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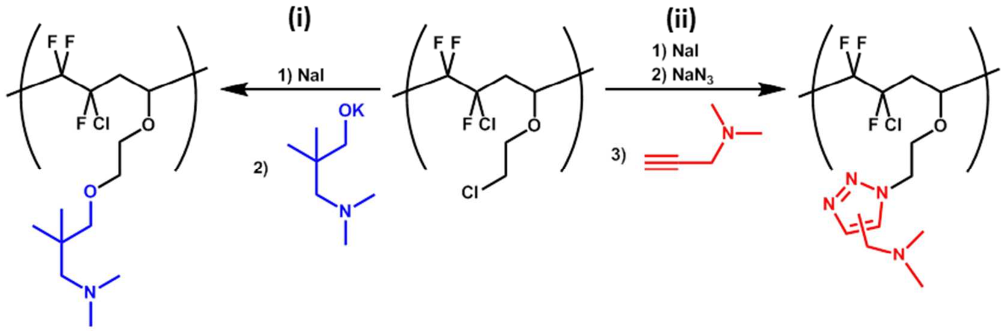
Graphical Abstract



Methods to prepare Quaternary Ammonium Groups-Containing Alternating Poly(chlorotrifluoroethylene-*alt*-vinyl ether) Copolymers

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Abstract

The radical copolymerisation of electron-acceptor chlorotrifluoroethylene (CTFE) with electron-donor vinyl ethers (VEs) produced poly(CTFE-*alt*-VE) alternating fluorinated copolymers with a high content of functional groups. This article describes methods to synthesise poly(CTFE-*alt*-VE) copolymers that bear ammonium-groups insensitive to Hofmann degradation. Direct preparation and post-polymerisation functionalisation methods are presented. First, the radical copolymerisation of CTFE with a tertiary amine-carrying vinyl ether led to low molecular weight-copolymers with imperfect structure. That copolymerisation and the quaternisation of the amino groups using methyl iodide were however accompanied by side reactions, including transfer reactions and significant loss of functionality. In contrast, the second strategy dealt with the post functionalisation of an alternated poly(CTFE-*alt*-2-chloroethyl vinyl ether) copolymer. Halogen exchange of poly(CTFE-*alt*-CEVE) copolymers was carried out using the efficient Finkelstein reaction. Then, the nucleophilic substitution of the iodine atoms on the obtained poly(CTFE-*alt*-IEVE) copolymer led to poor yield of functionalisation and was accompanied by a substantial amount of side reactions. Then, the iodine atoms in poly(CTFE-*alt*-IEVE) copolymers were chemically changed quantitatively into azides (especially from microwave activation) and the resulting azido-containing copolymer was reacted with 1-dimethylamino-2-propyne. An optimisation of this Huisgen's or thermal cycloaddition showed that i) a copper catalyst led to cross-linked copolymers, ii) whereas in the absence of the copper catalyst, the cycloaddition was slow and only converted ca. 60 % of the azides; iii) then, microwave activation led to high yield in a few minutes. Dimethylamino groups were inserted onto the copolymeric backbone and subsequently quaternised using iodomethane efficiently. Such copolymers, potentially resistant to alkaline media and able to promote hydroxide anions conduction, may exhibit interesting properties as component of solid alkaline fuel cell membranes.

1. Introduction

Fluoropolymers (i.e. polymers bearing highly electronegative fluorine atoms on their backbone) display a wide range of remarkable properties.[1] They can be elastomers (case of poly poly(vinylidene fluoride-*co*-hexafluoropropylene) copolymers, poly(VDF-*co*-HFP), or poly(VDF-*ter*-HFP-*ter*-tetrafluoroethylene) terpolymers, poly(tetrafluoroethylene-*alt*-propylene), poly(chlorotrifluoroethyene-*alt*-vinyl ethers), poly(CTFE-*alt*-VE) copolymers, thermoplastics such as the semicrystalline poly tetrafluoroethylene (PTFE), PCTFE, or PVDF, and also thermoplastic elastomers ((PVDF-*b*-poly(VDF-*co*-HFP)-*b*-PVDF) for examples.[1] The very high bond dissociation energy of the C-F bond endows fluoropolymers with exceptional high resistance to temperature, aging, and chemical (bases, acids or oxidants) aggressions. Their fluorinated backbones also confers fluoropolymers both hydrophobicity and lipophobicity. Moreover, their refractive indices are very low and some of them display remarkable electroactivity (ferroelectricity, piezoelectricity, electrostriction…).[2] These unusual properties allow fluoropolymers to find niche applications in numerous High-Tech areas such as aerospace and aeronautics, high performance elastomers and surfaces, coatings, textile finishings, electronics, energy, etc… However, fluoropolymers are relatively expensive and, in their vast majority, difficult to functionalise or to cross-link. Main fluoroolefins, such as TFE, VDF, CTFE, HFP are indeed non-functional. The monomer of the NAFION® membrane, a perfluorinated olefin that bears an ω- sulfonyl fluoride end-group, is one of the rare example of functional fluoroolefins. Thus, the preparation of functional fluoropolymers is a major challenge.

Copolymerisation of fluoroolefins with functional comonomers is arguably the simplest method to prepare functional fluoropolymers. Fluoroolefins are in general electron poor and have peculiar reactivity. Indeed, fluoroolefins occupy a special place in Alfrey and Price[3a-b] semi-empirical reactivity Q and e scale where Q represents the extent of the conjugation of the carbon-carbon double bond with its substituents, and e characterises the electron-donating ($e<0$) or electron-attracting ($e>0$) behaviour of the monomer. Fluoroolefins exhibit very low Q (close to zero) and very positive e values (VDF: Q= 0.008-0.036, e= 0.4-1.2; TFE: Q= 0.031-0.049, e = 1.22-1.84; CTFE: Q= 0.020-0.031, e= 1.48-1.84).[3-5] Monomer with similar Q values copolymerise well. If in addition their e values are also high and of opposite sign, monomers tend to copolymerise in an alternating fashion. Usually, fluoroolefins do not copolymerise well with non-fluorinated monomers. However, strong electron-donating monomers do copolymerise with fluoroolefins with a high tendency to alternation. Chlorotrifluoroethylene (CTFE) and vinyl ethers, for example, are proven to copolymerise easily and to produce highly alternating copolymers.[6] PCTFE has excellent film forming properties,[6] flame retardency,[7] resistance to chemical attack and interesting gas barrier property and is thus used in a large range of applications from valves and O-rings in the petrochemical industry, as packaging materials for drugs in the pharmaceutical industry,[8] and in advanced coatings.[1,6, 9-11] PCTFE has a very high melting temperature (214-220 °C) and only oligomers are soluble in common organic solvents. It is very crystalline and difficult to crosslink. In contrast, vinyl ethers are easy to crosslink or functionalise. Functional vinyl ethers are indeed synthesized easily *via* transetherification.[6, 12-16] Usually polymerized by cationic polymerization with HI/I_2[17] or triflic acid/tetrahydrothiophene,[18] vinyl ethers do not homopolymerize under radical polymerization conditions.[19-22] The copolymerisation of strongly electron-donating vinyl ethers (e.g. vinyloxyethane: Q=0.018, e=-1.80)[4] with fluoroolefins leads to near perfect alternating copolymers.[6,11,21] Studies by Boutevin *et al.*[5,22] have shown that the alternating copolymerisation of CTFE and vinyl ethers proceeds *via* a free monomer mechanism[23,24] although charge transfer complexes are readily formed in solution.[25-28] Indeed, in these studies[5,22], Boutevin et al. did not observe any head-to-head or tail-to-tail addition which would have been produced if the charge transfer complexes had polymerized. Poly(CTFE-*alt*-VE) copolymers are thus very interesting for their alternating structure and their ease of functionalization. This class of copolymers has found applications in high performance paints and coatings,[11, 29-34] such as Lumiflon® product marketed by the Asahi Glass Co. Ltd.[35-39] Poly(CTFE-*alt*-VE) copolymers are also interesting for applications in energy, in fuel-cells membranes,[40-43] lithium-ion batteries,[44-45] and in photovoltaic materials.[46]

