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Radical telomerization of 3,3,3-trifluoropropene with diethyl hydrogen phosphonate: Characterization of the first telomeric adducts and assessment of the transfer constants

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Abstract

The radical telomerization of 3,3,3-trifluoropropene (TFP) with diethyl phosphate (or diethyl hydrogen phosphonate, DEHP) was investigated to synthesize fluorinated telomers bearing a phosphonate end-group, as $H(TFP)_nP(O)(OEt)_2$. Di-*tert*-butyl peroxide was the most efficient radical initiator. A careful structural study of typical TFP/DEHP telomers was performed by ^1H, ^{19}F, and ^{31}P nuclear magnetic resonance spectroscopies. These analytical methods allowed us to prove the selective addition of the phosphonyl radical onto the hydrogenated side of TFP, while the telomers containing more than two TFP units were composed of TFP isomers containing normal and reversed adducts. The kinetics of telomerization led to the assessment of the first four order transfer constants giving an infinite transfer constant of 0.75 at 140 °C for DEHP.

Keywords: 3,3,3-Trifluoropropene; Radical telomerization; Diethyl hydrogen phosphonate; Transfer constant; Nuclear magnetic resonance; Kinetics of telomerization

1. Introduction

Fluorinated derivatives bearing phosphorus atoms are known for their applications in the field of surfactants [1,2], lubricants, oleophobic textile treatment [3], fire fighting agents, insecticides [4], complexing agents [5] and electrolytes [6,7]. They can also act as additives for polymers [8,9]. Many investigations dealing with the synthesis of $R_FP(O)(OR)_2$ have been described in the literature [10–19]. Among these methods, the telomerization reaction has proved to be an easy method to prepare such derivatives. Early examples include the redox telomerization of vinyl or allyl phosphonate with chlorofluorinated chains bearing a CCl_3 end-group, which led to original phosphonic acids [15].

Fluoroalkenes can also undergo radical telomerization, e.g. tetrafluoroethylene (TFE) [10–12], chlorotrifluoroethylene (CTFE) [20], and vinylidene fluoride (VDF) [21] with phosphonate-containing transfer agents (e.g., dialkyl hydrogen phosphonates). They also react with monomers bearing phosphonate functionality (e.g. vinyl or allyl phosphonates) and with fluorinated telogens (mercaptans [22,23] or perfluoroalkyl iodides [24]).

It is also possible that 3,3,3-trifluoropropene (TFP) and its telomers can be used as precursors to well-defined fluoropolymers. Previously, this monomer was used by several authors for homopolymerization [25–27] and in copolymerization [28–31] reactions with different fluorinated and non-fluorinated monomers. Many initiations have been used: metal complexes [26,28], γ-rays [27], peroxides [29,30], persulfates [30], and azo compounds [25].

Although the telomerization of TFP with various chain transfer agents (halogenated compounds [32–35], alcohols [36], esters [37]) has been demonstrated, very few examples exist in the literature involving the use of diethyl hydrogen phosphonate (DEHP) [13]. Telomerization of various fluoroalkenes with dialkyl hydrogen phosphonate as the functional transfer agent [31] is well known and is summarized in Table 1.

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Table 1
Radical telomerization of various fluoroalkenes with dialkyl hydrogen phosphonate (DEHP): experimental conditions, degree of polymerization, $\overline{DP}_n$ and infinite transfer constant C_T^∞ (n.d. stands for not determined)

Fluoroalkene	Initiation conditions	R_0 [a]	$\overline{DP}_n$	C_T^∞ [b]	Reference
$F_2C{=}CF_2$	AIBN	0.1–2.0	n = 1–10	0.2/80 °C	[11]
	Peroxide	–	n = 1–6	n.d.	[10]
$F_2C{=}CFCF_3$	Peroxide, therm.	–	n = 1	n.d.	[13]
$F_2C{=}CFCl$	Peroxides, 140 °C	0.3–2.0	n = 1–10	0.34/140 °C	[20]
$F_2C{=}CH_2$	DTBP, 140 °C; DBP, 92 °C; AIBN, 80 °C	0.1–2.0	n = 1–15	0.34/140 °C	[21]
$FClC{=}CFCl$	γ-Rays, 9 days	3.0	n.d.	n.d.	[12]
$F_2C{=}CCl_2$	γ-Rays, 16 days	2.1	n.d.	n.d.	[12]
$CFCl{=}CCl_2$	γ-Rays, 15 days	2.0	n.d.	n.d.	[12]
$H_2C{=}CHR_F$	Peroxide, AIBN	1.0	Monoadduct 39%	n.d.	[24]
$H_2C{=}CHCF_3$	130 °C/DTBP	1.0	Variable	n.d.	[13]
$H_2C{=}CHCF_3$	140 °C/DTBP	Variable		0.75/140 °C	This work

[a] $R_0 = [DEHP]_0/[fluoroalkene]_0$.
[b] C_T^∞ is defined as the infinite transfer constant to DEHP.

