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Comparison of epoxy- and cyclocarbonate-functionalised vinyl ethers in radical copolymerisation with chlorotrifluoroethylene

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ABSTRACT

The synthesis of functional fluoropolymers is a challenging and highly sought-after objective. Fluoroolefins are indeed in their vast majority non-functional. Their specific reactivity however, can be turned into an advantage. Alternating copolymerisation of electron-acceptor chlorotrifluoroethylene (CTFE) and electron-donor vinyl ethers (VEs) is indeed efficient to prepare poly(CTFE-*alt-VE*) fluoropolymers with a very high density of functional groups. This article deals with the synthesis of two original functional vinyl ethers (oxirane and cyclocarbonate), and describes two methods to synthesise ammonium-containing Hofmannn degradation-insensitive fluoro-copolymers, that may display interesting properties as component of solid alkaline fuel cell membranes. Both functional vinyl ethers copolymerised to high yield with CTFE. The oxirane-based monomers led to better defined alternating copolymers using amines afforded well-defined ammonium-functionalised fluoro-copolymers.

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1. Introduction

Fluoropolymers (i.e. polymers bearing fluorine atoms on the backbone) are a family of niche polymers which display a wide range of remarkable properties for high tech applications. Some are elastomers, thermoplastic such as polyvinylidene fluoride (PVDF), or thermoplastic elastomers (e.g. PVDF-b-poly(VDF-co-hexafluoropropylene)-b-PVDF) [1]. They can be semicrystalline like PVDF, or completely amorphous like poly(chlorotrifluoroethylene-alt-vinyl ethers) (poly(CTFE-alt-VE)) copolymers. Thanks to the very high energy required to break the C-F bond, they generally have very high resistance to temperature, aging, and chemical aggressions (oxidant, acid and base, except vinylidene fluoride copolymers and some CTFE-containg copolymers such as poly(CTFE-co-vinylacetate)). The fluorinated backbones also endow fluoropolymers with both hydrophobicity and lipophobicity. In addition, they have generally very low refractive indices and some of them show very high electroactivity (ferroelectricity, piezoelectricity, etc). Hence, these excellent and rare properties enable fluoropolymers to find high added-value applications in numerous technological fields

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http://dx.doi.org/10.1016/j.jfluchem.2014.08.014 0022-1139/© 2014 Elsevier B.V. All rights reserved. such as high performance elastomers, coatings and textiles, electronics, aerospace and aeronautics, energy, *etc.* One of the main drawbacks of fluoropolymers (that is directly related to their remarkable properties) is their relative lack of functionalities. Indeed, the main fluoroolefins, such as TFE (tetrafluoroethylene), VDF, CTFE, HFP (hexafluoropropene) are non-functional. Preparing functional fluoropolymers is a major challenge. Functional fluoroolefins exist but are rare. For example, the monomer of the NAFION[®] membrane is a perfluorinated vinyl ether that bears a sulfonyl fluoride end-group.

One of the easiest ways of preparing functional fluoropolymers is to copolymerise the desired fluoroolefin with a functional comonomer. Owing to the presence of very electronegative fluorine atoms, fluoroolefins are in general very electron poor and show very peculiar reactivity. Indeed, in Alfrey and Price [2,3] semi-empirical reactivity scale, fluoroolefins occupy a special place with their *Q* close to zero and their very positive *e* value (VDF: Q = 0.008-0.036, e = 0.4-0.52; TFE: Q = 0.031-0.049, e = 1.22-1.84; CTFE: Q = 0.020-0.031, e = 1.48-1.84) [2–5]. *Q* attempts to represent the extent of the conjugation of the carbon–carbon double bond with its substituents, while *e* characterises the electrondonating (e < 0) or electron-attracting (e > 0) behaviour of the monomer. Monomers copolymerise well if their *Q* values are similar and preferably high. Monomers with similar *Q* values and 2

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Scheme 1. General strategy for the synthesis of Hofmann degradation-insensitive poly(CTFE-alt-VE) copolymers using the cyclocarbonate-amine reaction.

