Synthesis of fluorinated telomers. Part 6. Telomerisation of chlorotrifluoroethylene with methanol†

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Bulk radical telomerisation of chlorotrifluoroethylene (CTFE) with methanol was investigated for the synthesis of fluorinated alcohols. Improvements in the conversion of CTFE and of the selectivity of the reaction were sought by using different radical initiators (peroxides, percarbonates, peresters) and an excess of methanol. These reactions were compared in terms of CTFE conversion, yield of monoadduct and formation of higher molecular weight telomers. Under these conditions, radical initiated telomerisations systematically led to low molecular weight CTFE telomers. 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) proved to be the most effective radical initiator. All these experiments revealed the low chain transfer activity of methanol in the presence of CTFE. A thorough structural study of typical CTFE–methanol telomers was performed by ^{19}F, ^{1}H and ^{13}C NMR spectroscopies. These analytical methods allowed us to prove the highly regioselective formation of $HOCH_2CF_2CFClH$ (produced with a 95% selectivity), showing the regioselectivity of the addition of hydroxymethyl radicals onto the difluoromethylene side of CTFE.

Fluorinated derivatives bearing a hydroxylated endgroup are of great interest for various applications such as surfactants, paints and coatings, block copolymers, *etc.* An easy way to synthesise such compounds is to polymerise a fluorinated olefin in the presence of a chain transfer agent, also called a *telogen*, to yield a series of low molecular weight products. Such a reaction is termed *telomerisation.*[1–4]

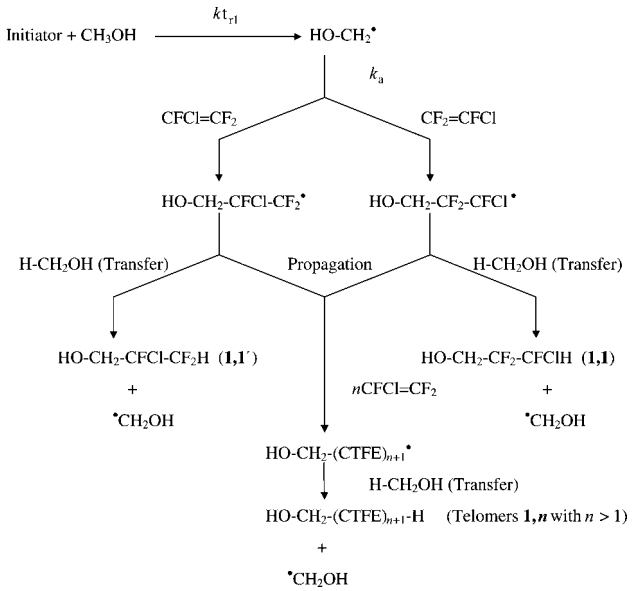
Telomerisation reactions of chlorotrifluoroethylene (CTFE) with many transfer agents have been investigated by numerous authors. Different kinds of transfer agents have been used. They contain cleavable bonds such as C–Cl (CCl_4,[5,6] CCl_3R[7]); C–Br (CCl_3Br,[8] $BrCF_2CFClBr$[9]); C–I (C_2F_5I,[10] $C_nF_{2n+1}I$ with $n = 4$ or 6,[11] CF_3CFClI,[11] ICF_2CFClI[12]); H–Br;[13] Br–Br;[14] Cl–F ($ClSO_2F$[15]); Cl–Cl ($ClSO_2Cl$[16]); I–F;[17] I–Cl;[18] I–Br;[19] I–I;[12] O–F (CF_3OF[20]), S–S (CF_3SSCF_3[21]), S–H (HOC_2H_4SH[22]), P–H [$HP(O)(OEt)_2$[23]]; B–H;[24] Si–H ($HSiCl_2CH_3$[25]); C–H [CCl_3H,[26] $(CH_3)_2CHOH$,[27] CH_3OH[28–30]]. A more exhaustive list of the transfer agents involved in the telomerisation of CTFE has already been presented.[31]

Alcohols are known to participate in chain transfer reactions essentially by hydrogen abstraction from available C–H groups on the carbinol carbon, the electron-withdrawing hydroxyl group making this chain transfer easier. However, their chain transfer coefficients are usually considered too low for these compounds to be efficient telogens, insofar as the "activation" in hydrogen abstraction is concerned, due to the hydroxy function that is, in most cases, of low importance. For this reason, few investigations involving alcohols as telogens and fluorinated alkenes have been described, and apparently excessive by-product formation, coupled with unfavourable product distributions, have deterred any commercial development.