Haszeldine et al. [13] studied the peroxide addition of DEHP to different fluoroalkenes, such as TFE, CTFE, VDF, hexafluoropropene (HFP), including TFP and found that the latter gave diethyl-3,3,3-trifluoropropyl-1-phosphonate only (monoadduct in 39% yield). A Bayer Company patent [38] demonstrates the synthesis of 2-perfluoroalkylalkanophosphonate esters (using $CH_3(CH_2)_6CO_2OC(CH_3)_3$ as the initiator) with general formula: $(R^1R^2O)_2P(X)–CH_2C(R^3)HR^F$ (where R^3 can be alkyl or fluoroalkyl group and R^F stands for a halogen or a fluorinated group) in 51–91% yield.

However, these investigations did not take into account the possiblity of formation of higher TFP adducts, their different isomers, detailed structural analysis, and the kinetics of the telomerization, which is the goal of this present paper.

2. Results and discussion

Radical telomerization of 3,3,3-trifluoropropene (TFP) with diethyl hydrogen phosphonate (DEHP) was initiated by di-*tert*-butyl peroxide (DTBP) at 140 °C, as follows:

$$HP(O)(OC_2H_5)_2 + nH_2C{=}CH(CF_3) \xrightarrow[140\,^\circ C]{DTBP} H[CH(CF_3)CH_2]_n\text{-}P(O)(OC_2H_5)_2$$

Indeed, this reaction is the result of four steps depicted in Scheme 1.

The first adducts of the telomerization of TFP were synthesized in an autoclave by using di-*tert*-butyl peroxide (DTBP) as the initiator (mainly 3% in initial molar ratio about TFP: $C_0 = [DTBP]_0/[TFP]_0 = 0.03$) and acetonitrile as the solvent. The initial mixture was composed of an equimolar amount of TFP and diethyl hydrogen phosphonate (DEHP) (defined as $R_0 = [DEHP]_0/[TFP]_0 = 1.0$). The use of solvent was required to improve the homogeneity of the liquid phase and the TFP dissolution in that medium. Acetonitrile was found to be the best solvent for this reaction because of its ability to dissolve the gas and its poor transfer activity in the presence of TFP. Thus, at 140 °C, the initial pressure in the 160 mL autoclave did not exceed 12.8 bar. It was also noted that the higher the initiator concentration, the higher the yield and the average degree of telomerization, $\overline{DP}_n$, i.e. the average number of TFP units in the telomers (Table 2).

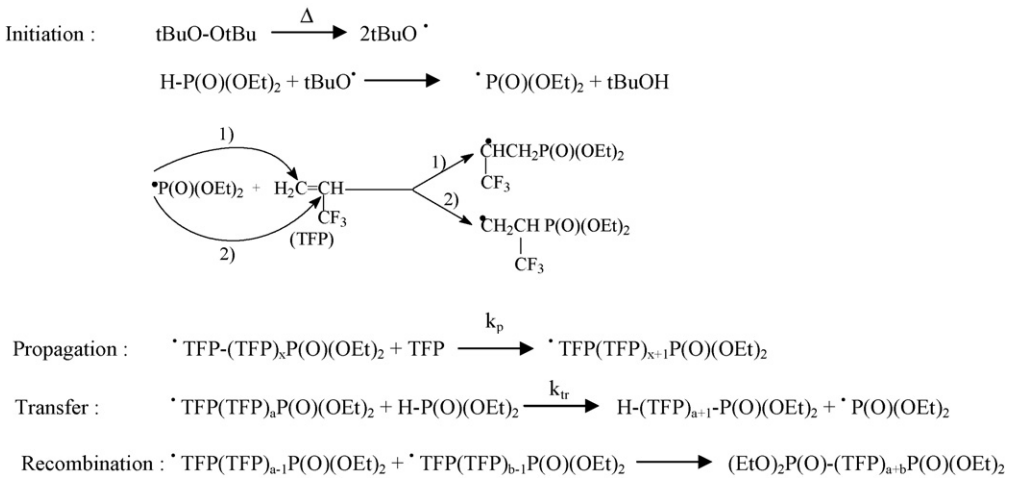
After evaporation of the solvent, the total product mixture was analyzed by gas chromatography (GC) showing the formation of a classical telomeric distribution. The gas chromatogram (Fig. 1) allowed us to identify the first seven adducts produced by such a telomerization.