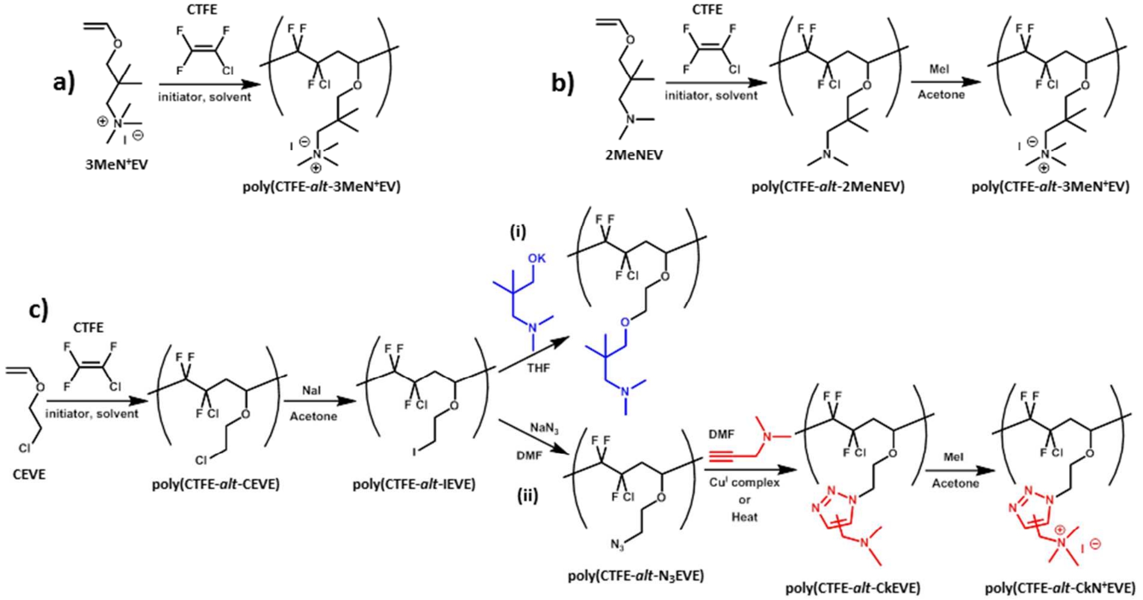
To prepare functional copolymers, two strategies can typically be used: (1) the direct copolymerisation of functional monomers and (2) the post-polymerisation functionalization of copolymers. Post-polymerisation functionalisation was successfully used with copolymers of CTFE with 2-chloroethyl vinyl ether (CEVE) to prepare copolymers bearing azoles[43,47] or phosphonic acid groups[42] for applications in fuel-cell membranes. Valade *et al.*[40] prepared electrodes binders with quaternary ammonium groups by nucleophilic sustitution. These polymers presented hydrogen atoms in β position of the ammonium groups and thus were sensitive to the Hofmann degradation[48] in alkaline media. The use of ATRP to prepare polystyrene grafts from poly(CTFE-*alt*-CEVE) copolymers which were subsequently chloromethylated and quaternised using trimethylamine partly overcame that issue.[49] This article aims at supplying improved methods to prepare poly(CTFE-*alt*-VE) copolymers that bear quaternary ammonium groups insensitive to Hofmann elimination. Such copolymers could be of interest to design original membranes for Solid Alkaline Fuel-Cells (SAFC).[50] To the best of our knowledge, Alaaeddine *et al.*[51,52] have so far reported the only examples of poly(CTFE-*co*-comonomer) copolymer with ammonium dangling groups resistant to Hofmann degradation for potential application in SAFC.

2. Results and discussion

Two synthesis strategies were used to prepare fluorinated copolymers that bear amine or ammonium groups: 1) Direct copolymerisation of chlorotrifluoroethylene (CTFE) and amine-functionalised vinyl ethers, and 2) Post polymerisation functionalisation of copolymers based on CTFE and vinyl ethers.

Note : Alternating copolymerisation of CTFE and vinyl ethers has been shown to proceed *via* polymerisation of the free monomers.[5, 22] Consequently, the copolymers only display head-to-tail addition as represented in all the drawings shown in this article.

Scheme 1. General synthesis scheme for a) Direct copolymerisation of CTFE and 3MeN$^+$EV, b) Post-polymerisation functionalisation of copolymers based on poly(CTFE-*alt*-2MeNEV), c) Post polymerisation functionalisation strategies: (i) Direct alkylation of poly(CTFE-*alt*-CEVE) copolymer and (ii) cycloaddition of azides and alkynes starting from poly(CTFE-*alt*-CEVE) copolymers



2.1. Direct radical copolymerisation of chlorotrifluoroethylene and amine-functionalised vinyl ethers.

The amine-functionalised vinyl ether, vinyloxy-3-dimethylamino-2,2-dimethylpropane (2MeNEV), was prepared by palladium acetate-catalysed transetherification of vinyloxyethane with 3-dimethylamino-2,2-dimethylpropan-1-ol. This vinyl ether, insensitive to Hofmann elimination, was obtained, after distillation, in relatively good yield (51%) and purity (92%). The presence of signals centered at 3.9, 4.2 and 6.5 ppm in the ^{1}H NMR spectrum (Figure S1) assigned to ethylenic protons attests the formation of such a vinyl ether that was also confirmed by the ^{13}C NMR spectrum (Figure S2) by signals at 86.2 and 153.1 ppm. This monomer was further quaternised using iodomethane to prepare the ammonium-bearing vinyl ether (3MeN$^+$EV). This reaction proceeded in quantitative yield.

The radical copolymerisation was carried out using various experimental conditions and the results are listed in Table 1. Attempts to copolymerise CTFE and 3MeN$^+$EV (Scheme 1.a) in different solvents using a variety of initiators were unsuccessful (entries 2-5, Table 1). This might arise from the reduction of the peroxide radicals by the iodide counter anion of the vinyl ether. Indeed, after reaction, the polymerisation medium acquired a yellow color which suggests the formation of molecular iodine. The hypothesis that iodide anions were responsible for the radical copolymerisation failures seems to be further supported by the fact that in the case of 2MeNEV, the copolymerisation in 1,1,1,3,3-pentafluorobutane (Scheme 1.b) proceeded with satisfactory conversions (entries 6-7, Table 1). However, the copolymers obtained were of surprisingly low molecular weights and of unexpected compositions. Indeed, elemental analysis used to calculate the copolymer compositions (supplementary information, Table S1), showed an excess of fluorine and conversely of CTFE. This discrepancy could be caused by the presence of PCTFE sequences in the copolymer or by side reactions occurring during the copolymerisation. The ^{19}F NMR spectrum of the copolymer (Figure 1.a.) did not exhibit any signals at -130 ppm characteristic of CTFE-CTFE dyads,[53] thus proving the perfect alternated structure of the copolymer. But, the ^{1}H NMR spectrum (Figure 1.b.) was quite complex. In addition to the broad peaks centered at 3.5 ppm and between 4.0 and 4.5 ppm characteristic of –CH_2-C$\underline{H}$O- and-O-C$\underline{H_2}$, this spectrum displays unexpected signals ranging between 6.1 and 6.7 ppm which may be ascribed to end-groups formed *via* transfer reactions (-CF_2-

CFClH and CFCl-CF_2H) as reported by Kumar and Améduri.[54] In addition, the ratio of the integrations of the ^1H NMR signals of CH_3-N and CH_3-C is surprisingly low (0.5 instead of 1) which suggests a loss of amino groups during the polymerisation. The ^{13}C NMR spectrum (Figure 2.a.) also reveals two unexpected signals at 47 and ca. 97 ppm which could be assigned to primary or tertiary carbon atoms. These observations and the low molecular weights of the copolymerssuggest that transfer reactions occurred during this copolymerisation.

In spite of the suboptimal structure, the poly(CTFE-*alt*-2MeNEV) copolymers were reacted with excess iodomethane in acetone at 20 °C to obtain poly(CTFE-*alt*-$3MeN^+EV$) copolymers (Scheme 1.b). After purification (precipitation from diethyl ether), the ^{13}C and ^1H NMR spectra (Figures 2 and 3) of the copolymer show the complete disappearance of $(CH_3)_2NCH_2$- signals (between 2.1 and 2.3 ppm in the ^1H NMR spectrum and at 48.9 ppm and 68.1 ppm in the ^{13}C NMR spectrum) and the appearance of new peaks centered at 3.6 ppm (^1H NMR) and 56.2 ppm (^{13}C NMR) characteristic of the $(CH_3)_3CH_2N^+$. The conversion of tertiary amine into ammonium groups was thus efficient. Nevertheless, the NMR spectra also display unexpected new signals at 1.4 ppm (in the ^1H NMR spectrum) and at 25.2 and 67.4 ppm (in the ^{13}C NMR spectrum). This suggests further that unidentified side reactions occurred concomitantly to the quaternization reaction.

In spite of its easy setup and relatively good efficiency, yielding perfectly alternating copolymers, this synthetic strategy led to copolymers with low molecular weights and was accompanied by significant amount of undesirable side reactions which decreased the number of amine functionalities. The obtained copolymers could still be interesting in blends with other copolymers or, if they could be partly cross-linked, to yield higher molecular mass polymers.