high *e* values of opposite sign tend to copolymerise in alternating fashion. In general, fluoroolefins, therefore tend to not copolymerise very well with non-fluorinated monomers. One exception is the case of strong electron-donating monomers with which fluoroolefins copolymerisation may occur with a high tendency to alternation. If the monomer partners are chosen well, it is actually possible to prepare nearly perfectly alternating copolymers. Such a couple is the CTFE/vinyl ether couple. PCTFE is a very interesting polymer due to its excellent film forming properties, its resistance to chemical attack and its gas barrier property. It is widely used, in the petrochemical industry in valves, O-rings, seals, shafts and joints, in the pharmaceutical industry as packaging material for drugs, in the fibre optics industry and for advanced coatings [1,6-8]. However, PCTFE is very insoluble in most organic solvents due to his high crystallinity (Mp = 214-220 °C) and is difficult to crosslink [9]. On the contrary, fluoropolymers based on vinyl ethers are easy to crosslink and functionalise. Functional vinyl ethers can be synthesised via transetherification [9-14]. Vinyl ethers are usually polymerised by cationic polymerisation using either HI/I₂ [15] or triflic acid/tetrahydrothiophene [16]. It is generally accepted that vinyl ethers do not homopolymerise under radical polymerisation conditions [17], although a few reports have shown that such homopolymerisation is indeed possible [18,19]. However, owing to their pronounced electron-donating

character (vinyloxyethane: Q = 0.018, e = -1.80) [4], vinyl ether do copolymerise easily with fluoroolefins and lead to near perfect alternating copolymers. Alternating copolymers schematically form via two possible mechanisms: (i) the monomers are free and add one after the other on the growing chain which reactivity depends on the last (or last two) monomer(s) added [20,21]. (ii) Charge transfer complexes are formed between electron-donating and electron-attracting monomers, and these complexes add to the growing polymer chain [22–26]. In the case of CTFE and vinyl ether, Boutevin et al. have suggested that charge transfer complexes do form readily, but that the copolymerisation proceeds via a free monomer mechanism [5,27]. Copolymers of CTFE and vinyl ethers are thus very interesting for their alternating structure and their easy functionalisation (thanks to the wide range of existing functional vinyl ethers). These copolymers are very useful for high performance paints and coatings [17,28-34]. Lumiflon[®] tradename, for example, are commercially available paints and coatings based on poly(CTFE-alt-VE) copolymers marketed by Asahi Glass Co. Ltd. [35–39]. In addition to these materials, poly(CTFE-alt-VE) copolymers have attracted interests for applications in the domain of energy, in particular in fuel-cells [40-42], in lithium-ion batteries [43], and in photovoltaic applications [44].

Typically, functional copolymers can be prepared by (i) direct copolymerisation of functional monomers; or by (ii)



Scheme 2. Synthesis routes of the preparation of cyclocarbonate-containing poly(CTFE-alt-CCEV) copolymer.

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Fig. 1. ¹H NMR of vinyloxy-2-methyloxirane (GcEV) recorded in acetone- d_{G} . The red arrow indicates residual glycidol. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

post-polymerisation functionalisation of copolymers. The postpolymerisation route was used successfully to prepare copolymers bearing azoles [42,45] and phosphonic acids [46] for applications in fuel-cell membrane, from copolymers of CTFE and vinyloxy-2chloroethane (CEVE). Similarly, Valade et al. [40] prepared electrodes binders carrying quaternary ammonium groups by nucleophilic substitution. These polymers however, presented hydrogen atoms in β position of the ammonium groups and were thus sensitive to Hofmann degradation [47]. This problem was partly circumvented using ATRP to prepare polystyrene grafts from poly(CTFE-*alt*-CEVE) which were subsequently chloromethylated and quaternised using trimethylamine [48]. To the best of our knowledge, there is only one reported example of poly(CTFE-*alt*-VE) copolymer bearing Hofmannn degradation insensitive ammonium groups [49].

The present article reports novel alternative methods to prepare poly(CTFE-*alt*-VE) copolymers bearing Hofmann elimination insensitive quaternary ammonium groups. CTFE was chosen for its high resistance to alkaline medium, while functional VEs were used to introduce functional groups into the copolymer backbone. Cyclocarbonate-functionalised poly(CTFE-*alt*-VE) copolymers were synthesised *via* two routes and subsequently functionalised with quaternary ammonium groups without hydrogen atoms in β position. Such copolymers if they proved to be sufficiently resistant to alkaline medium may be very interesting to design original membranes for solid alkaline fuel-cells (SAFC) [50].