The higher adducts were in negligible concentrations. The average cumulated degree of polymerization in number $\overline{DP}_{n\,cum}$ of these telomers was determined to be 2.1 or 2.6 according to the experimental conditions (Table 2), corresponding to an average cumulated molecular weight, $\overline{M}_{n\,cum}$, of about 330, assuming that each adduct has the following formulae $H(TFP)_nP(O)(OEt)_2$. Table 3 lists the relative amounts (in GC area) of these adducts *versus* their order. Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) chromatogram of the total product mixture also shows a telomeric distribution with a difference between each adduct of about 100 in molecular weight.

Table 2
Radical telomerization of TFP with $HP(O)(OC_2H_5)_2$ at high conversion

Run #	C_0	Conv. vs. TFP (wt.%)	Yield (dist.) (wt.%)	$\overline{DP}_n$ from GC	b.p. (°C)		
					n = 1	n = 2	n = 3
1	0.03	58	43	2.1	73–75	100–103	84–86
2	0.06	68	59	2.6	20 mmHg	20 mmHg	5 mmHg

Overall yield and degree of polymerization $\overline{DP}_n$. Reaction conditions: di-*tert*-butyl peroxide (DTBP) as the initiator; acetonitrile as the solvent (40 to 60 mol%); initial $[DEHP]_0/[TFP]_0$ molar ratio = 1; temperature 143 ± 3 °C; reaction time: 7 h;160 ml HC276 Hastelloy autoclave. $C_0 = [DTBP]_0/[TFP]_0$.



Scheme 1. General scheme of radical telomerization of 3,3,3-trifluoropropene with diethyl hydrogen phosphonate.

The first three adducts of the telomerization of TFP with diethyl hydrogen phosphonate were isolated by distillation under reduced pressure (Table 2). Although the mono- and diadduct could be easily purified by rectification, the higher order adducts required stronger vacuum to obtain reasonably pure fractions. Purity higher than 65% was typically observed. The boiling points of these three fractions are listed in Section 4. They are liquid in normal conditions (at STP) of temperature and pressure and soluble in common organic solvents. The structural analysis of the first three adducts was performed by means of ^{1}H, ^{19}F, and ^{31}P NMR spectroscopies (see Section 4) and confirm their general formulae: $H(TFP)_nP(O)(OC_2H_5)_2$.

Table 3
Proportions of TFP telomeric adducts (n) in % GC of the total product mixture *vs.* their order for TFP/DEHP telomers at $R_0 = 1$ (experimental conditions as those in Table 2)

C_0	n adducts							
	1	2	3	4	5	6	7	8
0.03	22.4	8.7	5.8	3.1	1.4	1.0	0.5	0.2
0.06	20.3	14.9	12.8	10.0	5.9	3.9	1.5	0.8

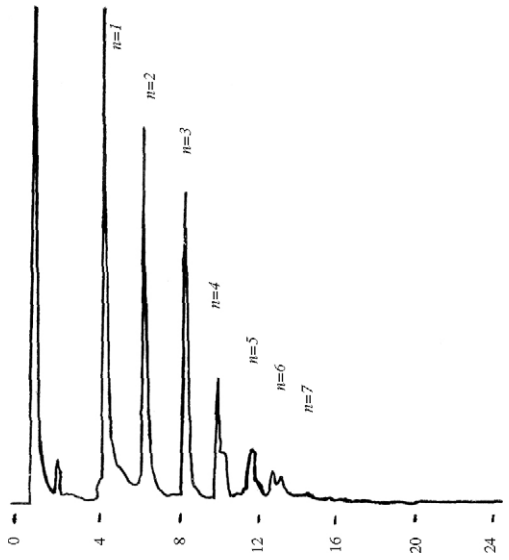


Fig. 1. Gas chromatogram of the total product mixture of the telomerization of 3,3,3-trifluoropropene with diethyl hydrogen phosphonate ($R_0 = 1$; $C_0 = 0.03$. Initiator di-*tert*-butyl peroxide; temperature 140 °C; $t_R = 7$ h; run #1 in Table 2).

2.1. Characterization of the first adducts of the telomerization of TFP with diethyl hydrogen phosphonate

2.1.1. Structure of the monoadduct

The ^{1}H NMR spectrum of the monoadduct shows the presence of both isomers, which exhibit the following formulae:

$CH_3–CH(CF_3)–P(O)(OC_2H_5)_2$ (**1.1**) (15%)

$CH_3–CH_2–CH_2–P(O)(OC_2H_5)_2$ (**1.2**) (85%)

The formation of both isomers can be deduced by NMR analysis.