Entry	VE	Feed composition		Solvent	Initiator	Yield (%)	Polymer composition[b]		Mn (g/mol)[c]	PDI
		CTFE	VE				CTFE	VE		
1	CEVE	60	40	PFB	TBPPI	77	46	54	20000	2.6
2	$3MeN^+EV$	67	33	H_2O/CH_3CN (1/1)	TBPPI	0	0	0	n.a.	n.a.
3		70	30	PFB/CH_3CN (1/1)	TBPPI	0	0	0	n.a.	n.a.
4		60	40	H_2O	$(NH_4)_2S_2O_8$	0	0	0	n.a.	n.a.
5		70	30	PFB/H_2O (1/1)	CF_3•[a]	0	0	0	n.a.	n.a.
6	2MeNEV	60	40	PFB	TBPPI	55	61	39	5600	1.7
7		60	40	PFB	TBPPI	64	58	42	3000	1.7

Table 1. Experimental conditions for the radical copolymerisations of CTFE and various vinyl ethers. Abbreviations: CEVE = 2-Chloroethylvinyl ether, $3MeN^+EV$ = vinyloxy-3-trimethylammonium-2,2-dimethylpropane, 2MeNEV = vinyloxy-3-dimethylamino-2,2-dimethylpropane, PFB =1,1,1,3,3-pentafluorobutane, TBPPI = *tert*-butyl peroxypivalate, [a]CF_3• this radical was generated using perfluoro-3-ethyl-2,4-dimethyl-3-pentyl[55,56] [b]calculated from elemental analysis (see Table S1 in supplementary information), [c]measured by SEC-HPLC using polystyrene calibration standards, n.a.: not applicable.

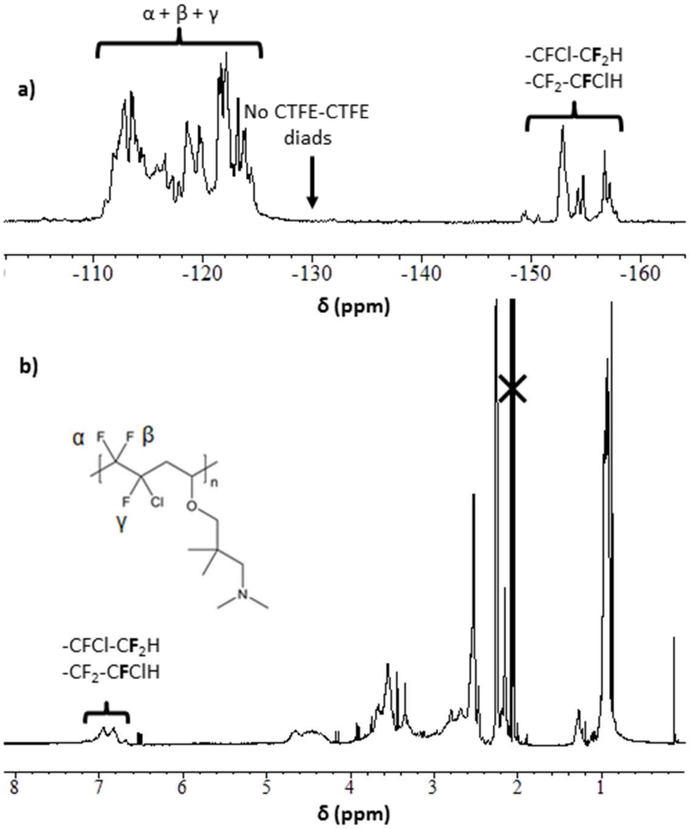
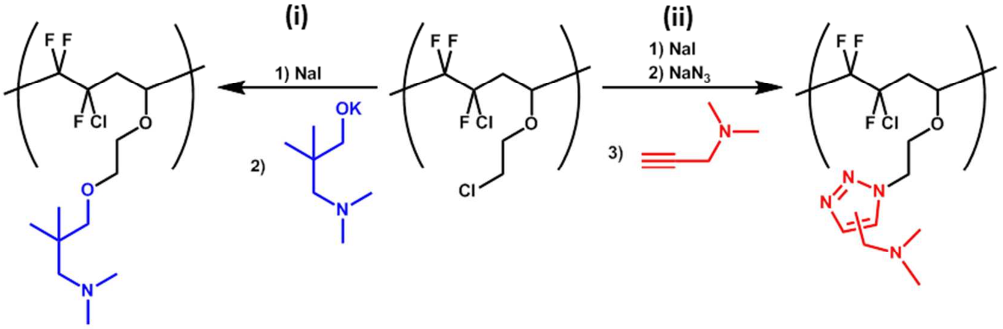


Figure 1. a) ^{19}F NMR and b) ^{1}H NMR spectra in acetone-d$_6$ of poly(CTFE-*alt*-2MeNEV) copolymer (Entry 6, Table 1) Multiplets around 6.9 ppm in ^{1}H NMR and between -150 and -160 ppm in ^{19}F NMR are characteristic of -CF$_2$H and -CFClH end-groups induced by transfer reactions.[54] The crossed-out signal is assigned to acetone.

2.2. Post-polymerization functionalization of copolymers based on chlorotrifluoroethylene and vinyl ethers

Scheme 1.c presents the strategies of examined post-polymerization functionalization to prepare ammonium-containing copolymers from alternating poly[CTFE-*alt*-2-chloroethyl vinyl ether (CEVE)] copolymers: (i) Alkylation using alcoholates and (ii) use of the cycloaddition of azides and alkynes.



Scheme 1. Post polymerization functionalization strategies: (i) Direct alkylation of poly(CTFE-*alt*-CEVE) copolymer and (ii) cycloaddition of azides and alkynes starting from poly(CTFE-*alt*-CEVE) copolymers.

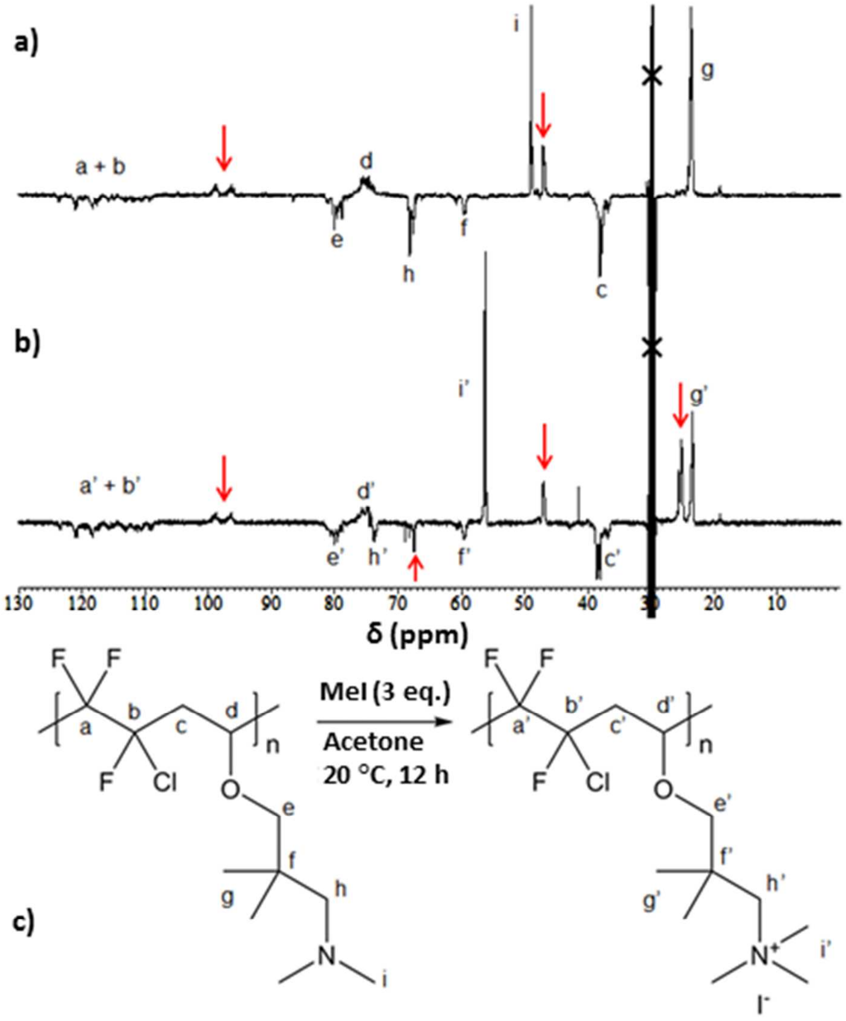


Figure 2. DEPT-135 ^{13}C NMR spectra (recorded in acetone-d$_6$) of a) the poly(CTFE-*alt*-2MeNEV) copolymer and b) the poly(CTFE-*alt*-3MeN+EV) copolymer obtained by methylation of poly(CTFE-*alt*-2MeNEV) copolymer. c) Reaction scheme of the methylation of the poly(CTFE-*alt*-2MeNEV) copolymer. The red arrows indicate unexpected signals that may be caused by side reactions occurring during the copolymerisation and the methylation. The crossed-out signals are assigned to acetone.

2.2.1. Synthesis of poly(CTFE-*alt*-CEVE) copolymer and halogen exchange.

The radical copolymerisation of CTFE with CEVE performed in 1,1,1,3,3-pentafluorobutane (Scheme 1.c) proceeded in good yields (Entry 1, Table 1) and afforded an alternating poly(CTFE-*alt*-CEVE) copolymer. The alternating structure was confirmed by ^{1}H NMR and ^{19}F NMR (no CTFE–CTFE dyads around -127 ppm in ^{19}F NMR,[53] Figure 4). The copolymer composition calculated using elemental analysis also confirmed this alternating structure (Table S1). Finally, the relatively high molecular weight (20,000 g mol^{-1}) suggests that no significant transfer reactions occurred during the copolymerisation.