In fact, one of the most important steps in the telomerisation process is the homolytic cleavage of the C–H bond in the α-position of the alcohol during the initiation steps. The dissociation energy of this bond (BDE) varies, depending on the structure of the telogen, with the lowest among the linear aliphatic alcohols being in methanol (393 kJ mol^{-1}[32]). Thus, methanol appears to be a convenient and readily available telogen for the synthesis of fluorinated telomers bearing a functional endgroup. In this way, the radical addition of methanol to chlorotrifluoroethylene (CTFE), initiated by di-*t*-butyl peroxide, γ or UV radiation, gave a telomeric distribution having a low degree of polymerisation, as shown by Liska and Simek.[30] In any case, products resulting from radical rearrangements during telomerisation were observed. Nevertheless, these experiments demonstrated the low activity of methanol as a chain transfer agent in the presence of CTFE.

Concerning the reaction of hexafluoropropene (HFP) with methanol, Haszeldine *et al.*[33] reported that under thermal, photochemical or peroxide-initiated conditions the monoadduct was obtained in high yield *via* a radical chain mechanism. Moreover, methanol shows an intermediate activity in chain transfer when reacting with tetrafluoroethylene (TFE): several research works initiated by Joyce[34] proved this alcohol to be an excellent telogen with TFE under radical conditions, yielding wide telomeric distributions having the general formula: $H(C_2F_4)_nCH_2OH$, with $\overline{DP}_n \approx 6$ when starting with twice as much methanol as TFE. Sotokawa *et al.*[35] confirmed these results forty years later, whereas Blickle *et al.*[36] achieved the telomerisation of TFE with methanol, using perester initiators. The first two adducts, $HOCH_2CF_2CF_2H$ and $HOCH_2(C_2F_4)_2H$, were successfully isolated by Paleta and Dedek,[37] who used a continuous flow of TFE bubbling through a methanol solution, with AIBN or benzoyl peroxide as radical initiators, at very low reaction temperatures. The kinetics of telomerisation of TFE with methanol was investigated by Kostov *et. al.*[38] Telomers of low molecular weights ($\overline{DP}_{n\,cum} = 3$–8) were also successfully prepared (over 70% yield) by Chambers and Powell,[39] from methanol and trifluoroethylene by irradiating the reactive medium with gamma rays. In the case of the telomerisation of vinylidene fluoride (VDF) with methanol, Oku *et al.*[40] proved that the

† For part 5, see: ref. 41.



Scheme 1 Mechanism of the radical addition of methanol to CTFE.

di-*t*-butyl peroxide initiated telomerisation of VDF with methanol is feasible. This was later confirmed,[41] although only leading to fair yields, with the remaining products arising from the concomitant formation of non-functional oligomers produced from the direct initiation of tertiobutoxy and even methyl radicals onto VDF.

The present work intends to complete the above results by performing a thorough investigation of the telomerisation of CTFE with methanol. This involves a study on the influence of the experimental parameters, especially the initial $[methanol]_0/[CTFE]_0$ molar ratio, on the reaction in terms of monomer conversion and average molecular weights of the products and a structural study of the CTFE–methanol telomers (in terms of regiochemistry and functionality of the telomers).

Results and discussion

Various aspects of the radical addition of methanol to chlorotrifluoroethylene (CTFE) were studied. Our goal was to find the best experimental conditions to obtain the highest yield of chlorofluorinated propanol (*i.e.*, the monoadduct) and to direct the selectivity of the addition. Indeed, as shown in Scheme 1, radical addition of the hydroxymethyl radical to the double bond of the fluoroalkene can be expected to proceed in two different ways. So far, only Joyce[34] and Liska and Simek[30] have studied this reaction. Recently, Wakselman *et al.*[42] confirmed these results to synthesise deuterated and hydrogenated analogues of 3-chloro-2,2,3-trifluoropropanol,[30] and then chlorofluoroallylic alcohols by dehydrofluorination of these compounds.[43] The synthesis of 3-chloro-2,2,3-trifluoropropanol, as described in their work, was not selective and led to poor yields. Liska and Simek[30] gave evidence for the formation of a mixture of two monoadducts (**1,1** and **1,1′**), telomers (**1,*n*** with $n > 1$) and other products formed by side reactions. Taking into account these observations and previous work on the radical addition of methanol to fluoroolefins (TrFE,[35] HFP[29]), we expected to obtain better results with CTFE. In our opinion, different parameters should influence the selectivity and the reaction yield. These are the reaction temperature, the nature of the radicals generated from the

