-*co*-HFP)-*alt*-VE] and poly[(CTFE-*alt*-VE)-*co*-(HFP-*alt*-VE)].

The copolymer composition was assessed from ^1H and ^{19}F NMR spectra (see Supporting Information).[30,60−63]

Elemental Analysis. Weight percentages of carbon and hydrogen atoms were assessed by elemental analysis at the CNRS−Service Central d'Analyze (Solaize, France) on a CH elemental analyzer equipped with a CO_2/H_2O infrared detector. Theoretical carbon and hydrogen compositions were calculated according to the polymer compositions assessed by ^1H and ^{19}F NMR spectroscopy and considering that co- or terpolymers have alternating structures (with 50% of fluorinated olefins and 50% of vinyl ethers). Equations 1 and 2 were used to determine these theoretical values:

$$\%C = \sum_i \left(\%\text{monomer}_i \times \frac{M_C}{M_{\text{monomer}_i}} \right) \quad (1)$$

$$\%H = \sum_i \left(\%\text{monomer}_i \times \frac{M_H}{M_{\text{monomer}_i}} \right) \quad (2)$$

where % monomer$_i$ is the molar fraction of the monomer i in the polymer and M_H, M_C, and M_{monomer_i} are the respective molecular weights of the hydrogen and carbon atoms and of the monomer.

Electrochemical Properties. Water uptake was calculated at 25 °C from the equation

$$\text{water uptake } (\%) = \frac{m_h - m_s}{m_h} \times 100 \quad (3)$$

where m_h and m_s stand for the weight (in grams) of the hydrated membrane and of the dry membrane before immersion in water, respectively. The experimental ionic exchange capacity (IEC) was calculated at 25 °C from eq 4 as follows:

$$\mathrm{IEC}_{\mathrm{exp}} = \frac{[\mathrm{Cl}^-]V}{m_s} \tag{4}$$

where $[\mathrm{Cl}^-]$, V, and m_s stand for the concentration of the exchange solution in anions Cl^- (mol L^{-1}), the volume of the exchange solution (mL), and the weight of the dry membranes (g), respectively. The membrane conductivity was determined from the following equation:

$$\sigma = \frac{l}{RS} \tag{5}$$

where l, R, and S represent the membrane thickness, the resistance measured by impedance spectroscopy, and the active surface of the membrane (0.785 cm^2), respectively. The experimental device used for the resistance measurement was a Teflon two-compartment cell clamping the humid membrane (100% relative humidity). Each compartment was filled with liquid mercury and contained a platinum electrode.

TGA. Thermogravimetric analyses (TGA) were performed with a TGA 51 apparatus from TA Instruments, under air, at the heating rate of 10 °C min^{-1} from room temperature up to a maximum of 500 °C. The sample size varied between 10 and 15 mg.

DSC. Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 apparatus. Scans were recorded at a heating rate of 20 °C min^{-1} from −100 to +100 °C, and the cooling rate was 20 °C min^{-1}. A second scan was required for the assessment of the T_g, defined as the inflection point in the heat capacity jump. The sample size was about 10 mg.

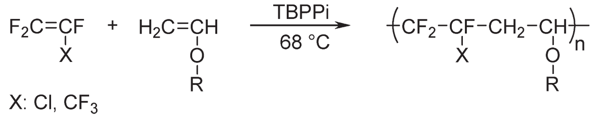
Results and Discussion

Synthesis and Modification of Poly[(CTFE-*alt*-VE)-*co*-(HFP-*alt*-VE)] Terpolymers. *Terpolymerization.* Radical copolymerizations of hexafluoropropylene (HFP) or chlorotrifluoroethylene (CTFE) with vinyl ethers (VEs) and radical terpolymerization of CTFE with HFP and VE, initiated by *tert*-butylperoxypivalate (TBPPi), were achieved as depicted in Scheme 1 and in the Experimental Section. The radical copolymerization of CTFE with vinyl ethers is an exothermic reaction, and a rapid increase of pressure in the autoclave was observed, followed by a sharp drop of pressure.

Several co- and terpolymerizations were carried out with different molar feed compositions in CTFE, HFP, and VE (Table 2). HFP is usually incorporated to lower the crystallinity[62] of the resulting copolymer and to favor its film forming character. To the best of our knowledge, HFP has never been used in the copolymerization with vinyl ethers. The introduction of a second vinyl, such as CHVE, BVE, or VE, with CEVE allowed to decrease the amount of CEVE incorporated in the polymer, which was useful to further control the amount of ammonium groups in the final material. Besides, the introduction of cyclohexylvinyl ether (CHVE) led to a less hydrophilic polymer, limiting the risk of water solubility of the final binder. On the other hand, the incorporation of butyl vinyl ether (BVE) and ethyl vinyl ether (EVE) can improve the mechanical properties necessary for the preparation of the membranes.[23]

The composition of the copolymers (Table 1) was determined by elemental analysis for the poly(CTFE-*alt*-VE) copolymers and by ^{19}F NMR spectroscopy for the poly[(CTFE *alt*-VE)-*co*-(HFP-*alt*-VE)] terpolymers.

Scheme 1. Radical Copolymerization between Fluorinated Monomers (Chlorotrifluoroethylene and/or Hexafluoropropylene) and Vinyl Ethers



X: Cl, CF_3
R: $-CH_2CH_2Cl$, alkyl, cyclohexyl.
TBPPi: *tert*-butylperoxypivalate

Copolymers and terpolymers of fluorinated olefins and vinyl ethers were obtained in high yields (close to 85%), in agreement with the literature.[23,51,52] For some copolymerizations (**P2**, **P3**, and **P10**), the reactions were stopped after a short reaction time due to a large exotherm (resulting in a fast increase of the pressure in the autoclave).