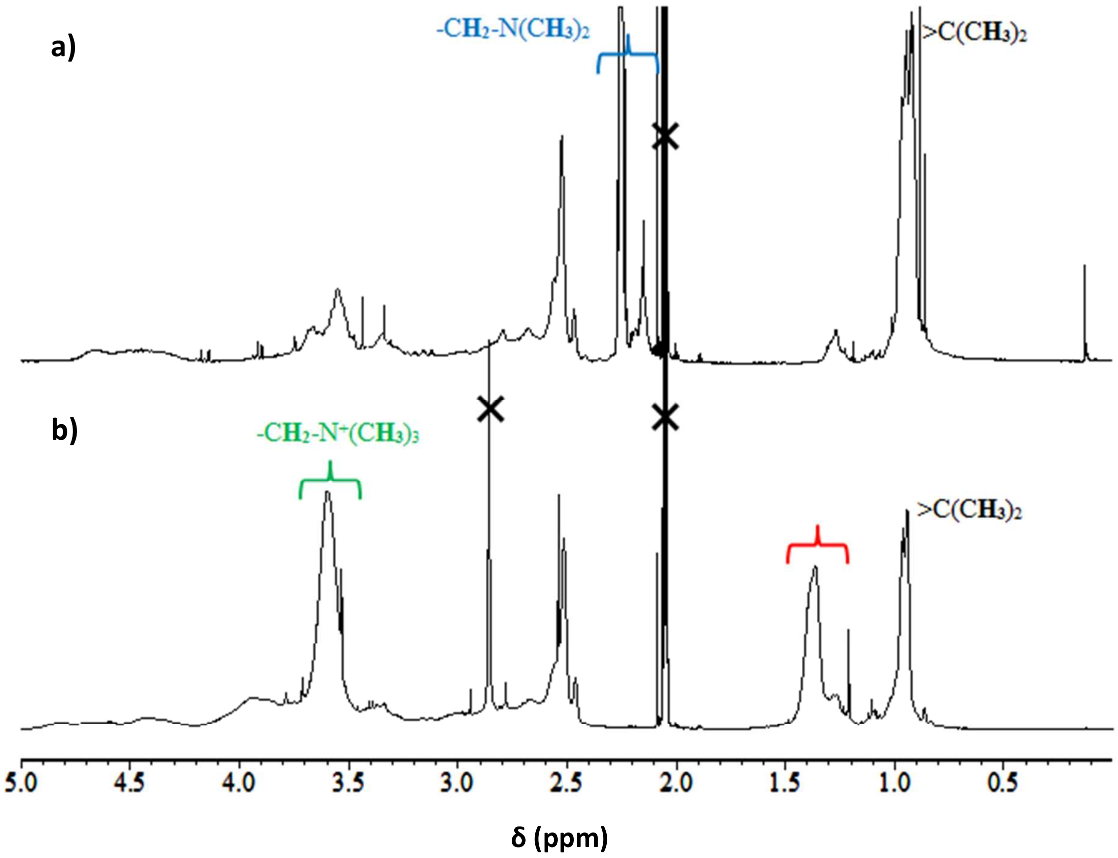


Figure 3. ^{1}**H NMR spectra in acetone-d$_6$ of: a) poly(CTFE-*alt*-2MeNEV) copolymer before methylation (entry 6 , Table 1), and of b) poly(CTFE-*alt*-3MeN$^+$EV) copolymer, obtained after methylation. The red bracket designates a new signal that may be caused by unidentified side-reactions. The crossed-out signals are assigned to acetone and residual water (2.84 ppm)**

Direct nucleophilic substitution of chlorine atoms in primary alkyl chlorides is usually difficult because chlorine is a relatively poor leaving group. Prior to performing the desired nucleophilic substitution, chlorine atoms are thus usually replaced with iodine atoms due to the lower bond dissociation energy of the C-I bond compared to the C-Cl bond (E(C-I) = 180 kJ mol^{-1} for CH_3I whereas E(C-Cl) = 297 kJ mol^{-1} for CH_3Cl).[57] Halogen replacement reaction was thus performed on the poly(CTFE-*alt*-CEVE) copolymer. After seven day-reaction in acetone at 65 °C in the presence of three equivalents of sodium iodide, the resulting poly(CTFE-*alt*-iodoethyl vinyl ether), poly(CTFE-*alt*-IEVE), was isolated by precipitation from cold methanol. The long reaction time ensured a high degree of halogen exchange.[40] A conversion of chlorine to iodine of 93 % was calculated from the ^{1}H NMR spectrum (Figure 5.a.) using the integrals of the methylene groups adjacent to the chlorine atom, at 3.52 ppm, and to the iodine atom, at 3.35 ppm.

Copolymer	yield (%)	% Iodination	Mn (g mol^{-1})	PDI	T_g (°C)	$T_{d,10\%}$ (°C)
Poly(CTFE-*alt*-CEVE)	n.a.	n.a.	20,000	2.6	33	287
Poly(CTFE-*alt*-IEVE)	85	93	20,200	3.5	31	323

Table 2. Chromatographic and thermal analyses (under air at 20 °C/min) of poly(CTFE-*alt*-IEVE) copolymers.

The iodinated polymer has a slightly higher molecular weight than its precursor in agreement with previous studies.[41,58] Its glass transition temperature (Table 2) was not significantly higher than that of its chlorinated copolymeric precursor. Finally, the iodinated copolymer showed a superior thermal stability (Table 2) compared to its chlorinated homologue contrarily to Tayouo's observation.[58]

The iodinated poly(CTFE-*alt*-IEVE) copolymer was then further transformed by nucleophilic substitution.

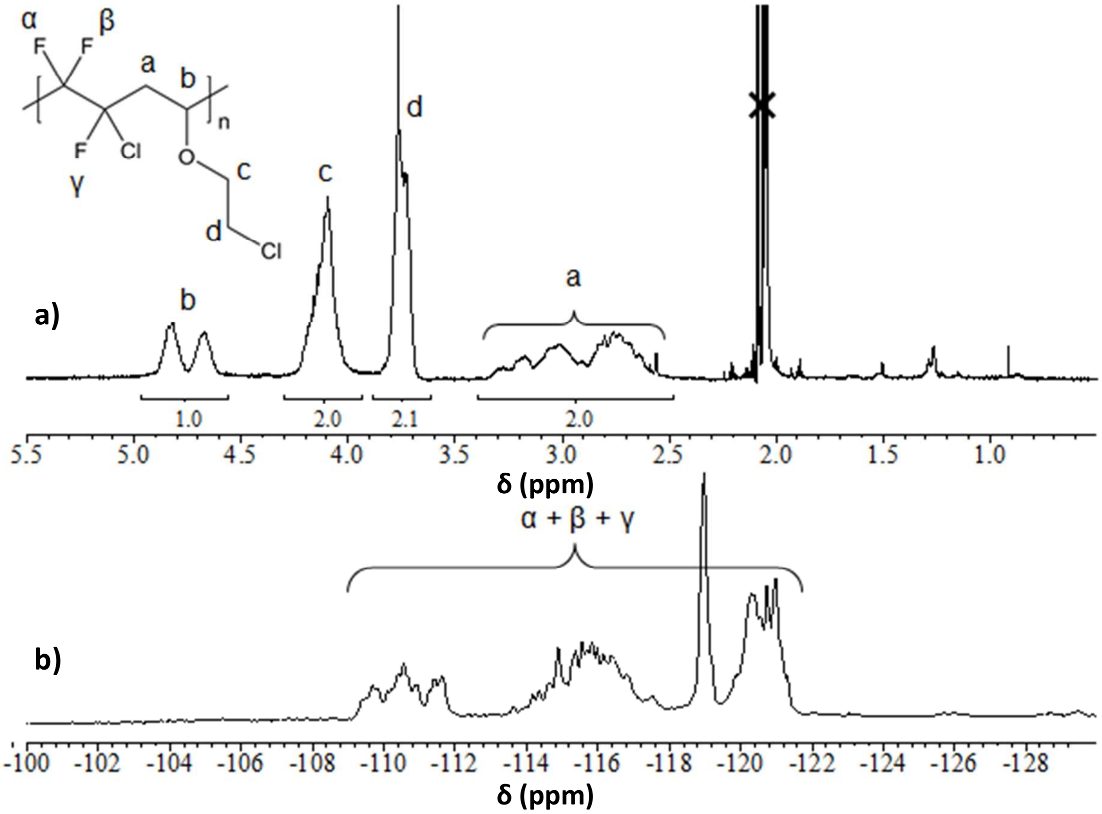


Figure 4. a) ^{1}H NMR spectrum and b) ^{19}F NMR spectrum in acetone-d$_6$ of poly(CTFE-*alt*-CEVE) copolymer (Entry 1, Table 1). The crossed-out signal is assigned to acetone

2.2.2. Alkylation of poly(CTFE-*alt*-IEVE) copolymer

This strategy consists in introducing the amine functions by nucleophilic substitution of the iodine atoms of poly(CTFE-*alt*-IEVE) copolymer using potassium 3-(dimethylamino)-2,2-dimethylpropan-1-olate (Scheme 1.c (i)). The reaction was first successfully tested on a model (small) molecule such as benzyl chloride (Figure S4). Figure S5 compares the ^{1}H NMR spectra of benzyl chloride, 3-(dimethylamino)-2,2-dimethylpropan-1-ol and the expected product. That figure exhibits the presence of the characteristic signals centered at 7.45, 4.65, 2.30 and 0.84 ppm assigned to aromatic protons, methylene in benzyl group, both methyls borne by amino end-group, and both central methyl groups, respectively. The signal of methylene group adjacent to the ether bridge underwent a high field shift from 3.38 (Figure S5 Bottom) to 3.22 ppm (Figure S5 Top). Then, the reaction was carried out on the poly(CTFE-*alt*-IEVE) copolymer using a similar experimental protocol. The alcoholate was prepared by reaction of 3-(dimethylamino)-2,2-dimethylpropan-1-ol with potassium *tert*-butoxide at 20 °C and added dropwise onto a THF solution of the copolymer. The reaction medium was then left at various temperatures (0-60 °C), even under microwave activation (Table 3).