2. Results and discussion

Scheme 1 presents the general strategy to prepare the poly(CTFE-*alt*-VE) copolymers carrying quaternary ammonium groups without hydrogen atoms in β position. A cyclocarbonate-functionalised poly(CTFE-*alt*-VE) copolymer is first reacted with a suitable primary amine bearing dimethylamino groups. In a second step, the tertiary amines are quaternised using methyl iodide.

Cyclocarbonate-functionalised poly(CTFE-alt-VE) copolymers can be obtained via 2 routes: (1) the copolymerisation of CTFE with a cyclocarbonate-functionalised vinyl ether (Route A, Scheme 2) and (2) the carbonation of a preformed copolymer carrying epoxide moieties (Route B, Scheme 2). Both routes were examined.

2.1. Syntheses of the functional monomers: Vinyloxy-2-methyloxiran (GcEV) vinyloxy-4-methyl-1,3-dioxolan-2-one (CCEV)

GCEV was first prepared by transetherification of vinyloxyethane with glycidol in the presence of palladium acetate and 1,10-phenantroline [43(a)]. The reaction yield (63%) was relatively good after vacuum distillation. GCEV monomer was obtained in high purity (92%) (Fig. 1) as a racemic mixture of two isomers (Fig. 2). Residual glycidol could not be completely eliminated by distillation, but since glycidol is inert in the conditions of polymerisation, GCEV was not further purified.

The cyclocarbonate-containing vinyl ether (CCEV) was synthesised by carbonation of vinyloxy-2-methyloxiran (GcEV) as shown in Scheme 2 (Route A). The carbonation reaction was performed using the protocol designed by Endo et al. [51] (Fig. 3) by reaction of CO_2 in DMF in the presence of LiBr. The reaction was very efficient, and a very pure cyclocarbonate vinyl ether (CCEV) was obtained in high yields (97%) (Figs. S1 and S2).

2.2. Radical copolymerisation of CTFE with CCEV and with GCEV

The copolymerisation of CTFE and CCEV was carried out in dimethylcarbonate at 74 °C using *tert*-butyl peroxypivalate as initiator. After precipitation, the poly(CTFE-*alt*-CCEV) copolymer was isolated in high yield (71%) and characterised by ¹H and ¹⁹F NMR (Fig. 4) and SEC-HPLC (Table 1, entry 2). The NMR spectra indicate a deviation from perfect alternating structure with signals between -126 and -130 ppm in the ¹⁹F NMR spectrum assigned to CFCl groups in CTFE-CTFE dyads [52]. These defects were also detected by calculation of the copolymer composition (from elemental analysis data, see supplementary info) which shows an excess of CTFE (Table 1, entry 2). Importantly, the peaks of the CH and of the CH₂ of the cyclocarbonate at 5.05 ppm and between



Fig. 2. Isomers of vinyloxy-2-methyloxirane (GCEV). Coupling constants for protons d, d' and e (1/) and for protons f, f' and e (2/).

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Fig. 3. Mechanism of the carbonation of epoxydes as proposed by Kihara et al. [51]. MX represents an alkaline metal salt (e.g. Nal, LiBr, LiCl, . .).



Fig. 4. (a) ¹H NMR spectrum and (b) ¹⁹F NMR spectrum of poly(CTFE-alt-CCEV) copolymer, recorded in acetone-d₆.

4.3 and 4.7 ppm, respectively are still present and the intensity of their integration indicates that the cyclocarbonate rings were not opened during the polymerisation. In addition, the ¹H NMR spectrum did not display any signals between 6.1 and 6.7 ppm, ascribed to end-groups formed via transfer reactions ($-CF_2-CFCLH$ and CFCl $-CF_2H$) as suggested by Kumar et al. [53]. This copolymer is further referred to as poly(CTFE-*alt*-CCEV)_A.

The radical copolymerisation of CTFE and GcEV was carried out under the same conditions and the corresponding copolymer was also isolated with high yields (69%). Contrarily to poly(CTFE-*alt*-CCEV) copolymer, poly(CTFE-*alt*-GcEV) copolymer contained very few CTFE-CTFE dyads (Fig. 5) and the copolymer composition calculated from elemental analysis did not show any excess of CTFE in the copolymer (Table 1, entry 2). The epoxide rings were also left intact during the polymerisation as indicated by the presence of the expected signals of the epoxide ring between 2.5 and 3.3 ppm (Fig. 5).