As shown in Table 2, experimental weight percentages of carbon and hydrogen, assessed by elemental analysis, contained in co- and terpolymers were similar to the theoretical values expected in the case of an alternating structure between the fluoroolefins and vinyl ethers. For example, the difference between experimental and theoretical carbon contents was less than 1%. However, a higher discrepancy was noted in the case of hydrogen, because of its low content in the copolymer. The proportions of CTFE and HFP in the terpolymers were found to be identical to those of the feed compositions. This quasi-quantitative incorporation of both monomers can be explained by taking into account their close polarities ($e_{\mathrm{CTFE}} = 1.56$;[64,65] $e_{\mathrm{HFP}} = 1.50$[66]) but can appear as surprising when considering the lower reactivity of HFP compared to CTFE. The steric hindrance generated by the CF_3, and its smaller inductive effect compared to that of chlorine, may be responsible for this behavior. This terpolymerization is an example of termonomer-induced copolymerization (TIC),[67] which associates monomers that do not copolymerize (CTFE and HFP), and a termonomer (VE) that exhibits a good reactivity with both of them. Hence, polymerization reactions between CTFE, HFP, and CHVE were monitored by NMR spectroscopy to understand how both these fluorooolefins terpolymerized with vinyl ethers. The reaction was carried out in similar conditions as for the poly[(CTFE-*alt*-CHVE)-*co*-(HFP-*alt*-CHVE)] terpolymer (**P3**), but by substituting the water by 1,1,1,3,3-pentafluorobutane. Samples were taken off the reaction media at regular time intervals to monitor the evolution of the incorporation of HFP in the polymer by NMR spectroscopy versus the conversion in CHVE (considering that the resulting polymers is alternated, the conversion of CHVE can be used as a reference).

The results displayed in Figure 1 show that the first terpolymers were relatively rich in CTFE (22 mol % for a CHVE conversion below 10%) while the initial percentage of this monomer was 10 mol % (with 40 mol % of HFP and 50 mol % of CHVE). Thus, although at the end of the polymerization the amount of CTFE was ca. 15 mol % (a value close to the initial value), this evolution of the proportion of CTFE, and hence of HFP, in the terpolymer was the consequence of the lower reactivity of HFP toward CTFE. Furthermore, HFP does not homopolymerize,[6] and thus, copolymers with such a high content of HFP (> 30 mol %) are rare. In addition, the copolymers containing HFP have lower molecular weights than those of poly(CTFE-*alt*-VE) copolymers, though both types of copolymers were obtained with similar yields (> 80 wt %). In fact, the molecular weights of HFP-containing copolymers were high enough when HFP was the only fluoroolefin, while when HFP was copolymerized with CTFE, the molecular weights decreased. As expected, the polymerizations carried out in aqueous

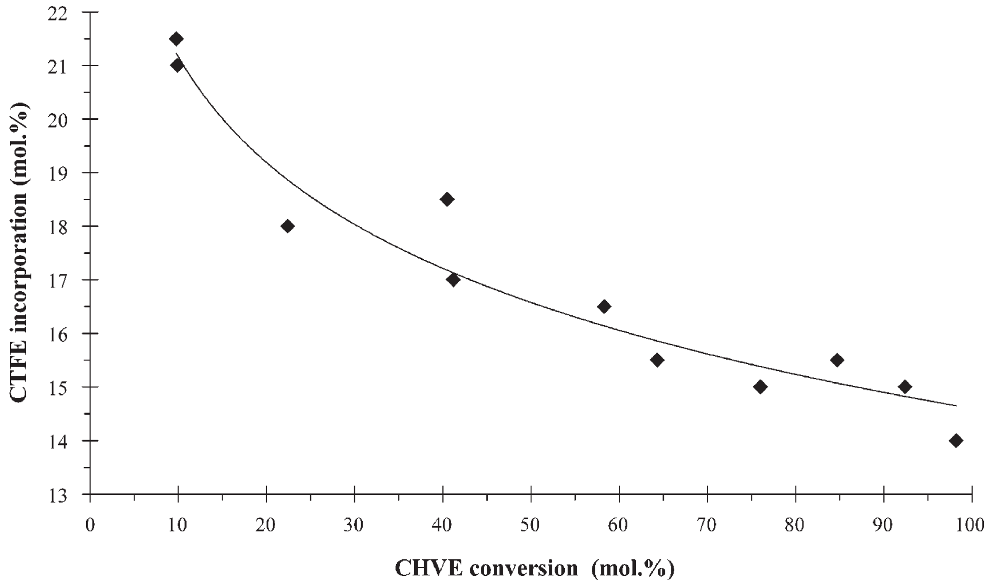


Figure 1. Evolution of the incorporation ratio of chlorotrifluoroethylene (CTFE) versus the cyclohexyl vinyl ether (CHVE) conversion during the terpolymerization between CTFE (10 mol %), hexafluoropropylene (HFP) (40 mol %), and CHVE (50 mol %), at 67 °C, initiated by *tert*-butylperoxypivalate (TBPPi) in $C_4F_5H_5$.