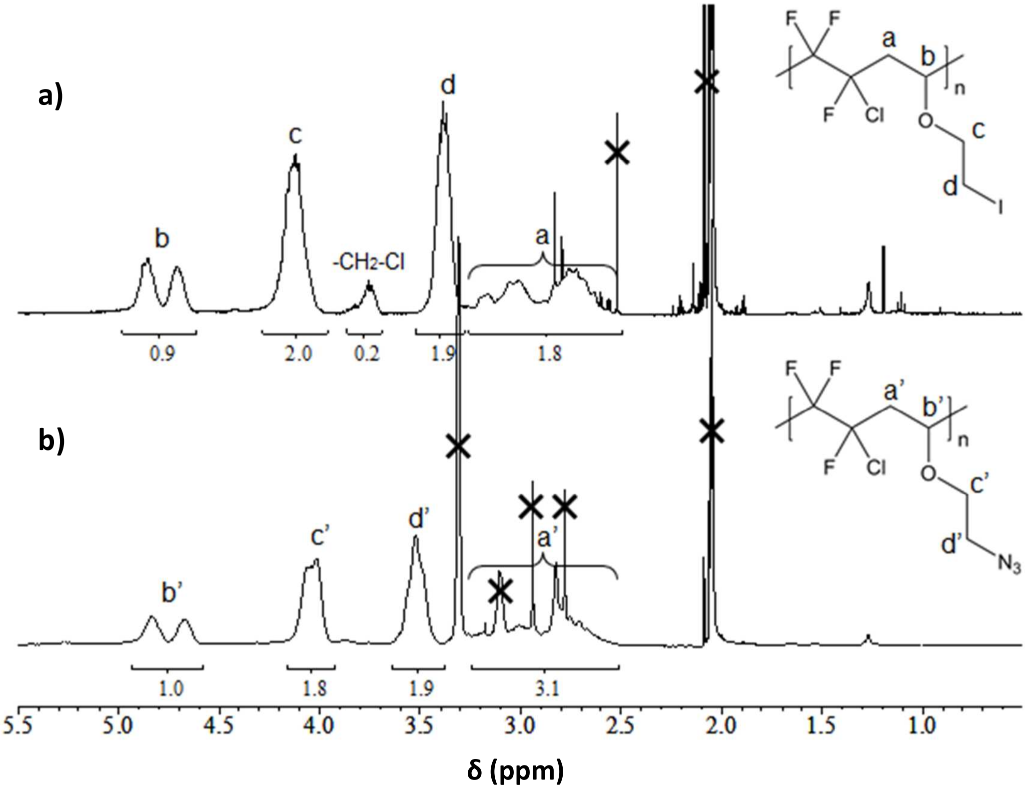


Figure 5. ^{1}**H NMR spectra in acetone-d$_6$ of a) poly(CTFE-*alt*-IEVE) copolymer and b) of poly(CTFE-*alt*-N$_3$EVE) copolymer (Entry 3, Table 4). The crossed-out signals are assigned to acetone (2.05 ppm), water (2.81 ppm), residual DMF (2.78 and 2.94 ppm) and residual methanol (3.12 and 3.31 ppm),**

Entry	Temperature (°C)	Solubility
1	20	Insoluble
2	0	Soluble
3[a]	n.a.	Soluble
4	60	Insoluble

Table 3. Experimental conditions for the nucleophilic substitution of poly(CTFE-*alt*-IEVE) copolymer using potassium 3-(dimethylamino)-2,2-dimethylpropan-1-olate. [a]**This reaction was carried out under microwave irradiation : P = 50 W, T$_{lim}$ = 200 °C, t = 5 min. T$_{max}$ = 99 °C**

The reactions carried out at 20 °C and 60 °C yielded a black residue insoluble in common organic solvents. This indicates that side reactions triggering significant crosslinking of the polymer chains occurred. These side reactions may be elimination reactions such as dehydrochlorination of the fluorinated polymer backbone or dehydroiodination of the pendent groups which both form reactive carbon-carbon double bonds. In contrast, the reactions performed under microwave irradiation or at 0 °C led to a soluble product which was characterised by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum (Figure 6) of the product corresponding to entry 2 (Table 3) shows the presence of new signals at 1.0 ppm and 2.3 ppm assigned to the methyl groups connected to the carbon and the nitrogen atoms in 3-dimethylamino-2,2-dimethylpropan-1-ol, respectively. However, the intensity of these new signals is rather small and the peak at 3.4 ppm characteristic of the –CH$_2$-I (Figure 6) is still present and has not significantly decreased in intensity. Moreover, new signals of lower intensity appeared between 3.5 and 7 ppm. These new peaks may be ascribed to the formation of carbon-carbon double bonds by dehydroiodination induced by the strong alkaline reaction medium. ^{19}F NMR spectra (not shown) are identical to that of the starting material, proving that dehydrochlorination and dehydrofluorination did not take place. Campagne *et al.*[43] had successfully reported nucleophilic substitution on poly(CTFE-*alt*-IEVE) copolymer using thiols in the presence of potassium *tert*-butoxide. The superior hardness of the alcoholate compared to that of the thiol may explain the completely different observed results. Thiols with the desired structure (similar to 3-(dimethylamino)-2,2-dimethylpropan-1-ol) are not commercially available. This strategy was thus abandonned and the cycloaddition of azides and alkynes was investigated.

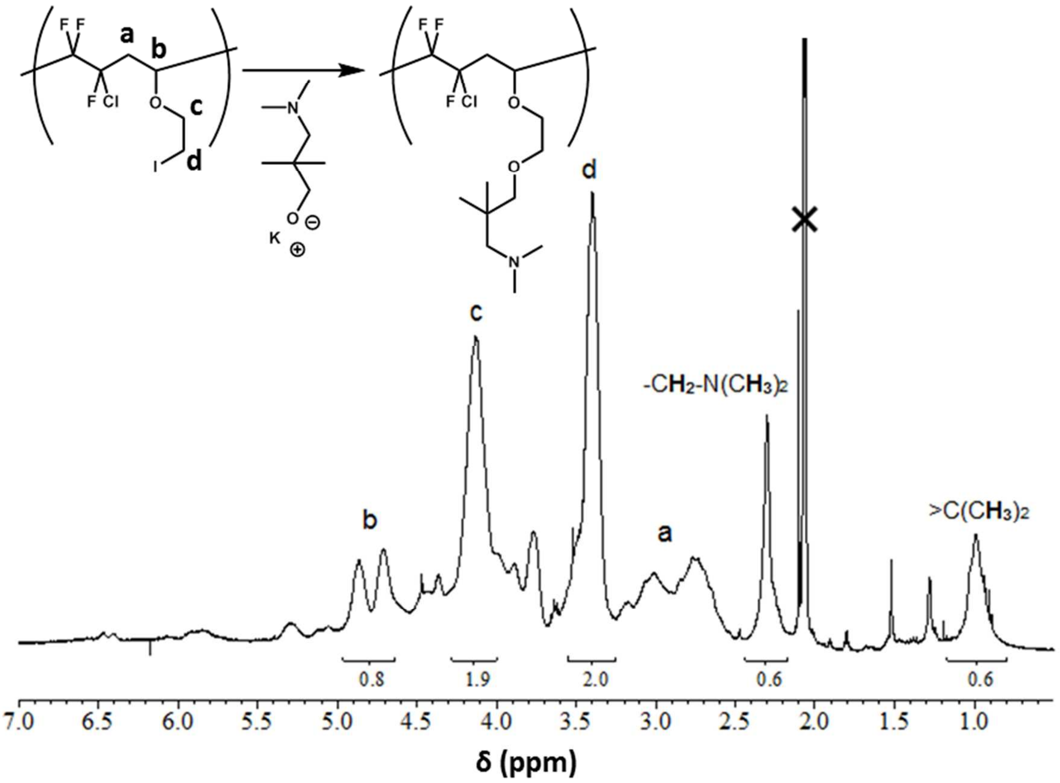


Figure 6. ^{1}H NMR spectrum in acetone-d$_6$ of the nucleophilic substitution product of potassium 3-(dimethylamino)-2,2-dimethylpropan-1-olate on poly(CTFE-*alt*-IEVE) copolymer (Entry 2, Table 3). The spectrum of the product achieved from Entry 3, Table 3 is identical. The crossed-out signal is due to acetone.