2.3. Carbonation of poly(CTFE-alt-GcEV) copolymer

The carbonation of the poly(CTFE-*alt*-GCEV) copolymer was performed using the conditions used for the carbonation of GCEV monomer. The resulting copolymer was isolated by precipitation from cold methanol, dried and characterised by ¹H, ¹⁹F NMR, SEC-HPLC, DSC, and TGA (Table 2.). This copolymer will be further referred to as poly(CTFE-*alt*-CCEV)_B.

Both poly(CTFE-*alt*-CCEV)_A and poly(CTFE-*alt*-CCEV)_B copolymers showed almost identical ¹⁹F NMR spectra with a slight presence of signals assigned to CFCl groups in CTFE-CTFE dyads. The ¹H NMR spectra (Fig. S3) were also quite similar but in the case of poly(CTFE-*alt*-CCEV)_B copolymer, small signals between 3.5 and 4 ppm attributed to the presence of unreacted epoxide groups can be observed.

Overall, both preparation routes led to very similar polymers and are thus both usable. Route A, the direct copolymerisation of CTFE with CCEV, produces a copolymer with lower molecular

Table 1

Experimental conditions for the copolymerisations of CTFE and functional cyclic vinyl ethers.

Entry	VE	Feed composition		Solvent Initiator	Yield (%)	Polymer composition ^a		'Mn (g/mol) ^b	PDI	
		CTFE	VE				CTFE	VE		
1	GcEV	60	40	DMC	TBPPI	69	51.5	48.5	13,500	2.2
2	CCEV	60	40	DMC	TBPPI	71	63.8	36.2	9600	1.5

Abbreviations: GcEV = vinyloxy-2-methyloxiran, CCEV = vinyloxy-4-methyl-1,3-dioxolan-2-one, DMC = dimethylcarbonate, TBPPI = tert-butyl peroxypivalate.

^a Calculated from elemental analysis (see Table S1 in Supplementary information).

^b Measured by SEC-HPLC using PS calibration standards.

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δ (ppm)

Fig. 5. (a) ¹H NMR spectrum and (b) ¹⁹F NMR spectrum in acetone-d₆ of poly(CTFE-alt-GcEV) copolymer.

Table 2								
SEC-HPLC	data	and	thermal	properties	of	the	resulting	poly(CTFE-alt-CCEV
copolymer	s.							

Route	Yield (%)	Mn (g/mol)	PDI	T_g (°C)	$T_{d,10\%}$ (°C)
А	71	9600	1.5	35	307
В	69	13,500	1.5	35	271

weight and with an imperfect alternating structure, while Route B, the carbonation of the epoxide-containing copolymer, yields a higher molecular weight-copolymer with a more regular alternating structure. However, it was obtained in lower yield (due to the loss during precipitation) and with a slightly lower number of cyclocarbonate functions. Poly(CTFE-alt-CCEV)_B copolymer also

exhibited a slightly lower decomposition temperature than $poly(CTFE-alt-CCEV)_A$ copolymer although their glass transition temperatures were identical (Table 2).

2.3.1. Functionalisation of poly(CTFE-alt-CCEV) copolymer using the amine ring-opening of cyclocarbonate reaction

Cyclocarbonates are known to react with nucleophiles [54]. The reaction with amines is one of the best known example of these ring-opening reaction and leads to the formation of hydroxyurethane. This reaction which can be catalysed by tertiary amines such as triethylamine (Scheme 3) [55] usually leads to the formation of two isomers, one isomer bearing a secondary alcohol (major product) and one isomer bearing a primary alcohol (minor product). The goal here was to use this reaction to functionalise poly(CTFE-*alt*-CCEV) copolymers and introduce tertiary amine into the polymer. *N*,*N*,2,2-tetramethylpropane-1,3-diamine was used



Scheme 3. Mechanism of the reaction of cyclocarbonate ring-opening by amines, catalysed by triethylamine [55].

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Table 3

Experimental conditions of the amine-poly(CTFE-alt-CCEV) reaction.