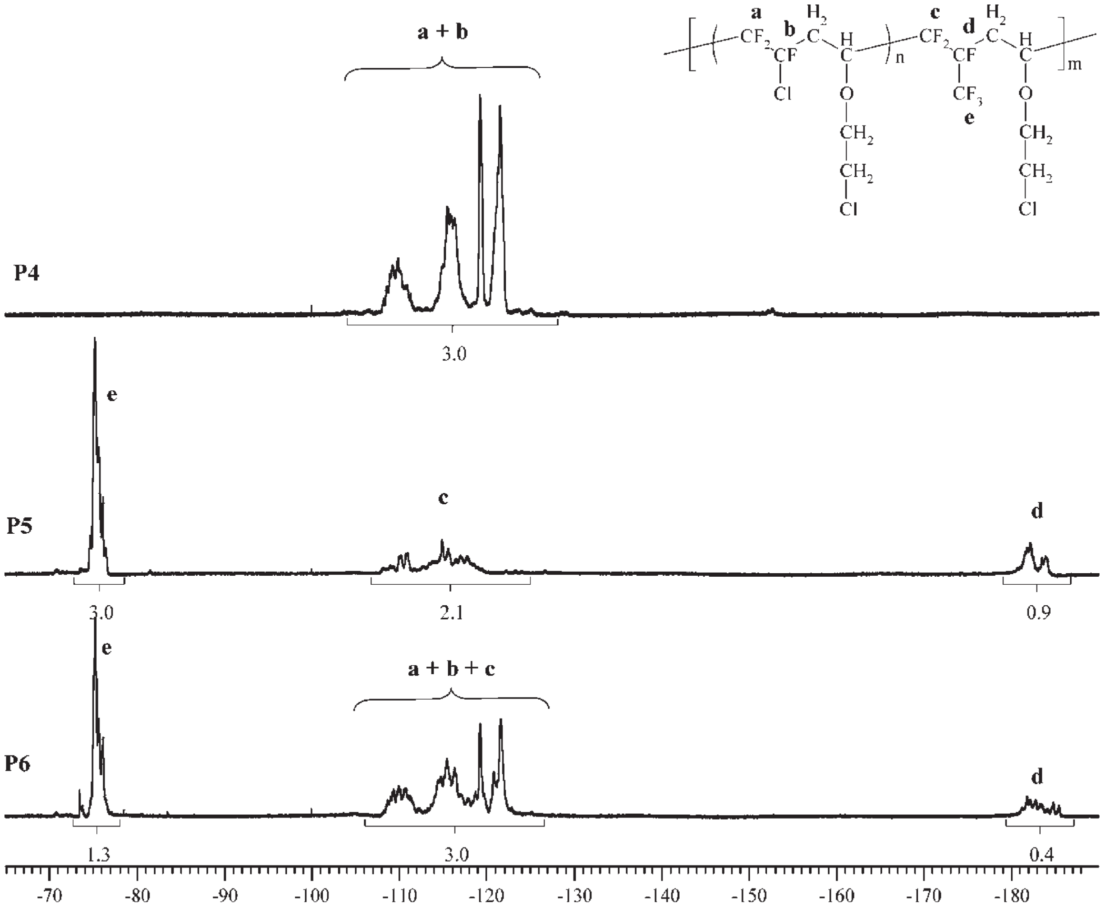


Figure 2. ^{19}F NMR spectra of poly(CTFE-*alt*-CEVE) (**P4**), poly(HFP-*alt*-CEVE) (**P5**), and poly[(CTFE *alt*-CEVE)-*co*-(HFP-*alt*-CEVE)] (**P6**) copolymers in $CDCl_3$ (CEVE and HFP stand for 2-chloroethyl vinyl ether and hexafluoropropylene, respectively).

media[22,24] led to much higher molecular weights than the polymerizations in solution.[68,69] However, the hypothesis of the transfer to the solvent during the terpolymerization to explain the lower molecular weight could not be considered since 1,1,1,3,3-pentafluorobutane has a negligible transfer constant.[70,71]

Figure 2 represents the ^{19}F NMR spectra of some poly(CTFE-*alt*-CEVE) and poly(HFP-*alt*-CEVE) copolymers and of poly[(CTFE *alt*-CEVE)-*co*-(HFP-*alt*-CEVE)] terpolymers. Though the CF_3- and $-CF-$ signals were well separated (−75 ppm vs −183 ppm), it was difficult to separate the integrals of the signals of the $-CF_2-$ (ranging from −109 to −123 ppm)[72] assigned to both HFP and CTFE.

Similarly, the ^1H NMR spectrum (Figure A, Supporting Information) allowed to assess the proportion of vinyl ethers in the polymer.[63] This figure shows the methylene and methyne protons of the main chain centered at 4.6 and 2.8 ppm, respectively. The other peaks were assigned to the alkyl pendant chain of the vinyl ether (alkyl groups between 0.8 and 2.2 ppm and CH_2X (where X = O or halogen) between 3.5 and 4.2 ppm). The incorporation of CEVE and CHVE units in the polymers fits with the feed composition (see Tables 1 and 2). This good agreement is not surprising considering the relatively close polarity of those vinyl ethers ($e_{CEVE} = -1.80$; $e_{CHVE} = -1.55$).[65] The molar masses of these copolymers assessed by SEC are listed in Table 2, and they vary from 3300 to 42 200 g mol^{-1}, similar to those of Lumiflon or Zeffle.[23] Although they could be considered as low molecular weights, they are sufficient for binder application that does not require outstanding mechanical properties.

From various vinyl ethers, different copolymers were produced, endowed with glass transition temperatures (T_g) ranging from −20 to +55 °C (Table 2). For example, copolymers containing BVE, which are known to lower the T_g, present the lowest T_g (**P7**, **P9**, and **P12**), although **P5** also exhibits a low T_g (−9 °C) due to the absence of CTFE. The synthesis of polymers with different T_g is of interest to obtain, after chemical modification, polymers with different film forming properties, which is an essential aspect for the determination of the electrochemical properties. Indeed, the membrane must be neither too soft to prevent flowing in water nor too brittle for its suitable processing such as casting and handling during the characterization. Several equations can be used to assess the T_g of a copolymer as a function of its composition.[73−77] Theoretical values of the glass transition temperature of the copolymers were calculated according to the Fox equation[74] which was developed for copolymers. This equation links the reverse of the T_g of a copolymer to the weight fraction, w_i, and the glass transition temperature, T_{gi} (in kelvin), of the corresponding homopolymer considering each monomer i as indicated in the equation

$$\frac{1}{T_g} = \sum_i \frac{w_i}{T_{gi}} \tag{6}$$

The theoretical T_g values of each homopolymer based on CTFE, CHVE, EVE, and BVE were +52, +81, −43, and −55 °C, respectively. The T_g of poly(CEVE), determined by Schappacher and Deffieux,[78,79] was used (T_g(poly(CEVE)) = −21 °C). As HFP does not homopolymerize, it is not possible to use an experimental value though the literature reports several calculated values,[80−82] and we have considered those determined by Bonardelli et al.[80] (T_g(poly(HFP)) = +160 °C), Gelin and Ameduri[81] (T_g(poly(HFP)) = −9 °C), and Rodriguez et al.[82] (T_g(poly(HFP)) = +11 °C). The experimental values of the glass transition temperatures are listed in Table 2 and were found generally to be identical (**P1**, **P5**, **P6**, **P7**, **P8**, **P9**) or close (**P2**, **P3**, **P4**, **P10**, **P11**, **P12**) to the calculated ones. It was found that calculations based on the value determined by Rodriguez et al.[82] for poly(HFP) gave the best agreement. If the copolymerizations carried out by Gelin and Ameduri[81] were achieved in similar conditions as those of the present copolymerizations, those of Bonardelli et al.[80] were carried out in emulsion. As the glass transition temperature is related to the morphology, and hence to the microstructure (conformation, molecular weight, ...) which depends on the polymerization method, some variations in the T_g values can be expected (from −9 to +160 °C).