2.2.3. Functionalization of poly(CTFE-*alt*-IEVE) copolymers *via* click chemistry

The present strategy was to use the copper-catalysed cycloaddition of azides and alkynes (CuAAC), probably the most versatile example of click chemistry,[59,60] to covalently attach tertiary amine functional groups to the poly(CTFE-*alt*-VE) copolymer.

The first step in this strategy was to substitute the iodine atoms of poly(CTFE-*alt*-IEVE) copolymer with azides (Scheme 1.c (ii)). Tillet *et al.*[46] reported the efficient azidation of poly(CTFE-*alt*-IEVE) copolymer (90 % of azidation and 65% yield) by reaction of the polymer in DMSO at 55 °C for 24 h in the presence of an excess of sodium azide. In this study, the azidation under microwave irradiation was investigated in order to shorten the reaction times. The results of this study are presented in Table 4. The reactions were performed in DMF with a slight excess of NaN_3 (1.1 equivalents per iodine atom). Poly(CTFE-*alt*-CEVE) copolymer was first tested. In the case of this chlorinated polymer, a black insoluble residue was obtained that may arise from cross-linking. On the contrary, the reactions carried out on poly(CTFE-*alt*-IEVE) copolymers did not show any sign of degradation, but the near quantitative substitution of the iodine atoms with azido groups. The IR spectrum (Figure 7) of the product corresponding to entry 3 (Table 4) clearly shows the characteristic signal of the substituted N=N=N group at 2095 cm^{-1}. The conversion of the iodine atoms into azides was quantitative and calculated using the integrals of the ^1H NMR signals at 3.4 ppm and 3.5 ppm (Figure 5) corresponding to the methylenes in CH_2I and CH_2N_3 groups, respectively. This microwave protocol proved to be very efficient, quick and very easy to set-up. A temperature of 150 °C was sufficient to afford near complete chemical modification and after simple filtration, the azide-functionalised polymer solution was pure enough for further reaction.

Entry	Copolymer	P (W)	T_{max} (°C)[a]	P_{max} (bar)	Duration	% Conversion[b]
1	poly(CTFE-*alt*-CEVE)	50	223 (220)	14	3 min 30 s	Insoluble
2	poly(CTFE-*alt*-IEVE)	50	221 (220)	6	1 min 30 s	> 90
3	poly(CTFE-*alt*-IEVE)	50	159 (150)	3	1 min 15 s	> 95
4	poly(CTFE-*alt*-IEVE)	30	147 (150)	3	5 min 05 s	> 95

Table 4. Experimental conditions and results of the azidation of poly(CTFE-*alt*-IEVE) copolymer The reaction vessels were irradiated with constant power until a set temperature was reached. The reaction vessels were then cooled down under air.
[a] The limit temperature is indicated in brackets. [b]Yields were not measured; the resulting polymers were used without any purification in the following step.

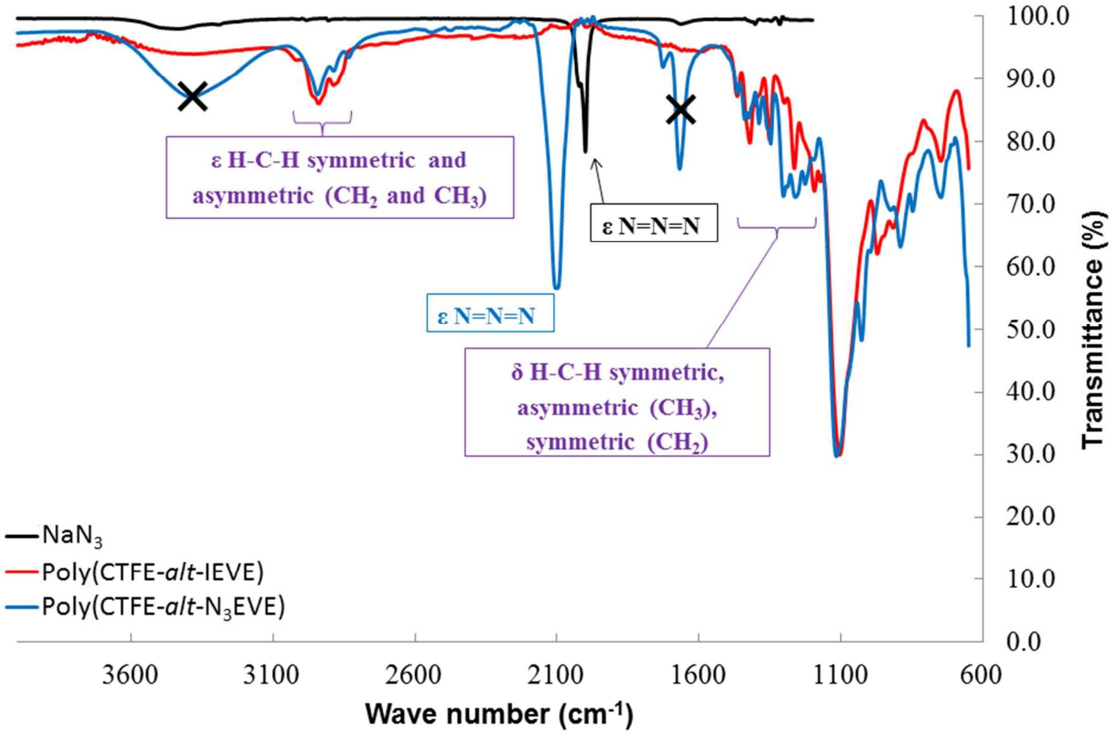


Figure 7. FTIR spectra in transmittance of sodium azide (black), poly(CTFE-*alt*-IEVE) copolymer (red) and poly(CTFE-*alt*-N_3EVE) copolymer (entry 3, Table 4, blue). The crossed out bands are assigned to residual methanol (3100-3600 cm^{-1}) and DMF (1700 cm^{-1}).

The second step consists in « clicking » 1-dimethylamino-2-propyne onto the azide-carrying dangling groups in poly(CTFE-*alt*-N_3EVE) copolymer. This step was carried out in DMF, under inert atmosphere at 20 °C in the presence of a copper complex (CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine) for 12 hr. These reactions yielded a dark solid material which proved to be insoluble in any solvents. On the contrary, the Huisgen cycloaddition performed *via* thermal activation (without any copper complex) where a DMF solution of the polymer and the alkyne was heated at 80 °C for 96 h, afforded a soluble polymer. It is thought that the insoluble materials obtained when the copper salts were used, were highly cross-linked polymer and that the cross-linking was caused by the copper salt. It is hypothesised that the azide-alkyne coupling did take place with high efficiency and that the numerous tertiary amine groups then attached to the backbone of the polymer chain acted as strong ligands for the copper cations. The resulting multidentate polymeric chains could then be cross-linked *via* multiple complexations of the copper.

The soluble product (on designated as poly(CTFE-*alt*-CkEVE) copolymer) obtained *via* the classical Huisgen cycloaddition protocol was purified by precipitation in cold water and characterised by ^{1}H NMR (Figure 8). The appearance of characteristic signals of $(CH_3)_2N$- at 2.2 ppm along with the vanishing of CH_2N_3 peak at 3.5 ppm indicates that the cycloaddition did take place but was incomplete. Both new signals at 7.5 and 7.8 ppm assigned to the proton of the triazole ring in the 1,5 and 1,4 isomers, respectively, further confirmed that the cycloaddition occurred. As expected, in contrast to the copper-catalysed version of the reaction, the thermal Huisgen cycloaddition was not complete (58 %) in spite of the long reaction time and led to a mixture of 1,4 (60 %) and 1,5 (40 %) isomers (Figures S6 and the calculation method is supplied in the supplementary information).