Entry	Solvent	<i>T</i> (°C)	Duration (h)	[carbonate] _o /[amine] _o	Catalyst (mol%)	Yield (mol%)
1	DMF	80	24	1.00:1.05	2	43
2	DMF	80	48	1.00:1.50	6	41



Fig. 6. FTIR transmittance spectra of poly(CTFE-*alt*-CCEV) (blue), poly(CTFE-*alt*-UrEV) (entry 1, Table 6, red), and poly(CTFE-*alt*-UrEV) (entry 2, Table 6, green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as it is non sensitive to Hofmann degradation thanks to its two methyl groups, should be very reactive via its primary amine function and could later be quaternised by methylation of its dimethylamino group.

Two reactions between *N*,*N*,2,2-tetramethylpropane-1,3-diamine and poly(CTFE-*alt*-CCEV) were carried out in DMF at 80 °C in the presence of catalyst (TEA) (Table 3) and yielded the amino-containing poly(CTFE-*alt*-UrEV) copolymer [56].

When a ratio of amine/carbonate of 1.05 was used, the reaction was not complete. IR spectrometry (Fig. 6) showed that the peak of the carbonyl of the cyclocarbonate at 1786 cm⁻¹ significantly decreased, but was still present in the polymer. The formation of hydroxyurethane was nonetheless confirmed by the presence of new peaks characteristic of the $-CH_2$ and CH_3 of *N*,*N*,2,2-tetramethylpropane-1,3-diamine (1300–1600 cm⁻¹ and 2700–3000 cm⁻¹), of the O–H and N–H bonds (3100–3700 cm⁻¹) and of the carbonyl of the urethane at 1698 cm⁻¹. The introduction of amine groups and the formation of hydroxyurethane were also confirmed by ¹H NMR (Fig. 7) which showed new signals at



Fig. 7. (a) Scheme of the cyclocarbonate ring-opening reaction of poly(CTFE-*alt*-CCEV) copolymer by *N*,*N*,*2*,2-tetramethylpropane-1,3-diamine. (b) ¹H NMR spectrum in acetone-d₆ of the resulting poly(CTFE-*alt*-UTEV) copolymer. (c) ¹H NMR spectrum in acetone-d₆ of the precursor poly(CTFE-*alt*-CCEV) copolymer.

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Fig. 8. Mechanism for the degradation by basic hydrolysis of primary (1/) and secondary (2/) urethanes as proposed by Larson and Weber [59]. R₁ and R₂ represent alkyl or aryl groups.

0.9 ppm and between 2.1 and 2.5 ppm for the $-C(CH_3)_2$ and $-N(CH_3)_2$, respectively, and at 3.1 and 6.5 ppm for the $-C\underline{H_2}$ -NH- and $-CH_2$ -N \underline{H} - of the urethane functions, respectively. It was nonetheless not possible to determine the ratio of the different isomers or the actual extent of the ring-opening reaction. Increasing the amount of amine and the reaction time did improve the conversion, but still did not afford quantitative conversion of the cyclocarbonates.

Urethane linkages can be hydrolysed in alkaline medium [57] (Fig. 8), which could be a problem for applications (including in alkaline fuel cells). However, Kalinina et al.[58] did not observe degradation of N-phenylmaleimide/cyclocarbonate-bearing vinyl ether copolymers cross-linked via hydroxyurethane linkages after 3 h at 150 °C in concentrated sodium hydroxide solutions. Mabey and Mill [59] reported a very different stability between primary and secondary carbamates. While primary carbamates can be hydrolysed very quickly without heating, secondary carbamates can be strongly stabilised depending on the substituents present on the nitrogen atom [59] (Table 4). Electron-donating methyl group, for example, can considerably stabilise carbamates. Methylation of carbamates are usually performed using a combination of iodomethane and a strong base such as sodium hydride or lithium bis(trimethylsilyl)amide [60–62]. In this work however, to avoid side reactions, mild conditions (absence of strong base) were used for the methylation reaction. The poly(CTFE-alt-UrEV) copolymer was dissolved in acetone and iodomethane was added to the solution. After purification, a watersoluble material was isolated in high yields (85%). ¹H NMR and ¹³C NMR (DEPT 135 experiment) spectra (Figs. S4 and S5, respectively) showed the complete shift of the signals of the $-CH_2-N(CH_3)_2$ groups upon quaternisation. Indeed, the complete disappearance of peaks between 2.0 and 2.5 ppm in ¹H NMR, and at 48.6 and 69.5 ppm in ¹³C NMR due to $N(CH_3)_2$ and $-CH_2-N(CH_3)_2$), and the formation of new peaks between 3.0 and 3.5 ppm in ¹H NMR and at 55.9 and 73.7 ppm in 13 C NMR caused by $-CH_2-N(CH_3)_3^+$ are