^{1}H NMR spectrum shows a multiplet, centered at 3.3 ppm, assigned to CH_2 group adjacent to trifluoromethyl CF_3 end-group ($^{3}J_{HF} = 12.6$ Hz) (formula **1.2**) for which the hydrogen is coupled to the phosphorus atom in the β-position ($^{3}J_{HP} = 8.5$ Hz), linked to a methylene group ($^{3}J_{HH} = 4.7$ Hz) in the α-position. The signals centered at 2.1 ppm characterize the methylene group adjacent to phosphorus atom ($^{2}J_{HP} = 15.3$ Hz) and linked to $–CH_2CF_3$ end-group ($^{3}J_{HH} = 5.7$ Hz). It confirms that this telomer arises from the addition of a phosphonyl radical toward the non-substituted carbon atom of TFP. The diethyl phosphonate function is identifiable by a quartet ($^{3}J_{HH} = 7.1$ Hz) of doublets ($^{3}J_{HP} = 8.1$ Hz) centered at 3.8 ppm for $–OCH_2–$ group and a triplet ($^{3}J_{HH} = 6.9$ Hz) of doublets ($^{4}J_{HP} = 0.4$ Hz) at 1.05 ppm assigned to the methyl group. It is noted the weak signal of a triplet centered at ca. 1.8 and 2.9 ppm assigned to the protons in $CH_3–$ and $–C^*H(CF_3)$ groups of $H_3C–CH(CF_3)–P(O)(OEt)_2$ monoadduct (formula **1.1**).

The structure was further evidenced by ^{19}F NMR spectroscopy (see Section 4), the ^{19}F NMR spectrum of which exhibits a triplet of doublets ($^{3}J_{FH} = 10.7$ Hz) from −66.7 to −69.7 ppm

for the fluorine atoms in CF_3 group [39] of isomer **1.2** (85%), while the signals ranging from −70.8 to −72.7 ppm are assigned to CF_3 group of isomer **1.1** in minor amount (15%).

^{31}P NMR spectrum shows a quartet centered at 28 ppm for isomer **1.2** with a coupling constant $^3J_{FP}$ = 29.7 Hz, a weak signal at 32.0 ppm for the **1.1** isomer and a signal having a very weak integral at 6.5–8.0 ppm assigned to non-reacted DEHP telogen.

This structural study demonstrates evidence that the major path (85%) of attack of the phosphonyl radical onto the non-fluorinated carbon atom of TFP (Scheme 1). On the contrary, previous work [21] dealing with the radical telomerization of vinylidene fluoride (VDF) with DEHP has shown that the phosphonyl radical was exclusively added onto H_2C site of VDF, while that of the $HOCH_2^{\bullet}$ radical produced from methanol [40] was not regioselective onto VDF. This may arise from the electrophilic phosphonyl radical, which is more selectively added onto the less electrophilic site of VDF (which exhibits a negative dipole moment) while TFP is regarded as less electrophilic than VDF. Hence, that addition led to a secondary and a primary carbon radical intermediates, the secondary one being the more stable and led to the expected isomer (85%) majorly.

2.1.2. Structure of the diadduct

As anticipated, a very interesting structural regioselectivity would be observed for the telomerization of TFP with diethyl hydrogen phosphonate. As the gross formula anticipates $H(TFP)_2P(O)(OEt)_2$, the existence of four types of diadduct (**2.1**–**2.4**) should be observed, resulting from TFP propagations, sketched in Scheme 2.

These four isomers representing the expected TFP diadducts exhibit the following formulae:

$CF_3CH_2CH_2$–$CH(CF_3)CH_2$–$P(O)(OCH_2CH_3)_2$ (5,5,5-trifluoro-2-trifluoromethyl-1-diethyl phosphonate pentane) (**2.1**)

$CH_3CH(CF_3)$–$CH(CF_3)CH_2$–$P(O)(OCH_2CH_3)_2$ (2,3-bis-trifluoromethyl-1-diethyl phosphonate butane) (**2.2**)

$CH_3CH(CF_3)CH_2CH(CF_3)P(O)(OCH_2CH_3)_2$ (1,3-bis-trifluoromethyl-1-diethyl phosphonate butane) (**2.3**)

$CF_3CH_2CH_2CH_2CH(CF_3)P(O)(OCH_2CH_3)_2$ (5,5,5-trifluoro-1-trifluoromethyl-1-diethyl phosphonate pentane) (**2.4**)