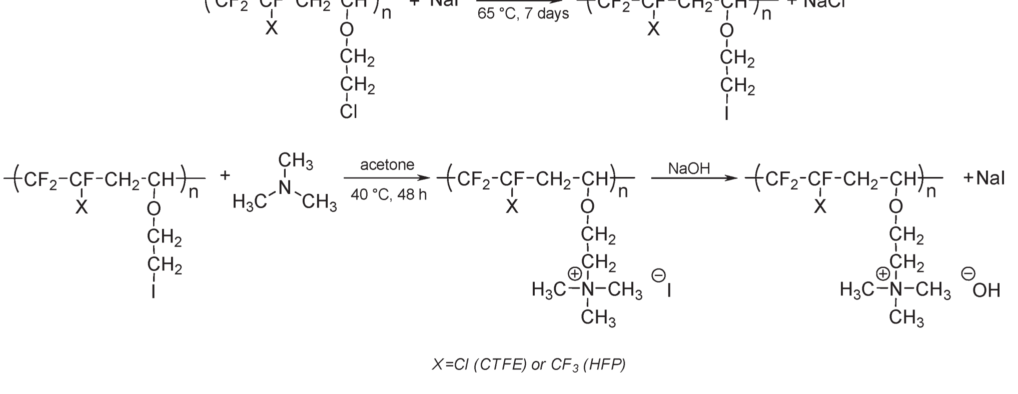
Finally, the existence of only one T_g for each terpolymer is an important observation proving that the product is indeed a terpolymer and not a mixture of two (poly[CTFE-*alt*-VE] and poly[HFP-*alt*-VE]) copolymers. Neither NMR spectroscopy, nor elemental analysis, nor SEC chromatography (especially because the PDI of the polymers is generally large) could underline this point.

Chemical Modification of the Copolymers. Three steps were required to modify the above copolymers starting from replacing the chlorine atom by an iodine one, then by trimethylamine. Finally, the iodine counterion was exchanged with hydroxide ions (Scheme 2).

Iodination of the Copolymers. When the direct amination of the chlorine atoms by trimethylamine was carried out, no substitution was observed. Thus, since the dissociation energy of CH_2-Cl bond is higher than that of CH_2-I, an intermediate step of iodination of CEVE-based copolymers and terpolymers was performed. This reaction has been described in the literature on the same monomer (2-chloroethyl vinyl ether).[83,84] This intermediate step enables the further cationization since the chlorine atom is not reactive enough to be substituted by a tertiary amine. The low solubility in acetone of the sodium chloride formed during the substitution compared to those of the sodium iodide enabled to reach high conversions.

Hence, the iodination was initially tested and monitored by ^1H NMR on CEVE monomer to determine and to apply the optimal conditions for the modification of the

Scheme 2. Modification of the Poly(CTFE-*alt*-VE) Alternating Copolymers by Iodination, Cationization by Trimethylamine (TMA), and Then Counterion Exchange by Sodium Hydroxide



X=Cl (CTFE) or CF_3 (HFP)

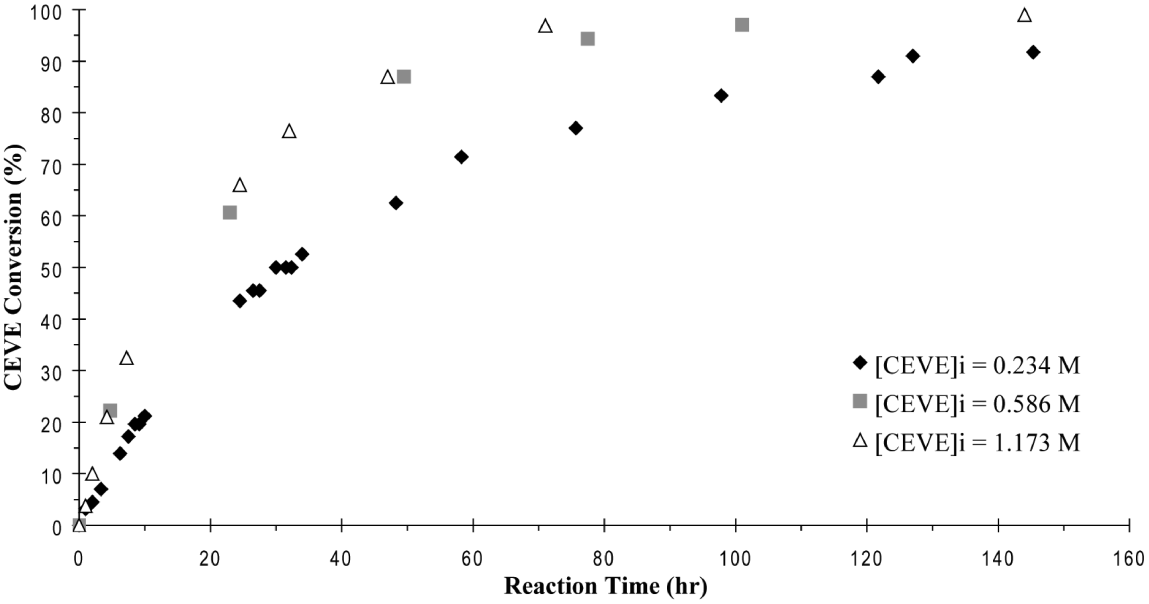


Figure 3. Conversion of 2-chloroethyl vinyl ether (CEVE) monomer into 2-iodoethyl vinyl ether (IEVE) versus time for different initial CEVE concentrations at 65 °C, in the presence of a 3-fold excess of NaI with respect to CEVE.

copolymers containing CEVE (Figure B, Supporting Information). The evaluation of the conversion, α_{IEVE}, was noted from the high field shift of the triplet from 3.82 to 3.45 ppm assigned to CH_2Cl into CH_2I (Figure 4), as follows:

$$\alpha_{\mathrm{IEVE}} = \frac{\int_{3.45} CH_2I}{\int_{3.45} CH_2I + \int_{3.82} CH_2Cl} \tag{7}$$

where $\int CH_2X$ represents the integral of the signal assigned to the CH_2X group.

Figure 3 represents the conversion of CEVE into 2-iodoethyl vinyl ether (IEVE), α_{CEVE}, versus time according to the concentration of monomer obtained with 3 equiv of NaI, in acetone, at 65 °C.