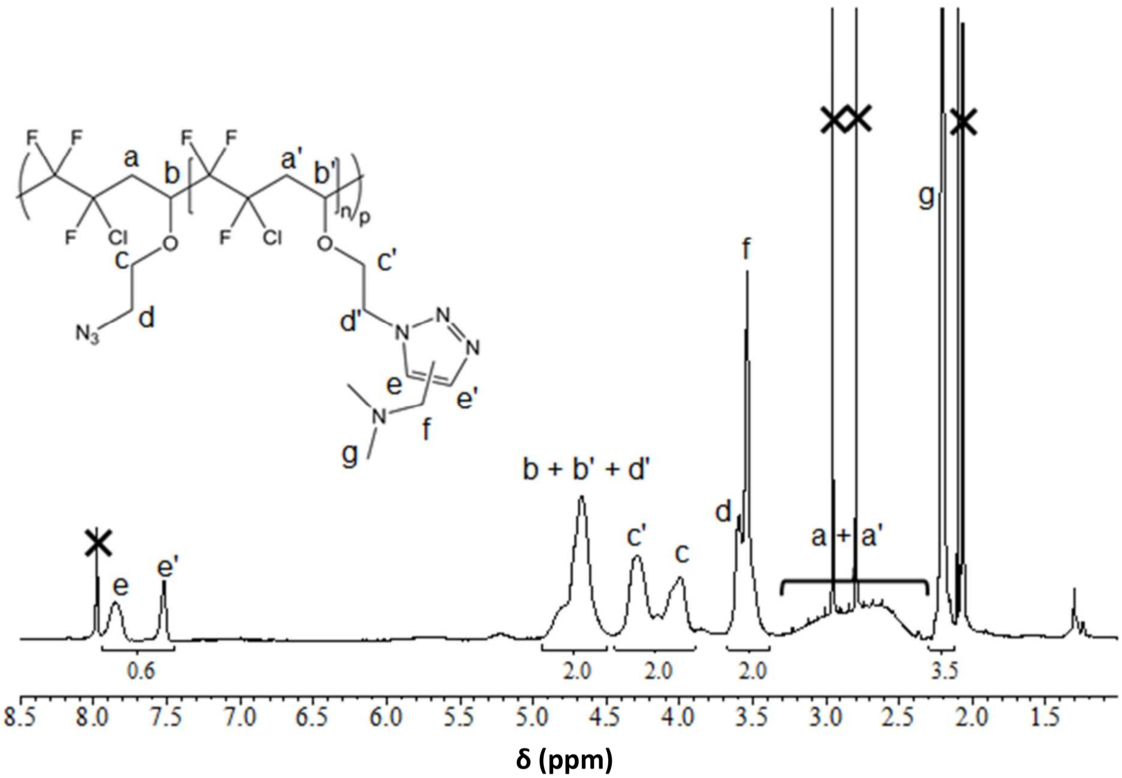


Figure 8. ^{1}H NMR spectrum of poly(CTFE-*alt*-CkEVE) copolymer recorded in acetone-d$_6$. The crossed-out signals are assigned to acetone (2.05 ppm) and residual DMF.

Quaternary ammonium groups were then formed onto the poly(CTFE-*alt*-CkEVE) copolymer by methylation of the tertiary amine pendent groups using iodomethane. This reaction afforded the quaternised poly(CTFE-*alt*-CkN$^+$EVE) copolymer in good yields (87 %) and with a high degree of quaternization as shown in the ^{1}H NMR spectrum (Figure S7). The copolymer obtained was water-soluble probably due to the high degree of quaternization. This solubility may be a limitation for application of this polymer as component of a membrane. Strategies of cross-linking using the residual azide groups are under investigation.

3. Conclusions

The preparation of functional fluoropolymers is a challenge to synthetic chemist owing to the scarcity of commercially available functional fluoroolefins. This article demonstrates that alternating copolymerisation of CTFE and functional vinyl ether is a very efficient way to prepare highly functional fluorinated copolymers. This method allows preparing ammonium-functionalised fluoropolymers resistant to the Hofmann elimination reaction (i.e. without any hydrogen in β position). These copolymers able to conduct hydroxide anions may be interesting as components (e.g. binders) of SAFC membranes. Two general strategies were examined: 1) the direct radical copolymerisation of CTFE with suitable functional vinyl ethers and 2) the post-polymerisation functionalisation of poly(CTFE-*alt*-VE) alternating copolymers. The copolymerisation of CTFE with ammonium-carrying vinyl ether did not proceed. In contrast, tertiary amine-containing vinyl ether copolymerised with CTFE and afforded functional copolymers. However, the copolymerisation and the quaternisation of the amino groups using methyl iodide were accompanied by side reactions, including transfer reactions leading to low molecular weight-copolymers and significant loss of functionality. Two post-polymerisation functionalisation methods were then studied. A perfectly alternating poly(CTFE-*alt*-CEVE) copolymer (where CEVE stands for 2-chloroethyl vinyl ether) was iodinated using the Finkelstein reaction. Nucleophilic substitution of iodine atoms in the resulting poly(CTFE-*alt*-IEVE) copolymers in the presence of potassium 3-(dimethylamino)-2,2-dimethylpropan-1-olate led to a poor functionalisation and was accompanied by substantial amount of side reactions (probably dehydroiodination). Second, the iodine atoms of the poly(CTFE-*alt*-IEVE) copolymer could be quantitatively modified into azides and the obtained copolymer was reacted with 1-dimethylamino-2-propyne. In the presence of copper catalyst, the cycloaddition yielded cross-linked copolymers. This cross-linking was most likely caused by the strong complexation of the copper cations by the numerous dimethylamino groups attached to the backbone of the polymer resulting from the cycloaddition reaction. As expected, the absence of copper catalyst, the cycloaddition was slow, and only converted ca. 60 % of the azides. Dimethylamino groups could nonetheless be introduced onto the fluorocopolymeric backbone and subsequently efficiently quaternised using iodomethane. The ammonium-functionalised copolymers obtained were all water-soluble which could be an issue for the desired application. More work is thus required to prepare non-water soluble copolymers with higher molecular weights. Controlled cross-linking strategies are under investigation.

4. Experimental

Analyses: ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired using a Bruker AC 400 at 25 °C. FTIR analyses were performed in ATR mode using a Perkin-Elmer Spectrum 1000. SEC-HPLC analyses were carried out on a Polymer Laboratories PL-GPC 50 instrument using 2 PL Mixed C 5 µm columns thermostated at 35 °C, THF as eluent (1.0 ml.min^{-1}) and a refractive index detector. Calibration was achieved using Varian monodispersed polystyrene standards. Elemental analyses were realized by the Service Central d'Analyses of CNRS (Villeurbanne, France). TGA analyses were performed on 10-15 mg samples on a TGA 51 instrument (TA Instruments) from 20 °C to 700 °C using a 20 °C/min heating ramp under air flow. DSC measurements were achieved on 15 mg samples on a Perkin-Elmer Pyris 1 instrument using the following heating/cooling cycle: Heating from -50 °C to + 150 °C at 20 °C/min, isotherm plateau at 150 °C for 3 minutes, cooling from 150 °C to -50 °C at 20 °C/min, isotherm plateau at -50 °C for 3 minutes. The heating/cooling cycle was performed twice per sample. T_g were determined at the inflexion point of the calorific capacity jump.

Chemicals: 3-(dimethylamino)-2,2-dimethylpropan-1-ol , 1-dimethylamino-2-propyne, *N*,*N*,2,2-tetramethylpropane-1,3-diamine, palladium acetate and iodomethane were purchased from ABCR, vinyloxyethane (or 2-chloroethyl vinyl ether, CEVE), 1,10-phenanthroline, vinyloxy-2-chloroethane, potassium *tert*-butoxide, benzyl chloride, sodium azide, copper bromide(I), HMTETA, sodium iodide, and all the solvents were purchased from Sigma-Aldrich. Chlorotrifluoroethylene was kindly provided by Honeywell (Buffalo, NY, USA). *Tert*-butylperoxypivalate (TBPPi) was supplied by Akzo Nobel (Compiègne, France). 1,1,1,3,3-pentafluorobutane (Solkane®365mfc) was supplied by Solvay S.A.

(Tavaux, France) and distilled over CaH_2 before use. Deuterated solvents for NMR were purchased from Euroiso-top. All chemicals and solvents were used as received unless otherwise noted.

Vinyl ether synthesis: All vinyl ethers were synthesised by transetherification of vinyloxyethane catalysed by palladium acetate in the presence of 1,10-phenantroline.

Typically for the vinyloxy-3-dimethylamino-2,2-dimethylpropane (**2MeNEV**):
The palladium acetate (34.42 mg, 1.52×10^{-3} mol) and the 1,10 phenantroline (41.2 mg, $2{,}29 \times 10^{-3}$ mol) were dissolved separately in 10 mL of dichloromethane and mixed together at 20 °C for 15 minutes. 20.018 g (0.152 mol) of 3-(dimethylamino)-2,2-dimethylpropan-1-ol and 263.00 g (2.29 mol) of vinyloxyethane were placed along with the catalyst solution into a pressure reactor. The reactor was closed and the reaction mixture was heated under stirring at 60 °C for 48 hours. The volatiles were removed using a rotary evaporator. Diethyl ether was added to the residue, and the precipitated catalyst was filtered off. The desired vinyl ether (19.40 g) was then isolated by distillation under reduced pressure (Bp = 45-47 °C/10 mbar) and obtained as a transparent colorless liquid.