The presence of three or four isomers was shown by ^1H, ^{19}F and ^{31}P NMR spectroscopies. The TFP isomers characterized by ^1H NMR had a complex structure at 3.3 and 1.6 ppm, as triplet of quartets ($^2J_{HF}$ = 19.7 Hz, $^3J_{HH}$ = 7.1 Hz) centered at 3.3 ppm and a quintet centered at 1.6 ppm corresponding to methylene groups of TFP located in δ- and α-positions, respectively about the phosphorus atom. The multiplet at 1.8 ppm overlapping with that at 1.6 ppm is assigned to $–CH_2$ protons between two asymmetric carbons in isomer **2.3** whereas a multiplet at 2.2 ppm is assigned to the proton in $–C^*H(CF_3)$ of isomer **2.1**. Tail to tail addition (isomer **2.2**) may be assigned to $–C^*H(CF_3)–C^*H(CF_3)–$ units of multiplet at 1.9 ppm but it is overlapping with that of isomer **2.1**. The characteristics of chemical shifts assigned to the methyl and methylene group in diethyl phosphonate functions are unchanged about that of monoadduct, centered at 3.8 and 1.05 ppm, respectively. Because of the overlapping of signals of normal and reversed isomers, it was difficult to identify them by ^1H NMR.

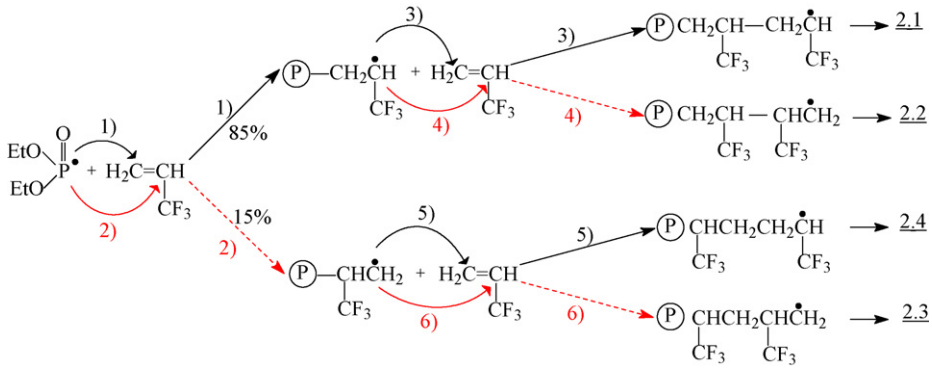
As it was noted in the case of the monoadduct, the signals assigned to fluorine atoms of normal **2.1** and reversed **2.4** diadducts bearing the $–CF_3$ end-group range from −66.3 to −68.3 ppm (24.9 wt.%). The normal addition of TFP isomer **2.1** (i.e. the addition of the telogenic radical on the less hindered side of TFP), was evidenced by the signal of $C^*H(CF_3)$ group centered at −69 ppm and its percentage in the reaction mixture was found to be ca. 62 wt.%. The reverse addition gave signals ranging from −71.0 to −73.2 ppm for **2.2**–**2.4** isomers.

^{31}P NMR spectrum (Fig. 2) shows the P–F and P–H couplings and the signals centered at 27.1, 28.0 and 31.7 ppm. The first one can be assigned to isomer **2.2** with a triplet ($^3J_{PF}$ = 29.3 Hz) (in 15% content), the second one to isomer **2.1** with 75% content, while the third one represents both **2.3** and **2.4** isomers with 10% content. However, the last two isomers cannot be distinguished in the ^1H NMR spectrum (see Scheme 2).

2.1.3. Structure of the triadduct

As for the triadducts obtained from the telomerization of TFP, eight possible isomers can be produced, the main ones having been identified with the following chemical structures:

$CF_3CH_2CH_2$–$CH(CF_3)CH_2$–$CH(CF_3)CH_2$–$P(O)(OCH_2CH_3)_2$ (7,7,7-trifluoro-2,4-bis(trifluoromethyl)-1-diethyl phosphonate heptane) (**3.1**)



Scheme 2. Reaction scheme of telomerization of 3,3,3-trifluoropropene with diethyl hydrogen phosphonate as a chain transfer agent where P represents $P(O)(OEt)_2$.

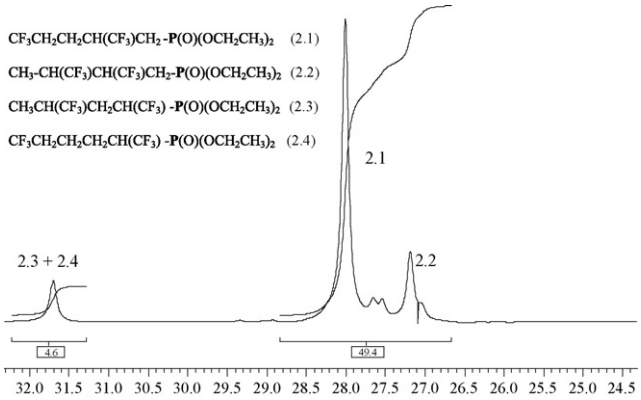


Fig. 2. ^{31}P NMR spectrum (recorded in $CDCl_3$) of $H(TFP)_2P(O)(OEt)_2$ telomer.