A CEVE concentration of 0.234 mol L^{-1} allowed a quasi-complete conversion after 7 days. As expected, the higher the concentration, the faster the reaction. However, beyond a concentration of 0.6 mol L^{-1}, the rate of the reaction did not increase further. Such an exchange reaction is called a Finkelstein reaction.[85] This S_N2 nucleophilic substitution occurs with a single-step mechanism, and when the solution is saturated in iodide salt, its concentration can be considered as constant, and the kinetics of that reaction is pseudo first order. Plotting ln([CEVE]/[CEVE]$_0$) versus the reaction time led to a straight line, the slope of which is the rate constant $k = 1.0 \times 10^{-5}\ s^{-1}$ at 65 °C (Figure C, Supporting Information). Hence, that reaction of iodination was transposed onto copolymers. They were analyzed by ^1H NMR spectroscopy (Figure 4). Spectra obtained showed a high field shift of the signal corresponding to the protons adjacent to the halogen atom from 3.5 ppm when linked to a chlorine atom to 3.1 ppm when located close to an iodine atom. From the comparison of the ^1H NMR spectra of **P5** and **P5i** products, a small remaining signal assigned to $-CH_2Cl$ groups (3.5 ppm) could be observed.

The yields, reported in Table 3, show the difficulty to modify the copolymers completely and the problems noted when adapting a reaction from a model compound to a polymer. These lower conversion values may arise from the lower solubility of the copolymer in acetone compared to the monomer. The lower access of the reagent to the $-CH_2Cl$ sites due to the entanglement of the polymer coils may also be responsible. Different reaction times were also attempted on the poly[(CTFE-*alt*-CEVE)-*co*-(CTFE-*alt*-CHVE)] terpolymer (**P1**) showing an increase of the yield from 2 days (**P1i1**) to 7 days (**P1i2**) (Table 3).

Amination of the Copolymers. The ammonium groups were introduced via a substitution of the iodoalkyl groups of the copolymers by trimethylamine (TMA). This type of nucleophilic substitution has successfully been achieved on copolymers bearing poly(vinylbenzyl chloride) side groups at 40 °C, and the reaction time between TMA and the iodine atom in the copolymer did not exceed 48 h.[86−91] Our reactions were carried out under that procedure. In some cases, a change of the solubility was observed after 24 h, corresponding to a deep change in the chemical nature of the polymer resulting in a modification of its behavior in solution. This drift in solubility can be considered as an evidence of the grafted ammonium groups. The evolution of the chemical structure of the copolymer was monitored by ^1H NMR spectroscopy and is shown in Figure 4. Originally centered at 3.1 ppm when linked to an iodine atom, the signal of the terminal methylene shifted to 3.3 ppm when adjacent to an ammonium group. Other signals, located between 2.3 and 2.9 ppm, at 3.8 ppm, and at 4.2 ppm corresponding to $-CTFE-CH_2-CH(OR)-CTFE-$, $-O-CH_2-CH_2$, and $-CTFE-CH_2-CH(OR)-CTFE-$, respectively, remained unchanged.

In addition, the ^1H NMR spectra showed that the substitution by TMA was not associated with an elimination reaction (dehydroiodination), which could have occurred due to the basicity of the amine and to the high reactivity of the iodine. Indeed, a dehydroiodination side reaction would have led to the formation of a vinyl group, which protons would have appeared in the 5−7 ppm range in the ^1H NMR spectrum.

Stability of Poly(CTFE-*alt*-VE) Copolymers in Basic Media. Poly(CTFE-*alt*-VE) alternating copolymers are composed of CTFE/VE diads which contain a succession of methylene and chlorofluoromethylene units. These diads may undergo a reaction of dehydrofluorination or dehydrochlorination under basic conditions, and it was necessary to study their behavior in highly basic media. Although the stability in such conditions of analogous polymers such as

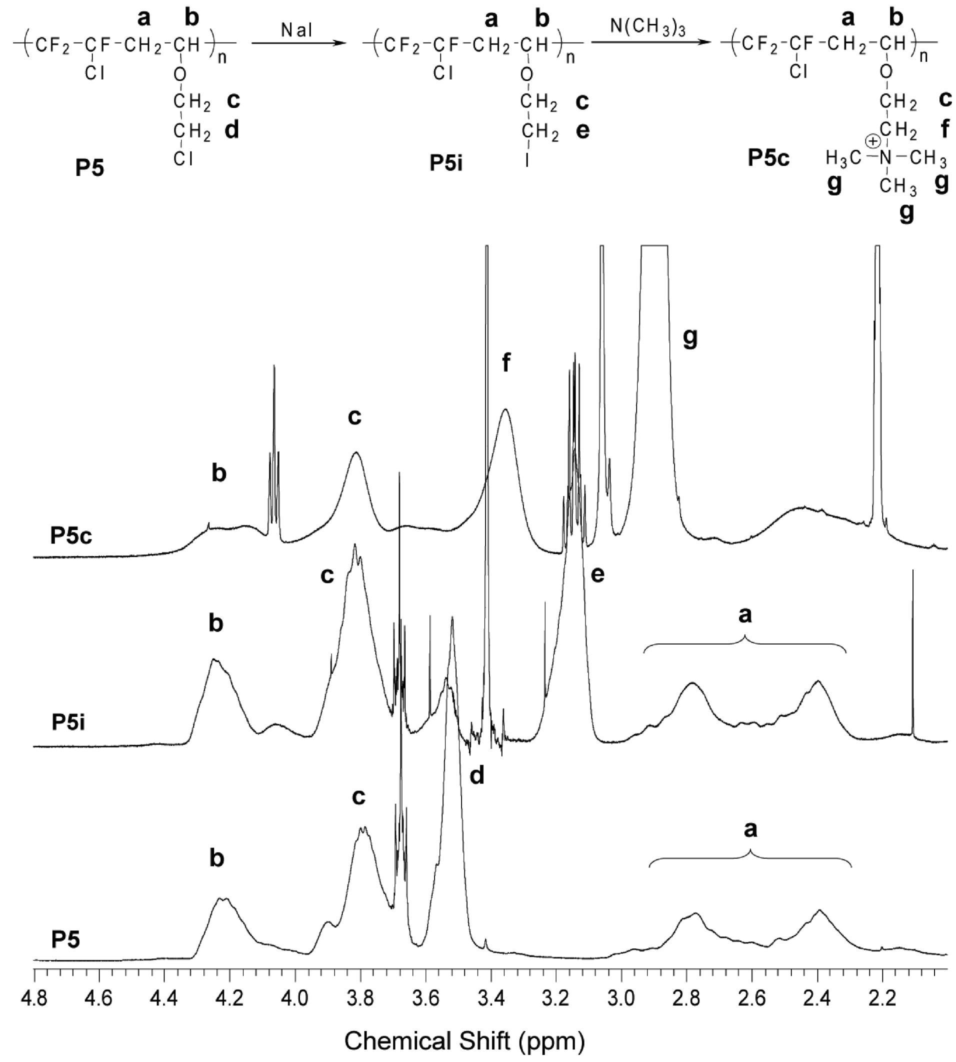


Figure 4. ^{1}H NMR spectra of the poly(HFP-*alt*-CEVE) copolymer (**P5**), iodinated (**P5i**), and cationized (**P5c**), in $CDCl_3$ for the first two and in DMSO-d_6 for the third one.