Table 4

Half-life of various carbamates under hydrolytic conditions at pH=7 and T=25 °C calculated by Mabey and Mill [3]. R_1 , R_2 and R_3 represent the groups connected to the carbamates as indicated in Fig. 8.

<i>R</i> ₃	R_1	R_2	t _{1/2}
C ₆ H ₅	C ₆ H ₅	Н	1.5 days
C ₆ H ₅	C ₆ H ₅	CH ₃	5200 years
$P-NO_2C_5H_4$	C ₆ H ₅	Н	26 s
$P-NO_2C_5H_4$	C ₆ H ₅	CH ₃	2700 years
1-C ₁₀ H ₉	CH ₃	Н	8.5 days
$1 - C_{10}H_9$	CH ₃	CH ₃	1200 years

observed (Figs. S4 and S5). No new signals corresponding to the methylation of the urethane linkages could be seen. As expected, iodomethane alone cannot methylate the carbamate groups. The copolymers obtained were water-soluble and even though they probably are non-sensitive to the Hofmann degradation, they may not be resistant to very alkaline medium (due to the alkaline sensitive urethane linkages). Films could be obtained from the quaternised copolymers. However, these films were very brittle presumably because of the low molecular weight of the copolymers. Studies to solve these problems are underway and will be reported in due course.

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. The goal was to prepare copolymers bearing Hofmann elimination insensitive quaternary ammonium groups from cyclocarbonate-containing copolymers using the cyclocarbonate amine reaction. Two functional vinyl ethers, GcEV (epoxide-containing) and CCEV (cyclocarbonatecontaining) monomers were synthesised in high yields an purity and copolymerised with CTFE. The copolymerisation of GCEV and CTFE led to a nearly perfect alternating copolymer whereas that of CCEV and CTFE led to copolymer with structural defects (CTFE-CTFE dyads). Both the epoxides and cyclocarbonates functional groups seemed unaffected by the polymerisation conditions. The carbonation of the poly(CTFE-alt-GcEV) proceeded with near quantitative yield. The ring-opening of the cyclocarbonates with N,N,2,2tetramethylpropane-1.3-diamine was relatively efficient and vielded a suitable amine-functionalised copolymer which could be easily quaternised without side reactions using iodomethane. More work is required however to prepare non water-soluble higher molecular weight copolymers. The combination of this donor-acceptor copolymerisation and the ring-opening of cyclocarbonates by amine is a very promising synthetic method to introduce a range of functional groups onto a copolymeric backbone.

4. Experimental

4.1. Analyses

NMR spectra ¹H, ¹³C, and ¹⁹F 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 performed

on a Polymer Laboratories PL-GPC 50 instrument using 2 PL Mixed C 5 μ m columns thermostated at 35 °C, THF as eluent (1.0 mL/min) and a refractive index detector. Calibration was done using Varian polystyrene narrow standards. Elemental analyses were performed 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 performed 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 min, cooling from 150 °C to –50 °C at 20 °C/min, isotherm plateau at –50 °C for 3 min. The heating/cooling cycle was performed twice per sample. T_g were measured at the inflexion point of the enthalpic jump.

4.2. Chemicals

N,*N*,2,2-tetramethylpropane-1,3-diamine, palladium acetate and iodomethane were purchased from ABCR. Glycidol, vinyloxyethane, 1,10-phenanthroline, and all the solvents were purchased from Sigma-Aldrich. Chlorotrifluoroethylene was provided by Honeywell (Buffalo, NY, USA). *Tert*-butylperoxypivalate was provided by AkzoNobel (Compiègne, France). Deuterated solvents for NMR were purchased from Euroiso-top. All chemicals and solvents were used as received unless otherwise noted.