CF_3CH_2–CH_2–$CH_2CH(CF_3)$–$CH(CF_3)CH_2$–$P(O)(OCH_2CH_3)_2$ (7,7,7-trifluoro-2,3-bis(trifluoromethyl)-1-diethyl phosphonate heptane) (**3.2**)

$CH_3CH(CF_3)$–$CH(CF_3)CH_2$–$CH(CF_3)CH_2$–$P(O)(OCH_2CH_3)_2$ 2,4,5-tris(trifluoromethyl)-1-diethyl phosphonate hexane (**3.3**)

Beside the expected major head to tail TFP chaining, head to head and/or tail to tail structures as those of the diadduct can be observed. The major difference, except the integrals, concerns the characteristic structures of methylene groups brought by TFP.

The structures of the five other isomers show a change on the position of CF_3–groups.

The ^{1}H NMR spectrum of the TFP-triadduct shows multiplets assigned to different isomers such as those of the diadducts but are more complex. It exhibits the characteristic signals attributed to CF_3CH_2– and CH_3– end-groups resulting from a normal (isomer **3.1**) and reversed (isomer **3.3**) addition of a TFP unit as evidenced by the presence of a triplet with a high coupling constant ($^3J_{HF}$ = 17.3 Hz) and centered at 3.3 and 1.65 ppm, respectively. Because of the complex structure of different triadducts, it is difficult to assess the amount of the defects of chaining (head to head or tail to tail) from the corresponding integrals in the range from 1.4 to 2.6 ppm.

In the ^{19}F NMR spectrum, the presence of a doublet of multiplets centered at −66.5 to −68 ppm and a multiplet between −72 and −73.4 ppm corresponds to the trifluoromethyl groups in the different isomers. The signal at −68.5 ppm is assigned to –C*H(CF_3) of normal adduct. Unfortunately, because of the complexity of isomers and of overlapping the signals, only fragmental structures of these isomers can be identified but not their ratio.

The main multiplet noted in the ^{31}P NMR spectrum has not undergone a shift about that of the diadduct, but it was observed a change in the ratio of the different isomers.

2.2. Kinetic study of the telomerization reaction of TFP with diethyl hydrogen phosphonate: assessment of the first C_T^n transfer constant

2.2.1. Assessment of transfer constants of first orders

The activity of transfer of diethyl hydrogen phosphonate in the presence of 3,3,3-trifluoropropene is characterized by the transfer constants (or coefficients), C_T^n, that may be defined for each growing telomeric radical as the ratio of the transfer rate constant of the telogen, k_{tr}^n, to the rate constant of propagation, k_p^n:

$$C_T^n = \frac{k_{tr}^n}{k_p^n} \quad (1)$$

These rate constants characterize reaction (1) of formation of telomers of (n) order from (n) order radicals, and reaction (2) of formation of telomeric radicals of (n + 1) order from these same radicals, respectively (Scheme 3). The telomers produced are unable to participate to new radical reactions, especially as potential transfer agents. Indeed, we have independently checked that the hydrogeno fluorophosphonates produced by this telomerization do not act as new chain transfer agents when they were reacted in the presence of an organic initiator and TFP. In contrast, this was possible in the case of the telomers of TFE [41], VDF [42] or TFP [35] with perfluoroalkyl iodides [31].

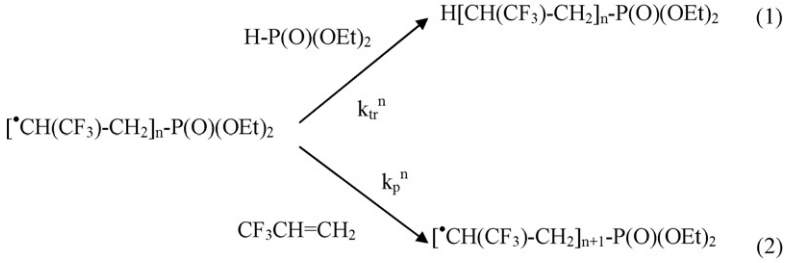
We have also shown that the telomerization in solution of TFP with diethyl hydrogen phosphonate, from equimolar amounts of these reactants, led to a mixture composed of the first adducts of the telomerization, $H(TFP)_nP(O)(OEt)_2$, for which the average cumulated degree of telomerization in number $\overline{DP}_{n\,cum}$ did not exceed 3. It should be noted that studies performed by Boutevin et al. [43] demonstrate the requirement to differentiate the rate constants characterizing each step of the telomerization, when it produces low $\overline{DP}_{n\,cum}$ (i.e., lower than 10) mainly.