Table 4. Chemical Stability of Poly(CTFE-*alt*-CHVE) Alternating Copolymers in Basic Media[a]

sample	basic media[b]	T (°C)	t (days)	solvent
S1	NaOH (2.5 mol L^{-1})	50	7.0	water (100 mL)
S2	NaOH (1.25 mol L^{-1})	50	7.0	water + DMF (1:1 vol, 100 mL)
S3	$H_2N-(CH_2)_3-N(CH_3)_2$ (2 equiv) + TEA (2 equiv)	90	2.2	toluene (100 mL)
S4	TEA (3 equiv)	90	7.0	DMF (40 mL)
S5	TMA (3 equiv)	25	7.0	toluene (40 mL)
S6	TEA (3 equiv)	90	3.2	acetonitrile (100 mL)
S7	$HO-(CH_2)_2-SH$ (2 equiv) + TEA (2 equiv)	90	7.0	DMF (40 mL)

[a] The "S" in the sample name stands for stability. TEA = triethylamine, TMA = trimethylamine, T = temperature, and t = time. [b] The amount of amines is noted as equivalent to the (CTFE−CHVE) units.

ECTFE has been demonstrated,[35,37,39] the stability of poly(CTFE-*alt*-VE) copolymers, satisfactory in acidic media,[92] remains unclear in basic media and was worth investigating. A poly(CTFE-*alt*-CHVE) alternating copolymer was synthesized by radical polymerization and obtained in 74% yield (**P2**, Table 1). The molecular weight, measured by SEC, led to $M_n = 12\,100$ g mol^{-1} with a polydispersity index of 1.9. To evaluate its stability in basic media, it was dipped into various basic solutions at different temperatures. The conditions are listed in Table 4. NMR and SEC analyses were performed to investigate any possible degradation/aging, and no changes were observed (see Supporting Information). Also, no change of color was observed whatever the conditions.

The ^{1}H NMR spectrum (Figure 5) clearly shows the methylene protons of the cyclohexyl groups in the region ranging from 0.9 to 2.3 ppm, while the methylene protons of the main chain are located between 2.4 and 3.5 ppm. The methyne are also clearly identified at 4.8 ppm (for the one from the main chain) and at 3.6 ppm for the cyclohexyl one. This difference of chemical shifts is a further evidence of the alternation in which the difluoromethylene group adjacent to the methyne in the backbone induces a low field shift. As evidenced from this ^{1}H NMR spectrum, no apparent degradation of the cyclohexyl group was observed since none of the corresponding signals have been affected. Furthermore, no modification of the backbone was observed either, especially at the junctions between methylene and