Table 1 Structure and kinetic data for the initiators used in the telomerisation of MeOH with CTFE

Trade name (AKZO)	Chemical name	Structure	Radicals formed	Physical state	T/K for a half-life of x h 0.1				
					1	10	A/l s^{-1}	E_a/kJ mol^{-1}	
Trigonox® 25	*tert*-Butylperoxypivalate (TBPPI)	^{t}BuOOC(O)^{t}Bu	^{t}BuO•, Me•, ^{t}Bu•, ^{t}BuCO$_2$•	Liquid	367	348	320	7.09×10^{14}	123.6
Lucidol®	Dibenzoyl peroxide (BP)	$[PhC(O)O]_2$	PhCO•, Ph•	Powder	386	364	345	6.94×10^{13}	122.3
Trigonox® 101	2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP)	$[^t$BuOOC(Me)$_2$CH$_2$–$]_2$	^{t}BuO•, Me• •CH$_2$CH$_2$	Liquid	429	407	387	1.69×10^{6}	155.4
Trigonox® B	Di-*tert*-butylperoxide (DTBP)	^{t}BuOO^{t}Bu	^{t}BuO^{-}•, Me•	Liquid	437	414	394	4.20×10^{15}	153.4
Trigonox® A-80	*tert*-Butylhydroperoxide (TBHP)	^{t}BuOOH	^{t}BuO•, Me•	Aq. solution	480	458	437	3.18×10^{17}	186.0

Table 2 Experimental conditions and overall yields for the radical addition of methanol to CTFE with $C_0 = [initiator]_0/[CTFE]_0 = 0.025$

Expt. no.	T/K	Initiator	Half-life/h	Reaction time/h	Initial amount of CTFE/g	R_0[a]	Overall yield[b] (%)	**1,1**[c] (%)	**1,1′**[c](%)	**1,*n*** ($n > 1$)[c] (%)
1	348	TBPPI	1.0	8	52	40	10	1	0	9
2	363	BP	1.0	8	40	40	16	8	0	8
3	388	DHBP	10.0	46	29	40	84	64	3	17
4	407	DHBP	1.0	7	72	5	20	8	0	12
5	407	DHBP	1.0	7	40	20	34	19	0	15
6	407	DHBP	1.0	7	30	40	92	73	3	16
7	407	DHBP	1.0	7	18	80	79	73	3	3
8	419	DTBP	1.0	7	29	40	86	67	3	16
9[d]	419	DTBP	1.0	7	31	40	79	67	3	9
10	432	DHBP	0.1	1	32	40	46	34	1	11
11	453	TBHP	1.0	8	30	40	36	24	1	11
12	473	TBHP	0.1	8	31	40	26	16	0	10

[a] $R_0 = [MeOH]_0/[CTFE]_0$. [b] Yield calculated from initial mol of CTFE. [c] $HOCH_2CF_2CFClH$ (**1,1**), $HOCH_2CFClCF_2H$ (**1,1′**), $HOCH_2(CTFE)_{n+1}H$ (**1,*n*** with $n > 1$). [d] $C_0 = [initiator]_0/[CTFE]_0 = 0.050$.

initiators, and also the initial $[methanol]_0/[CTFE]_0$ molar ratio. The observed results are reported herein.

Analyses of the products formed

The reactions were performed at various temperatures ranging between 348 and 473 K. In most cases, the required initiators were used in conditions in which they display a half-life close to 1 h,[44] as shown in Table 1. This table also lists the formation of various radicals arising from homolytic cleavages from the initiators. A minimum reaction time of 7 h was necessary to ensure that all the initiator decomposed. The results are listed in Table 2.

The chlorofluoroalcohol and telomer yields were assessed by ^{19}F NMR of an aliquot of the total product mixture (Fig. 1), using C_6F_6 as external standard. The CTFE conversion was determined by the sum of the yields of these products.