Thus

$$k_{tr}^1 \neq k_{tr}^2 \neq k_{tr}^3 \neq \cdots \neq k_{tr}^n, \quad n < 10 \quad (2)$$

$$k_p^1 \neq k_p^2 \neq k_p^3 \neq \cdots \neq k_p^n, \quad n < 10 \quad (3)$$

Obviously, it is deduced that $C_T^1 \neq C_T^2 \neq C_T^3 \neq \cdots \neq C_T^n$, for $n < 10$. Further, it is considered that the C_T^n values increase with n to reach a limit value C_T^∞, as a reference to characterize the



Scheme 3. Transfer and propagation steps for the 3,3,3-trifluoropropene telomerization with diethyl hydrogen phosphonate.

Table 4
Kinetics of radical telomerization of TFP with $HP(O)(OEt)_2$ (DEHP) at 140 °C initiated by DTBP

#	Run					
	3	4	5	6	7	8
R_0	0.25	0.50	1.00	2.25	2.50	3.00
n of $\overline{DP}_n$	4.2	2.8	1.9	1.6	1.3	1.0

R_0 stands for the initial $[DEHP]_0/[TFP]_0$ molar ratio.

activity of transfer of a telogen in the presence of a given monomer.

Several authors proposed various methods of determination of these constants taking into account the molecular distributions. We have chosen the David et Gosselain approach [44], that enabled us to direct the molar fractions, F_n, of each telomer to the C_T^n values and to the ratio R' of concentrations of telogen to that of monomer:

$$C_T^n = \frac{F_n}{R' \sum_{j=n+1}^{\infty} F_j} \quad (4)$$

where F_n, C_T^n, and R' represent molar fraction of nth telomer, transfer constant of n order and initial $[DEHP]_0/[TFP]_0$ molar ratio, respectively.

According to this relation, it is possible to assess the values of different constants C_T^n by plotting the ratios $F_n/\sum_{j=n+1}^{\infty} F_j$ *versus* the different values of R'. The slopes of these straight lines of the experimental data characterizing each n order hence give the C_T^n values.

Hence, the representation of the straight-lines determining $F_n/\sum_{j=n+1}^{\infty} F_j$ *versus* R should allow to assess within a good approximation the values of the transfer constants C_T^n of the first adducts, assuming that R remained constant in the course of the kinetics (i.e. for a short time less than 1 h [21]). We chose as a reaction time 30 min because of the lower reactivity of TFP *versus* that of VDF and TFE.

The experiments required for the assessment of the C_T^n, of the first adducts were investigated as indicated in the experimental part.

Several experiments were carried out at different R ratios and it is noted that the higher the R, the lower the $\overline{DP}_{n\,cum}$ (Table 4).

The transfer constants up to the fourth orders were determined from the experimental results and are listed in Table 5.

For example, for C_T^1 coefficient, the evolution of the ratio $F_1/\sum_{i=2}^{\infty} F_i$ *versus* R_0 was plotted. The experimental data are located onto a straight line, the slope of which is $C_T^1 \sim 0.32$. The

Table 5
Values of n order–transfer constants of DEHP for the telomerization of TFP with DEHP from 1 to 4 orders ($T = 140$ °C)

Order n_i	C_T^n
$n = 1$	0.32
$n = 2$	0.44
$n = 3$	0.62
$n = 4$	0.71

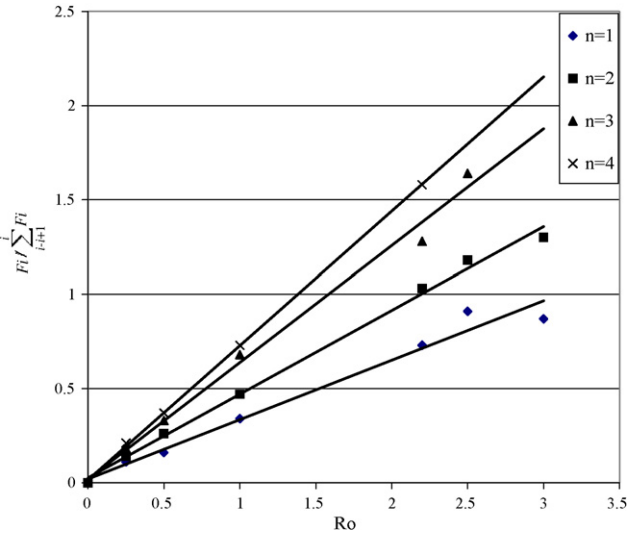


Fig. 3. Assessment of the transfer constants of n-order in the telomerization of 3,3,3-trifluoropropene with diethyl hydrogen phosphonate. (R_0 stands for the initial $[DEHP]_0/[TFP]_0$ molar ratio.)

other transfer constants were calculated according to the same procedure (Fig. 3).