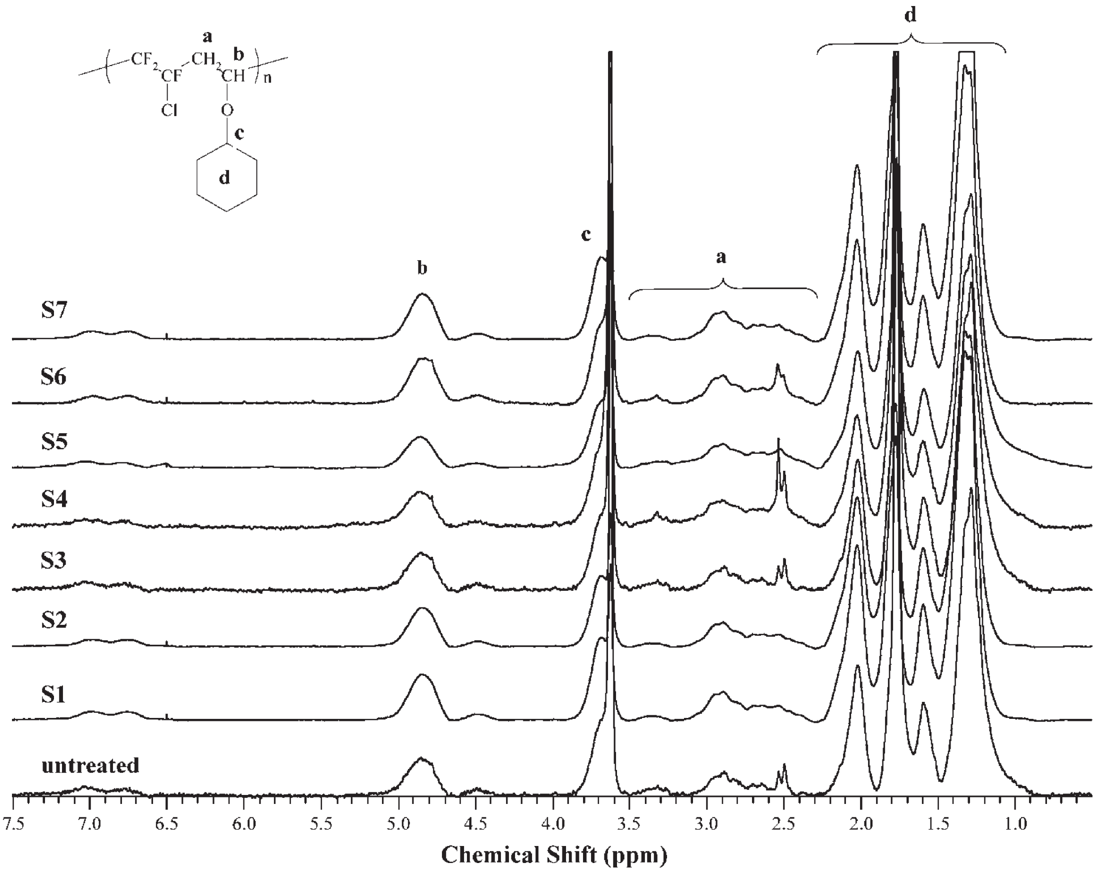


Figure 5. ^{1}H NMR spectra of the poly(CTFE-*alt*-CHVE) copolymer (untreated, lower spectrum) and exposed to various basic solutions (**S1**−**S7** in Table 4): **S1**: NaOH (2.5 mol L^{-1}), 7 days; **S2**: NaOH (1.25 mol L^{-1}), 7 days; **S3**: $H_2N-(CH_2)_3-N(CH_3)_2$ (2 equiv) + $N(CH_2CH_3)_3$ (2 equiv), 2.2 days; **S4**: $N(CH_2CH_3)_3$ (3 equiv), 7 days; **S5**: $N(CH_3)_3$ (3 equiv), 7 days; **S6**: $N(CH_2CH_3)_3$ (3 equiv), 3.2 days; **S7**: $HO-(CH_2)_2-SH$ (2 equiv) + $N(CH_2CH_3)_3$ (2 equiv), 7 days.

fluoromethylene groups where a dehydrofluorination reaction could be expected (the formation of a −CH=CF− double bond would induce the presence of the signal beyond 6.0 ppm).[93−98]

The ^{19}F NMR spectra (Figure D, Supporting Information) also confirm the stability of these copolymers since no evolution of the signals in the spectra has been observed (if fluorovinyl groups (−CH=CF−) would have been formed, a new signal should be present at −118 ppm).[98,99]

The SEC analyses of the different copolymers (untreated, **S1**−**S7**) (Figure E, Supporting Information) show in some cases a slight increase in molecular weight (13 200 vs 12 120 g/mol) accompanied by a slight decrease in the polydispersity index (1.70 vs 1.92). This phenomenon appeared for samples treated by amines or thiol solutions, where the reaction was carried out in an organic solvent, and a precipitation was necessary to isolate the product, which tends to eliminate the lowest molecular weight fraction. For sample treated by sodium hydroxide aqueous solution, a simple filtration was enough to recover all the product.

Under basic conditions, poly(CTFE-*alt*-CHVE) copolymers were clearly more stable than poly(VDF) polymers[93−98] which undergo a dehydrofluorination. This arises from the presence of two CF_2 groups, adjacent to the CH_2 groups in poly(VDF) which have an electron-withdrawing effect making the protons in methylene groups more acidic and consequently more sensitive to bases.

Electrochemical and Thermal Properties. Although these present poly[(CTFE *alt*-VE)-*co*-(HFP-*alt*-VE)] terpolymers did not require good mechanical properties to be cast as electrode binders, the characterization of the properties such as ionic exchange capacity (IEC), swelling ratio, or ionic conductivity implied the preparation of self-supporting membranes to assess such analyses.

Electrochemical Properties. Table 5 lists the obtained values for all electrochemical properties (IEC, swelling, and conductivity) of all the poly(CTFE-*alt*-CEVE) copolymers and poly[(CTFE *alt*-CEVE)-*co*-(CTFE-*alt*-VE)] terpolymers as well as their composition.

Some cationized copolymers were water-soluble (**P5c**, **P6c**, **P11c**, **P12c**) and could not be used as electrode binder while others were not water-soluble (**P1c1**, **P1c2**, and **P4c**) and did have the adequate solubility in DMSO to be tested as well. **P1c1** and **P1c2** probably owed their insolubility in water to their low ratio of hydrophilic ammonium groups compared to hydrophobic cyclohexyl groups. This hypothesis cannot be assumed in the case of **P4c** since this copolymer had the highest theoretical IEC (2.42 mequiv g^{-1}). In this case, the explanation may arise from the mechanical properties. Since the synthesized copolymers have similar molecular weights (7800 g mol^{-1} < M_n < 25 400 g mol^{-1}), the crystallinity and the glass transition temperature varied according to the nature of the incorporated monomers. Also, the accessibility to the ammonium sites on the polymer chains can also play a major role. Nevertheless, both **P1c2** and **P4c** got broken during the conductivity test.

The water content of the water insoluble quaternary ammonium-modified polymers varied between 13% and 25% with IEC values ranging from 0.5 to 0.72 mequiv g^{-1}. Regarding the conductivity, the brittleness of **P1c2** and **P4c** prevented from any measurement, and only **P1c1** could be assessed (0.13 mS cm^{-1}). Table 5 shows how difficult it was

Table 5. Membrane-Related Properties of the Different Cationized Poly[(CTFE *alt*-VE)-*co*-(HFP-*alt*-VE)] Terpolymers and a Recall of Their Composition[a]

	copolymer composition (%)							
sample	CTFE	HFP	CEVE	VE	IEC_{th}[c] (mequiv g^{-1})	IEC_{exp} (mequiv g^{-1})	water uptake (%)[b]	conductivity (mS cm^{-1})
P1c1	50		12	CHVE (38)	0.52	0.50	19	0.13
P1c2	50		12	CHVE (38)	0.81	0.72	25	
P4c	50		50		2.42	0.66	13	
P5c[d]	0	50	50		3.36		water-soluble	
P6c[d]	31.5	18.5	50		3.63		water-soluble	
P11c	50	0	26	EVE (24)	1.93		water-soluble	
P12c	50	0	27	BVE (23)	2.11		water-soluble	

[a] The "c" in the sample name stands for cationized copolymer. Standard deviation: conductivity: 12%; water content: 5%; IEC: 12.5%. Thickness **P1c1** = 125 μm. Solubility: 1 g of polymer for 2 g of dimethyl sulfoxide. [b] $(m_h - m_s)/m_S$ = mass of product relative to the mass of solvent. [c] Calculated regarding to the amount of CEVE, in the condition where all Cl have been substituted by ammonium groups: $IEC_{th} = [(\%CEVE \times 1000)/(\%CEVE \times M_{TMAEVE} + \%VE \times M_{VE} + \%CF_2CFX \times M_{CF_2CFX})] \times T_I$, where %VE and $\%CF_2CFX$ represent the vinyl ether fractions (CHVE, EVE, or BVE) and fluorinated olefins (CTFE and/or HFP) fractions in the copolymer, respectively, M_{TMAEVE} is the molar mass of cationized CEVE by TMA and washed with sodium hydroxide (TMAEVE = trimethylethyl vinyl ether ammonium), and T_I is the ratio iodinated of the copolymer. [d] Initial nonprecipitated copolymer.