In order to separate the monoadducts **1,1** and **1,1′** from the *n* adducts **1,*n***, the crude product was distilled. A colourless liquid was obtained and its ^{19}F and ^{1}H NMR spectra are shown in Fig. 2 and 3, respectively. Firstly, the ^{19}F NMR spectrum (Fig. 2) clearly shows the presence of two signals corresponding to the monoadducts **1,1** and **1,1′**, one of which is much more intense than the other. The ^{1}H NMR spectrum (Fig. 3) exhibits a doublet ($^2J_{HF} = 48.0$), of doublets ($^3J_{HF} = 8.5$) of doublets ($^3J_{HF} = 5.2$ Hz) centred at 6.3 ppm assigned to the –CFClH end group of the monoadduct **1,1**. However, the $-CF_2H$ endgroup of the **1,1′** monoadduct at 6.0 ppm [triplet ($^2J_{HF} = 54.3$) of doublets ($^3J_{HF} = 3.3$ Hz)] has a smaller integral than the –CFClH endgroup. We can therefore conclude that the radical addition of methanol to CTFE was very selective towards the formation of 3-chloro-2,2,3-trifluoropropanol (**1,1**). Indeed, when the overall yield was satisfactory (higher than 75%), the molar proportions of alcohols **1,1** and **1,1′** were 95 and 5%, respectively (experiments 3 and 6–9, Table 2).

As can be seen in Fig. 2, 3-chloro-2,2,3-trifluoropropanol (**1,1**) gives rise to an ABX system. Its two AB peaks are respectively located at −121.3 and −123.9 ppm, while its X signal is at −156.2 ppm. The spectrum of 2-chloro-2,3,3-trifluoropropanol (**1,1′**) also displays an ABX system. Its two AB resonances are located at −131.8 and −135.6 ppm, respectively, and its X peak is at −137.2 ppm. Furthermore, from the coupling constants, a simulated ^{19}F NMR analysis of 3-

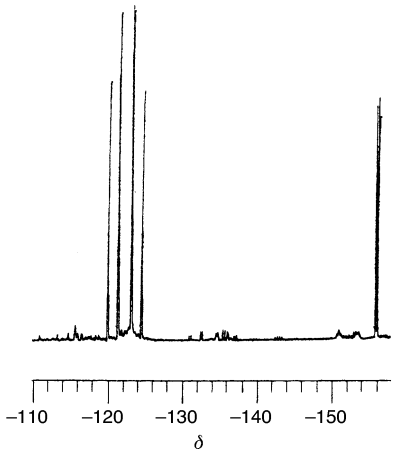


Fig. 1 ^{19}F NMR spectrum of the total product mixture produced from the telomerisation of chlorotrifluoroethylene with methanol (experiment 6, Table 1).

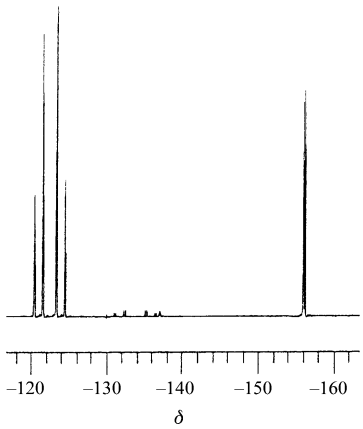


Fig. 2 ^{19}F NMR spectrum of the distilled chlorotrifluoroalcohol (monoadducts **1,1** and **1,1′**) produced from the telomerisation of chlorotrifluoroethylene with methanol (experiment 6, Table 1).

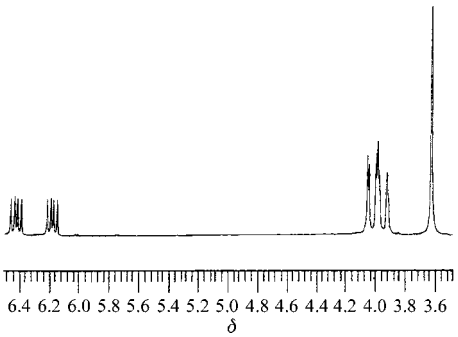


Fig. 3 ^{1}H NMR spectrum of the distilled chlorotrifluoroalcohol (monoadducts (**1,1**) and (**1,1′**) produced from the telomerisation of chlorotrifluoroethylene with methanol (experiment 6, Table 1).