4.3. Vinyl ether synthesis

4.3.1. Vinyloxy-2-methyloxiranne (GcEV)

Palladium acetate (34.42 mg, 1.52 mmol) and 1,10 phenantroline (41.2 mg, 2.29 mmol) were dissolved separately in 10 mL of dichloromethane and mixed together at 20 °C for 15 min. 20.00 g (269.99 mmol) of glycidol 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 h. The volatiles were removed using a rotary evaporator. Diethyl ether was added to the residue, and the precipitated catalyst was filtered off. 17.03 g (170.09 mmol) of GCEV was then isolated by distillation under reduced pressure and obtained as a transparent colourless liquid.

¹H NMR (Acetone-d₆) δ (ppm): 0.89 (s, C-CH₃, 6H), 2.15 (s, -CH₂-N, 2H), 2.23 (s, N-CH₃, 6H), 3.44 (s, -CH₂-O, 2H), 3.91 (dd, CHH-CH=(E), ²J_{gem} = 1.77 Hz, ³J_{cis} = 6.82 Hz, 1H), 4.16 (dd, CHH-CH=(Z), ²J_{gem} = 1.64 Hz, ³J_{trans} = 14.27 Hz, 1H), 6.51 (ddt, CH₂-CH=, ³J_{cis} = 6.82 Hz, ³J_{trans} = 14.27 Hz, ⁴J = 0.51 Hz, 1H).

¹³C NMR (Acetone-d₆) δ (ppm): 23.5 (CH₃-C, 2C), 37.1 ((CH₃)₂-C<, 1C), 48.8 (CH₃-N, 2C), 67.2 (CH₂-N, 1C), 74.7 (CH₂-O, 1C), 86.2 (H₂C=CH, 1C), 153.1 (H₂C=CH, 1C).

¹H NMR (Acetone-d₆) δ (ppm): 2.61 (dd, -CHH-O- epoxy, ²J_{gem} = 5.05 Hz, ³J_{trans} = 2.53, 1*H*), 2.77 (dd, -CHH-O- epoxy, ²J_{gem} = 5.05 Hz, ³J_{cis} = 4.17 Hz, 1*H*), 3.17 (m, -CH₂-CH<, 1*H*), 3.56 (dd, -O-CHH-, ²J_{gem} = 11.62 Hz, ³J_{cis} = 6.32 Hz, 1*H*), 3.99 (dd, CHH-CH = (E), ²J_{gem} = 2.02 Hz, ³J_{cis} = 6.82 Hz, 1*H*), 4.01 (dd, -O-CHH-, ²J_{gem} = 11.62 Hz, ³J_{trans} = 2.78 Hz, 1*H*), 4.22 (dd, CHH-CH = (Z), ²J_{gem} = 2.02 Hz, ³J_{trans} = 14.27 Hz, 1*H*), 6.50 (ddt, CH₂-CH=, ³J_{cis} = 6.82 Hz, ³J_{trans} = 14.27 Hz, ⁴J = 0.51 Hz, 1*H*).

¹³C NMR (Acetone-d₆) δ (ppm): 44.2 (CH–**C**H₂–O–, 1C), 50.3 (–CH₂–**C**H<, 1C), 70.1 (>HC–**C**H₂–O–, 1C), 87.4 (H₂**C**=CHO–, 1C), 152.6 (>**C**=CH₂, 1C).

4.3.2. Carbonation of vinyloxy-2-methyloxirane

5.003 g (50.0 mmol) of vinyloxy-2-methyloxiran and lithium bromide (21.7 mg, 2.50 mmol) were dissolved into 30 mL of DMF and place into a Parr pressure reactor. The reactor was closed and 15 bar of CO₂ were introduced. The reaction mixture was then heated at 80 °C for 16 h. The reactor was then cooled down and the gases were evacuated. DMF was removed under reduced pressure. 50 mL of dichloromethane were added and the organic solution was washed with deionised water (3×30 mL). The aqueous phases were extracted once with dichloromethane (20 mL). The organic phase was dried with MgSO₄ and the solvent was removed under reduced pressure. The product was isolated as a brown liquid.