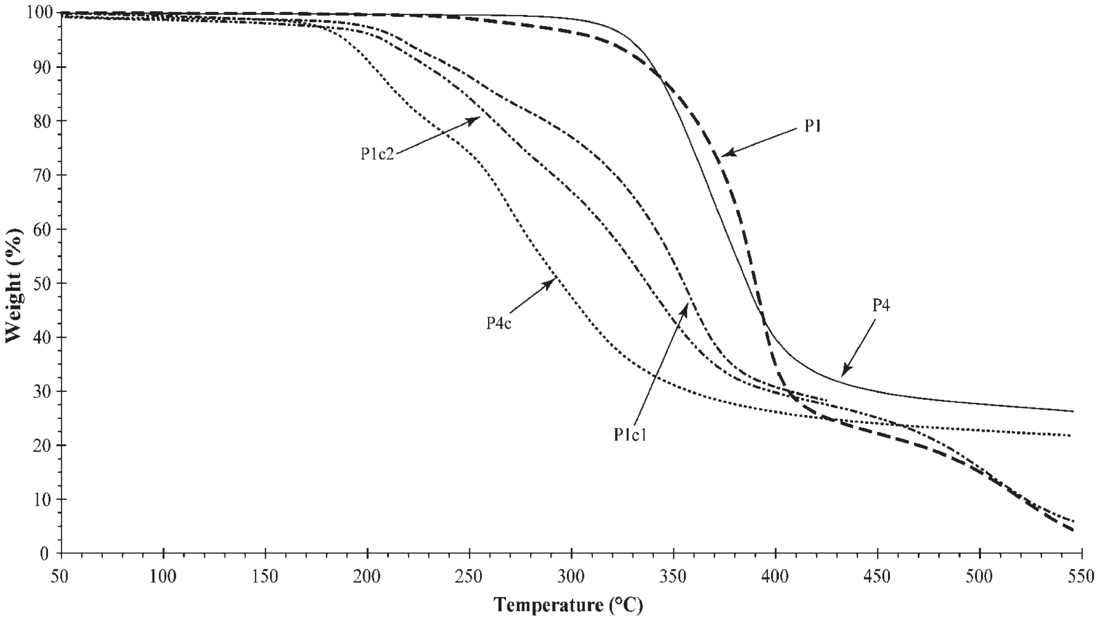


Figure 6. TGA thermograms (under air, at 10 °C min^{-1}) of the initial (**P4**) and cationized (**P4c**) poly(CTFE-*alt*-CEVE) copolymers and the original (**P1**), slightly cationized (**P1c1**), and highly cationized (**P1c2**) poly[(CTFE-*alt*-CHVE)-*co*-(CTFE-*alt*-CEVE)] terpolymers.

to find out the suitable compromise to obtain the optimal conductivity, favored by the largest amount of ammonium group and water insolubility. For example, **P1c1** copolymer, with the lowest amount of CEVE, and consequently the lowest amount of ammonium groups (IEC_{th} = 0.52 mequiv g^{-1}), was not water-soluble, which allowed to assess its IEC (0.5 mequiv g^{-1}) and its conductivity (0.13 mS cm^{-1}) values. The reverse case happened for **P5c**, **P6c**, **P11c**, and **P12c** copolymers where the ammonium content is higher, but this resulting water solubility made them impossible to be used as electrodes binders.

Thermal Analysis. Figure 6 represents the thermograms obtained by thermogravimetric analysis (TGA) for the **P1** and **P4** copolymers in its chlorinated or ammoniated forms. Under the conditions used for the TGA (25−550 at 10 °C min^{-1}, under air), the poly(CTFE-*alt*-CHVE) (**P2**) and poly(CTFE-*alt*-EVE) (**P8**) copolymers had an initial degradation temperature above 300 °C, in good agreement with the literature.[57,100] The decomposition temperatures at 10% weight loss (Table 2) show that most unmodified polymers do not decompose up to 300 °C. The comparison of the thermograms (Figure 6) clearly shows the thermal stability loss of the copolymers modified with the ammonium groups. The thermal stability was much affected when the ammonium ratio increased. This degradation is closely linked to the Hoffman type degradation reaction of these ammonium groups.[101]

Although no clear indication on the thermostability could be drawn from the TGA thermograms, it is safe to assume that these copolymers should resist at 50 °C regarded as the fuel cell operating conditions. In addition, during the preparation of the membranes, the samples were dried at 50 °C for 24 h, and no change was observed in the aspect of the membranes.

Conclusions

Alternating poly(CTFE-*alt*-EV) copolymers and poly[(CTFE *alt*-VE)-*co*-(HFP-*alt*-VE)] terpolymers were synthesized from fluorinated olefins (CTFE, HFP) and vinyl ethers (CEVE, CHVE, BE, and EVE) and were obtained in high yield (>85%). For the first time, copolymers based on HFP and VE were prepared. Most co- and terpolymers showed a good thermostability ($T_{d,10\%} \geq 300$ °C). Though not investigated, these copolymers should have potential application for coatings. Interestingly, the presence of 2-chloroethyl vinyl ether (CEVE) in these copolymers enabled, after two consecutive substitutions

(NaI and then trimethylamine), the introduction of ammonium groups in the chains. These copolymers bearing cationic sites are original and susceptible to conduct hydroxide ions. Considering their stability in basic media and their properties, these materials were a good choice as electrode binder for solid alkaline fuel cells. According to the grafting ratio in ammonium groups, these polyelectrolytes exhibited different solubility. Some of them were water-soluble, while others were not, but all were soluble in organic media and exhibited IEC values ranging from 0.5 mequiv g^{-1} to 0.72 mequiv g^{-1}. However, combining the more favorable CEVE content, molecular weight, mechanical properties, and hydrophobia, these electrochemical properties should be improved. The assessment of the membrane−electrode assembly performances is currently under progress.

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Supporting Information Available: Assessment of copolymer compositions, ^{1}H NMR spectra of copolymers with various vinyl ethers, iodination of 2-chloroethylvinyl ether monomer, ^{19}F NMR and SEC of copolymer exposed to various basic solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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