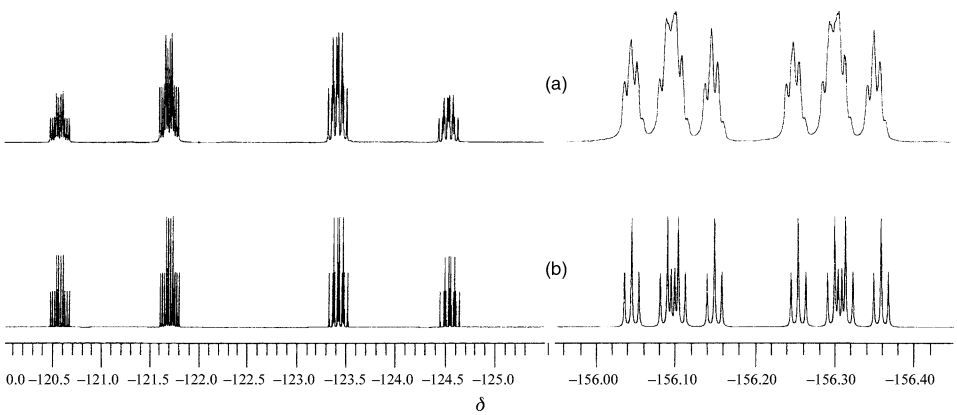


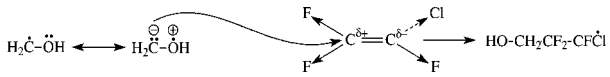
Fig. 4 Experimental (a) and simulated (b) ^{19}F NMR spectra of **1,1**.

chloro-2,2,3-trifluoropropanol was performed and is in good agreement with the experimental chemical shifts (Fig. 4).

Finally, the chemical shifts of the *n* adducts, also called telomers (**1,*n*** with $n > 1$) have been deduced by comparing the ^{19}F NMR spectra of both the crude product (Fig. 1) and the distillated monoadducts (Fig. 2). For these telomers, the difluoromethylene groups resonate in two different regions at -110 to -130 ppm and at -132 to -140 ppm, corresponding, respectively, to the normal PCTFE chaining (*i.e.*, head-to-tail CTFE blocks) and to the reversed PCTFE chaining (*i.e.*, head-to-head CTFE blocks).[45] The signals due to the –CFCl– groups of CTFE units and the –CFClH endgroups of the telomers appear at -152 to -156 ppm.

It is noteworthy that the yield of the monoadduct **1,1** is larger than the yield of the telomers, which did not exceed more than 17% under our conditions for a large excess of methanol ($R_o \approx 40$).

Hence, it can be concluded that the favoured addition of the hydroxymethyl radical, the carbon atom of which exhibits nucleophilic behaviour (since the hydroxyl group is an electron-donating substituent) as reported by Chambers *et al.*,[46] to the olefin, occurs onto the difluoromethylene group. Such an observation may be explained by two statements: on the one hand, the carbon is electronically poorer on the difluoromethylene part than on the fluorochlorinated side, because of the electronic attractive effect of the fluorine atoms. On the other hand, greater steric hindrance occurs on the fluorochlorinated side due to the bulky chlorine atom, which hampers the attack of the hydroxymethyl radical (Scheme 2).



Scheme 2 Radical addition of the hydroxymethyl radical to CTFE.

Influence of the initiator nature and reaction temperature

Several telomerisation reactions of CTFE with methanol were performed using various initial telogen concentrations keeping the initial amount of CTFE introduced into the autoclave constant.

As has been described for the radical addition of methanol to vinylidene fluoride,[40,41] the best experimental conditions were found to be 407 and 419 K with the peroxides 2,5-bis-(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) and di-*tert*-butyl peroxide (DTBP), respectively (experiments 3 and 6–9, Table 2). The best yield was obtained when the reaction was initiated by DHBP (experiment 6), which gave 73% 3-chloro-2,2,3-trifluoropropanol (**1,1**) (see also Experimental for NMR characterisation, and Fig. 1), 3% 2,3,3-trifluoro-2-chloropropanol (**1,1′**) and 16% telomers (**1,*n***). The gas chromatogram of the total product mixture of experiments 4 and 7 [Fig. 5(a) and (b), respectively] enabled us to confirm the formation of telomers with low average degrees of polymerisation ($n \leqslant 4$), even when the initial molar ratio R_0 was the lowest (*i.e.*, 5 in experiment 4). Actually, this chromatogram [Fig. 5(a)] shows a classical telomeric distribution with peaks corresponding to the monoadducts, diadducts, triadducts and tetraadducts having retention times of 2.5, 6.7, 10.4 and 13.9 min, respectively. However, the peak located at 11.0 min could not be assigned, although it is presumed to be recombination products.