^{1}H NMR (Acetone-d_6), Figure S1, δ (ppm) : 0.89 (s, C-C$\mathbf{H_3}$, 6H), 2.15 (s, -C$\mathbf{H_2}$-N, 2H), 2.23 (s, N-C$\mathbf{H_3}$, 6H), 3.44 (s, -C$\mathbf{H_2}$-O, 2H), 3.91 (dd, C**H**H-CH= (E), $^2J_{gem}$ = 1.77 Hz, $^3J_{cis}$ = 6.82 Hz, 1H), 4.16 (dd, CH**H**-CH= (Z), $^2J_{gem}$ = 1.64 Hz, $^3J_{trans}$ = 14.27 Hz, 1H), 6.51 (ddt, CH_2-C**H**=, $^3J_{cis}$ = 6.82 Hz, $^3J_{trans}$ = 14.27 Hz, ^4J = 0.51 Hz, 1H).
^{13}C NMR (Acetone-d_6), Figure S2, δ (ppm) : 23.5 (***C***H_3-C, 2C), 37.1 ($(CH_3)_2$-***C***<, 1C), 48.8 (***C***H_3-N, 2C), 67.2 (***C***H_2-N, 1C), 74.7 (***C***H_2-O, 1C), 86.2 (H_2***C***=CH, 1C), 153.1 (H_2C=***C***H, 1C).

Synthesis of 3MeN$^+$EV by methylation of vinyloxy-3-dimethylamino-2,2-dimethylpropane

Iodomethane (9.021 g, 6.36 10^{-2} mol) was added to a solution of vinyloxy-3-dimethylamino-2,2-dimethylpropane (5.00 g, 3.18 10^{-2} mol) in acetonitrile (31.8 mL). The mixture was stirred at 20 °C for 12 hr. After precipitation in diethyl ether, the white salt was filtered and dried at 60 °C for 12 h. Yield = 96 %

^{1}H NMR (D_2O) δ (ppm) : 1.20 (s, C-C$\mathbf{H_3}$, 6H), 3.20 (s, N^+-C$\mathbf{H_3}$, 9H), 3.42 (s, -C$\mathbf{H_2}$-N^+, 2H), 3.67 (s, -C$\mathbf{H_2}$-O, 2H), 4.13 (dd, C**H**H-CH= (E), $^2J_{gem}$ = 2.27 Hz, $^3J_{cis}$ = 6.82 Hz, 1H), 4.32 (dd, CH**H**-CH= (Z), $^2J_{gem}$ = 2.27 Hz, $^3J_{trans}$ = 14.40 Hz, 1H), 6.55 (dd, CH_2-C**H**=, $^3J_{cis}$ = 6.82 Hz, $^3J_{trans}$ = 14.40 Hz, 1H).
^{13}C NMR (D_2O) δ (ppm) : 24.6 (***C***H_3-C, 2C), 36.5 ($(CH_3)_2$-***C***<, 1C), 55.4 (***C***H_3-N^+, 3C), 73.2 (***C***H_2-N^+, 1C), 74.1 (***C***H_2-O, 1C), 88.0 (H_2***C***=CH, 1C), 151.3 (H_2C=***C***H, 1C).

Radical Copolymerisation of CTFE with vinyl ethers

All the copolymerisations were carried out using 100 or 300 mL Parr pressure reactors equipped with a rupture disc (3000 psi), mechanical stirring system, a manometer and 2 injection valves. Before reaction, all the solids were placed in the reactor which was then first pressurized with 20 bars of nitrogen (to detect leaks) and then put under vacuum (10^{-2} mbar) for 2 hr. The liquid phases (initiator, liquid monomer, solvent) were first degassed by argon or nitrogen bubbling and then introduced into the reactor *via* a funnel. The desired amount of CTFE was then transferred into the reactor using double weighing method (i.e. the difference of weight before and after transferring CTFE). The reaction mixture was then heated up to the desired temperature under stirring for the required time. At the end of the reaction, the reactor was cooled down to ambient temperature, cooled in an ice bath, the remaining gases were evacuated, and the resulting residue was dissolved into acetone, concentrated under vacuum and precipitated from cold methanol. The polymer was then dried under vacuum (10 mbar) at 60 °C for 12 h. In a typical reaction, 33.5 g (0.288 mol) of CTFE was added to a 300 mL pressure reactor containing 20.00 g (0.188 mol) of CEVE, 81.9 mg (4.70 mmol) of TBPPI, 75.5 mg (5.46 mmol) of potassium carbonate and 150 mL of 1,1,1,3,3-pentafluorobutane. The autoclave was then heated up to 74 °C for 16 hr. The polymer was then purified and dried as described above.

Iodination of poly(CTFE-*alt*-CEVE) copolymer

60.00 g (0.269 mmol) of poly(CTFE-*alt*-CEVE) copolymer was dissolved in freshly distilled acetone to obtain a 0.60 mol.L^{-1} solution which was placed into a Parr pressure reactor containing 121.0 g (0.807 mol) of sodium iodide. The reactor was then heated up to 65 °C under stirring for 7 days. After the reaction, acetone was removed under vacuum and the residue was redissolved in diethyl ether. The chlorine and iodine salts were filtered off while the clear solution was concentrated before precipitation in cold methanol. The resulting poly(CTFE-*alt*-IEVE) polymer was then dried under vacuum at 60 °C for 12 h. During the entire synthesis, the glassware containing the polymer was wrapped with aluminum sheet to shield the polymer from UV light.

$$\%\, Iodination = 100 * \frac{\int_{3.4}^{3.5} CH_2{-}I}{\int_{3.4}^{3.5} CH_2{-}I + \int_{3.7}^{3.8} CH_2{-}Cl} \qquad (7)$$

Azidation of poly(CTFE-*alt*-IEVE) copolymer

1.00 g (3.18 mmol) of poly(CTFE-*alt*-IEVE) copolymer was dissolved in DMF (5 mL). The DMF solution and 22.7 mg (3.5 mmol) of sodium azide were placed into a 10 mL glass tube. The tube was capped with a rubber septum and heated up using a microwave reactor TM CEM Discover. The microwave irradiation program was then started. After reaction, the suspension was filtered on filter paper and the poly(CTFE-*alt*-N_3EVE) copolymer was isolated by precipitation in cold methanol.

Nucleophilic substitution of poly(CTFE-*alt*-IEVE) copolymer

Tert-butoxide (1.180 g, 10.50 mmol) was inserted into a round bottom flask along with 20 mL of THF. 3-(Dimethylamino)-2,2-dimethylpropan-1-ol (1.25 g, 9.53 mmol) was then added dropwise to the solution over the course of 2 hr. The mixture was then added dropwise to a THF solution of poly(CTFE-*alt*-IEVE) copolymer (3.00 g, 9.50 mmol, 0.6 mol L^{-1}) at 0 °C. The reaction mixture was stirred at 0 °C for 12 hr. The resulting copolymer was isolated by precipitation in cold methanol and dried at 60 °C under vacuum for 12 h.

Functionalization of poly(CTFE-*alt*-N_3EVE) copolymer by CuAAC and thermal cycloaddition

Poly(CTFE-*alt*-N_3EVE) copolymer (5.00 g, 21.8 mmol of azide equivalent) was dissolved in DMF. In a separate flask the copper complex was formed by dissolution of CuBr (0.63 g, 4.37 mmol) and HMTETA (1.00 g, 4.37 mmol) in degassed DMF. 5.45 g (65.5 mmol) of 1-dimethyl-2-aminopropyne was added to the polymer solution. The complex was also added and the reaction mixture was again degassed by nitrogen bubbling for 30 minutes. The reaction was left at 40 °C for 12 hr. A green insoluble solid was obtained.

In the case of the thermal cycloaddition without any catalyst, 1-dimethyl-2-aminopropyne was added to the copolymer solution and after degassing by nitrogen bubbling. Then, the reaction mixture was placed in an oil bath thermostated at 80 °C for 72 hr. The resulting copolymer was isolated by precipitation from cold water and dried at 60 °C under vacuum for 12 hr.

Methylation of poly(CTFE-*alt*-CkEVE) copolymer

The poly(CTFE-*alt*-CkEVE) copolymer (2.00 g, 7.3 mmol of dimethylamino groups) was dissolved in distilled acetone to obtain a (0.6 mol L^{-1}) solution. Iodomethane (3.12 g, 22.0 mmol) was added to this solution and the reaction mixture was stirred at 20 °C for 12 hr. A brown solid was obtained. The acetone was removed under vacuum and the solid was redissolved in methanol, precipitated from cold diethyl ether, and then dried at 60 °C under vacuum for 12 h. A brown solid was isolated.

Methylation of poly(CTFE-alt-2MeNEV) copolymer

Poly(CTFE-*alt*-2MeNEV) copolymer (9.50 g, 33.2 mmol) was dissolved in 50 mL of distilled acetone at 20 °C in a 100 mL round bottom flask. Iodomethane (14.20 g, 99.5 mmol) was added and the reaction medium was stirred at 20 °C for 12 hr. The reaction mixture was then concentrated under reduced pressure and precipitated from cold diethyl ether. The solid was dried at 60 °C under vacuum for 12 hr.

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