Vinyloxy-4-methyl-1,3-dioxolan-2-one (CCEV)

¹H NMR (Acetone-d₆) δ (ppm): 3.97 (dd, -CHH-OCOO-, ²J_{gem} = 11.75 Hz, ³J_{trans} = 4.17, 1H), 4.05 (dd, -CHH-OCOO-, ²J_{gem} = 11.87 Hz, ³J_{trans} = 2.78, 1H), 4.06 (dd, CHH-CH=(E), ²J_{gem} = 2.27 Hz, ³J_{cis} = 6.82 Hz, 1H), 4.29 (dd, CHH-CH=(Z), ²J_{gem} = 2.27 Hz, ³J_{trans} = 14.27 Hz, 1H), 4.40 (dd, -O-CHH-Carbonate, ²J_{gem} = 8.46 Hz, ³J_{trans} = 5.94 Hz, 1H), 4.65 (dd (t), -O-CHH-Carbonate, ²J_{gem} = 8.59 Hz, ³J_{cis} = 8.59 Hz, 1H), 5.09 (m, -CH₂-CH<, 1H), 6.55 (ddt, CH₂-CH=, ³J_{cis} = 6.82 Hz, ³J_{trans} = 14.27 Hz, ⁴J = 0.51 Hz, 1H).

¹³C NMR (Acetone-d₆) δ (ppm): 66.7 (>HC-**C**H₂-carbonate, 1C), 68.2 (-O-**C**H₂-CH<, 1C), 75.5 (-CH₂-**C**H<, 1C), 88.0 (H₂**C**=CHO-, 1C), 152.2 (-**C**H=CH₂, 1C), 206.3 (>**C**=O, 1C).

4.4. Radical copolymerisation of CTFE with vinyl ethers

All the copolymerisations were carried out using 100 or 300 mL Parr pressure reactors fitted with a rupture disc (3000 psi), mechanical stirring system, a manometer and 2 injection valves. Before reaction, all the solids are placed in the reactor which is then first filled with 20 bar of nitrogen (to detect leaks) and then put under vacuum (10^{-2} mbar) for 2 h. The liquid phases (initiators, liquid monomers, solvent) are first degassed by argon or nitrogen bubbling and then introduced into the reactor via a funnel. The desired amount of CTFE is then transferred in the reactor using double weighing method. The reaction mixture is then heated up to the desired temperature under stirring for the required time. At the end of the reaction, the reactor is cooled down to ambient temperature, the remaining gases are evacuated, and the resulting residue is dissolved into acetone, concentrated under vacuum and precipitated in cold methanol. The polymer is 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 Parr pressure reactor containing 20.0 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 reactor was then heated up to 74 °C for 16 h. The polymer was then precipitated and dried as described above.

4.5. Carbonation of poly(CTFE-alt-GcEV) copolymer

Poly(CTFE-alt-GcEV) copolymer (2.005 g, 9.24 mmol) and LiBr (0.041 g, 0.46 mmol) were dissolved in 30 mL of DMF in a 50 mL Parr pressure reactor. The reactor was closed and 15 bar of CO_2 were introduced. The reaction mixture was then heated at 80 °C for 16 h. Gas in excess was then evacuated and the copolymer was precipitated in cold methanol. The solid was dried at 60 °C under vacuum for 12 h.

4.6. Functionalisation of poly(CTFE-alt-CCEV) copolymer by carbonate/amine reaction

1.006 g (3.84 mmol) of poly(CTFE-*alt*-CCEV) copolymer, dissolved in 20 mL of DMF, were placed into a 50 mL round bottom flask. *N*,*N*,2,2-tetramethylpropane-1,3-diamine (0.750 g, 5.76 mmol), and triethylamine (0.023 g, 0.23 mmol) were added to the DMF solution, and the reaction mixture was heated under stirring at 80 °C for 48 h.

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The polymer was isolated by precipitation in cold methanol, and dried at 60 °C under vacuum for 12 h.

4.7. Methylation of poly(CTFE-alt-UrEV) copolymer

500 mg (1.32 mmol) of poly(CTFE-alt-UrEV) copolymerwere dissolved in 20 mL of DMF in a 50 mL round bottom flask. Iodomethane (0.75 g, 5.3 mmol) was added to the reaction mixture and the reaction mixture was stirred at 20 °C for 12 h. Methanol was added to the reaction medium to dissolve the solid formed, and the polymer was precipitated in cold diethyl ether. The solid was dried at 60 °C under vacuum for 12 h.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.08.014.

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