The initiation in the presence of DHBP was more efficient than that involving DTBP in terms of overall and **1,1** yields, because of the chemical structure of the initiators. In the course of its thermal decomposition, one mol of di-*tert*-butyl peroxide (DTBP) produces two mol of *tert*-butoxy radicals whereas the thermal decomposition of 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) generates four radicals. For the same rate of decomposition, the initiation in the presence of DHBP produces twice as many radicals as DTBP

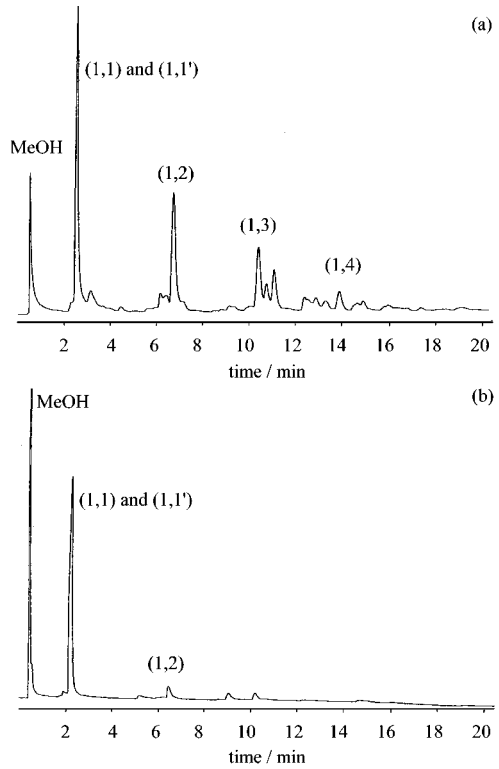


Fig. 5 Gas chromatograms of the total product mixture of the telomerisation of CTFE with methanol. Experimental conditions: $T = 407$ K; $t = 7$ h; $[MeOH]_0/[CTFE]_0 = 5$ (a) and 80 (b); $[DHBP]_0/[CTFE]_0 = 0.025$ (experiments 4 and 7 in Table 2).

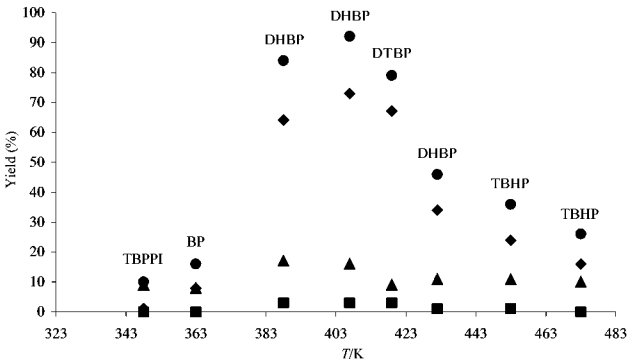


Fig. 6 Plots of the overall CTFE conversion (●), yields of monoadducts **1,1** (◆), **1,1′** (■) and higher adducts **1,*n*** (▲) *vs.* the temperature and the nature of the initiator.

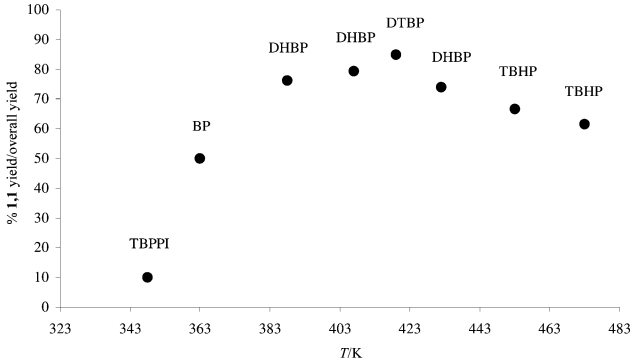


Fig. 7 Plot of the ratio of **1,1** yield to overall CTFE conversion *vs.* the temperature and the nature of the initiator.

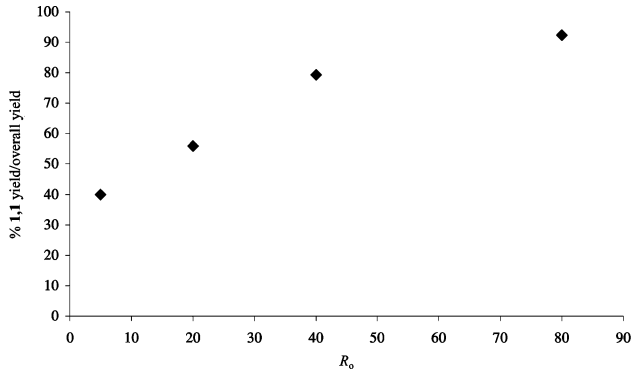


Fig. 8 Plot of the ratio of **1,1** yield to overall CTFE conversion *vs.* the initial $[MeOH]_0/[CTFE]_0$ molar ratio.

does. This is why we carried out experiment 9 with an initial $[DTBP]_0/[CTFE]_0 = C_0$ molar ratio of 0.05, so as to retain similar conditions as in the case of reactions initiated by DHBP, where C_0 was always set to 0.025. Although the same yields of alcohols **1,1** and **1,1′** were obtained, the amount of telomer formed was only 9% *vs.* 16% when the initial C_0 molar ratio was 0.025 (experiment 8). Consequently, the initiation with DHBP or DTBP (with $C_0 = 0.05$) significantly increased the selectivity of the radical addition.

The study of the reaction temperature, the nature and the amount of the initiator showed an increase in both the yield and the selectivity up to 407 and 419 K. Above these temperatures, the yields and the selectivity progressively decreased (experiments 10–12) as can been seen in Fig. 6 and 7. Fig. 6 shows the evolution of alcohol **1,1**, **1,1′** and telomer **1,*n*** overall yields *vs.* the temperature and the nature of the initiator. From 348 to 473 K, the amount of telomer **1,*n*** formed did not change significantively, but as already observed, the yield of **1,1** formed increased with the temperature up to 419 K (with a maximum value of 90%). Above this temperature, it decreased dramatically. In our opinion, side reactions between the hydroxymethyl radical and the initiator radicals could account for this decrease.

Fig. 7 shows the influences of the temperature and the nature of the initiator on the evolution of the selectivity of the radical addition of methanol to CTFE. The best selectivity was obtained at 419 K with DTBP, $C_0 = 0.05$ (experiment 9), although the yield of alcohol **1,1** was lower than that obtained from DHBP at 407 K (experiment 6).

Influence of the initial R_0 molar ratio

The radical addition of methanol to CTFE led to a high yield of chlorotrifluoroalcohol when the reaction was carried out at 407 K with DTBP as thermal initiator (experiment 6). To improve the selectivity of the addition and the formation of **1,1**, the initial molar ratio $R_0 = [CTFE]_0/[MeOH]_0$ was monitored. As expected, the higher the R_0 value, the lower the average degree of polymerisation of the telomers, in agreement with Mayo's law for radical telomerisation:[47]

$$\frac{1}{(\overline{DP_n})_i} = C_T \times \frac{[T]_0}{[M]_0}$$

where $(\overline{DP_n})_i$ represents the instantaneous degree of polymerisation, C_T the transfer constant of the radical to the transfer agent (or telogen), and $[T]_0$ and $[M]_0$ stand for the initial concentrations of telogen and monomer, respectively; $[T]_0/[M]_0$ is also represented by R_0.

First, it was noted that the overall yield and the yield of **1,1** increased with R_0 except for $R_0 = 80$ (experiment 7) where the overall yield was lower than that at $R_0 = 40$ (experiment 6). This can be attributed to the solubility of CTFE, which increased with the dilution of the reagents. Hence, the yield of **1,1** was 73% for $R_0 = 40$ (experiment 6), whereas it was only 8 and 19% for $R_0 = 5$ (experiment 4) and $R_0 = 20$ (experiment 5), respectively. For $R_0 = 80$ (experiment 7), the yield of **1,1** was not improved, but it is noteworthy that only 3% of the products formed were telomers. Fig. 8 shows the evolution of the ratio of the yield of **1,1** to the overall yield *vs.* the initial molar ratio R_0. As the yield of **1,1** increases more than the yield of telomers from $R_0 = 5$ to 80, the selectivity should reach almost 100% for higher R_0 (> 80).

Conclusion

The radical telomerisation of CTFE with methanol led to fair to good results, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) appearing to be the most efficient initiator. However, methanol exhibits a low transfer activity in the presence of CTFE, in contrast to the same transfer agent involved in the telomerisation of other commercially available fluorinated olefins such as TFE, HFP, or trifluoroethylene (TrFE), but in good agreement with the results obtained for VDF. Rather low molecular weight CTFE telomers were produced in fair to good yields, as in the case of the first three fluoroalkenes. Highly regioselective addition of hydroxymethyl radicals to the more fluorinated site of CTFE was also observed, which was confirmed by NMR simulation. The characterisation of higher adducts (*i.e.*, CTFE–methanol telomers) was complex and more thorough investigations have not yet been completed. However, the telomerisation of CTFE with methanol appears to be a good method to prepare novel macromonomers after chemical modification of the hydroxy end-group. This work is in progress.

Experimental

Materials

Chlorotrifluoroethylene was kindly supplied by Solvay S.A. (Tavaux, France). *tert*-Butylperoxypivalate (TBPPI) was a gift from La Charolaise des Peroxydes. Dibenzoyl peroxide (BP), 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP), di-*tert*-butyl peroxide (DTBP) and *tert*-butyl hydroperoxide (TBHP) were generously provided by Akzo (Compiègne, France). Methanol was of analytical purity grade and was obtained from Sigma-Aldrich Chimie (Saint Quentin-Fallavier, France). The reagents did not require any purification prior to use.

Apparatus and analysis

The reactions were carried out in a 1000 ml Hastelloy (C276) Parr Systems autoclave, fitted with a mechanical stirrer and a specific electric heating mantle. The agitation speed was fixed by an electronic driving device, which also controlled the temperature of the autoclave *via* a thermocouple and an integrated heating power regulator.

After reaction, the products were worked up and analysed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an OV1 column, (2 m × 1.8 in). Nitrogen pressure at the entrance to the column was maintained at 1 bar and the detector and injector temperatures were 533 and 528 K, respectively. The temperature program started from 308 K and attained 523 K at a heating rate of 10 K min^{-1}. The GC apparatus was connected to a Hewlett Packard integrator (model 3390), which automatically calculated the area of each peak in the chromatogram.

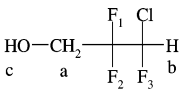
The products were characterised by ^1H, ^{13}C and ^{19}F NMR spectroscopy at room temperature. Spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated chloroform as the solvent and TMS (resp. $CFCl_3$) as the reference for ^1H (resp. ^{19}F) nuclei. The letters s, d, t, q and m stand

for singlet, doublet, triplet, quartet and multiplet, respectively. Coupling constants and chemicals shifts are given in hertz (Hz) and ppm, respectively. In all cases, the yields were calculated by using hexafluorobenzene of analytical purity grade provided by Aldrich, as external standard in the ^{19}F NMR spectra. NMR simulation was performed with gNMR software.[48]

Model reaction: radical addition of methanol to chlorotrifluoroethylene

The initiator and methanol were successively introduced into the 1000 ml Hastelloy autoclave. The autoclave was then left closed for 20 min and purged with 20 bar of nitrogen to prevent any leakage, and degassed afterwards. Next, CTFE was introduced by double weighing (see Table 2 for the required amounts of each starting material). The reaction was allowed to proceed for 7 h at the required temperature (Table 1), after which the autoclave was cooled to room temperature and then put in an ice bath. The total product mixture (pale yellow liquid) was analysed by GC and by ^{19}F NMR spectroscopy to assess the nature and the yield of the products formed. The mixture was then concentrated and 3-chloro-2,2,3-trifluoropropanol was obtained by distillation at 387 K under atmospheric pressure.

3-Chloro-2,2,3-trifluoropropanol (1,1). ^1H NMR ($CDCl_3$) δ: 2.97 (br s, shifted with dilution, Hc, 1H); 4.0 (ddd, $^3J_{HaF1} = 14.5$, $^3J_{HaF2} = 11.4$, $^4J_{HaF3} = 2.0$, Ha, 2H); 6.30 (ddd, $^2J_{HbF3} = 48.0$, $^3J_{HbF1} = 8.5$, $^3J_{HbF2} = 5.2$, Hb, 1H). ^{19}F NMR ($CDCl_3$) δ: -121.3 (ABX system, AB part dt, $^2J_{F1F2} = 263.8$, $^3J_{F1Ha} = 14.8$, $^3J_{F1F3} = 10.3$, $^3J_{F1Hb} = 5.0$, F_1, 1F); -123.8 (ABX system, AB part dt, $^2J_{F2F1} = 263.8$, $^3J_{F2F3} = 13.6$, $^3J_{F2Ha} = 11.2$, $^3J_{F2Hb} = 8.9$, F_2, 1F); -156.2 (ABX system, X part dt, $^2J_{F3Hb} = 48.0$, $^3J_{F3F2} = 13.6$, $^3J_{F3F1} = 10.3$, $^4J_{F3Ha} = 2.1$, F_3, 1F). ^{13}C NMR ($CDCl_3$) δ: 60.2 (t, $^2J_{CF} = 23.0$, $HOCH_2CF_2$–); 95.9 (dt, $^1J_{CF} = 247.0$, $^2J_{CF} = 32.6$, $–CH_2CF_2CFClH$); 116.4 (dt, $^1J_{CF} = 249.2$, $^2J_{CF} = 25.3$, $–CH_2CF_2CFClH$).



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