From these results, the transfer coefficients are in the same value as those obtained from order $n = 4$, i.e. the constant value was found equal to ca. 0.71 (Table 5). Only first both order constants are slightly different from that value. Such a phenomenon can be explained by the influence of the phosphonate end-function.

Nevertheless, the results obtained allowed us to define a value of C_T^{∞}, assigned to the limit value of calculated C_T^n by extrapolation of C_T^n *versus* n:

$$C^{\infty}_{T(HP(O)(OEt)_2/TFP)} = 0.75 \text{ at } 140\,^{\circ}C$$

These transfer constants, all lower than 1.0, evidence the preponderance of the propagation step toward the transfer at each step of the telomerization. It is also observed that the value of the transfer constant, C_T^{∞}, characteristic of the reactivity of the transfer of diethyl hydrogen phosphonate in the presence of TFP, is overall of the same order than those reported in the literature and obtained in the presence of CTFE ($C_T^{\infty} = 0.34$ at 140 °C [20]) or VDF ($C_T^{\infty} = 0.38$ at 140 °C [21]).

A C_T^{∞} lower than 1 also indicates that the telomers produced are not able to act as potential chain transfer agents as this was noted in the case where $R_F(CH_2CF_2)_nI$ for which C_T was found to be about 7 [45]. This also demonstrates that the C–P bond of $H(CF_2CH_2)_nP(O)(OR)_2$ telomers is too strong and cannot be cleaved to enable the synthesis of higher molecular weight telomers. This indicates that $H(CF_2CH_2)_nP(O)(OR)_2$ cannot act as a potential chain transfer agent for the radical telomerization of VDF initiated by DTBP.

3. Conclusion

The radical telomerization of 3,3,3-trifluoropropene (TFP) with diethyl hydrogen phosphonate (DEHP) allowed us to

synthesize TFP telomers bearing a phosphonate end-group. The first three adducts described above exhibit a major structure as $H(TFP)_nP(O)(OEt)_2$ where "n" represents the order of the considered adduct. Except for the monoadduct, the first TFP-diethyl hydrogen phosphonate telomers contain a rather high amount of different isomers of the TFP "microblocks" (head and tail additions). Further, these compounds are liquid at room temperature and have excellent solubility in common organic polar solvents such as acetone, chloroform, acetonitrile, or DMF. These properties could enable them to be used as novel hydrogenofluorinated solvents. In addition, these materials demonstrated excellent stability with no degradation even after being stored in the air for more than a year. Moreover, it was observed that the C–P bond appeared stable even at 150 °C, without any further reinitiation as shown by a total lack of reactivity of the telomers towards TFP in the presence of a peroxide initiator at 140 °C. The kinetics of this telomerization allowed us to determine the transfer constants of the first four telomers with an infinite value of 0.75 at 140 °C for DEHP, showing that medium to high telomers can be produced according to the initial $[DEHP]_0/[TFP]_0$ molar ratios. Assessment of C_T^n value for $HP(O)(OEt)_2$ shows that it is higher than in the case of telomerization of VDF and CTFE since propagation of TFP is lower. Potential original surfactants from these TFP telomers are under investigation.

4. Experimental details

4.1. General comments

4.1.1. Reactants

3,3,3-Trifluoropropene (TFP) was kindly supplied by the Chemtura Company (West Lafayette, IN, USA), acetonitrile from SDS (Peypin, France), diethyl hydrogen phosphonate and di-*tert*-butyl peroxide were purchased by Aldrich (Saint Quentin Fallavier, France), and were used as received.

4.1.2. Reactions

To obtain a suitable amount of TFP telomers, the telomerization was carried out in a 160 mL Parr Hastelloy Autoclave (height: 12 cm; internal diameter: 8.5 cm) equipped with a manometer, a rupture disk, inner and outlet valves. The open autoclave was then charged with 0.91 g (0.00624 mol) of di-*tert*-butyl peroxide, 28.8 g (0.208 mol) of diethyl hydrogen phosphonate and 35 g (0.85 mol) of acetonitrile, sealed and purged with nitrogen. After cooling in a liquid nitrogen/acetone mixture, the medium was evacuated and 20.0 g (0.208 mol) of TFP was introduced by double weighing (i.e., the difference of weight after and before feeding the autoclave with TFP). The mixture was heated to 140 °C for 7 h. The maximum pressure reached 12 bar for 20.0 g of TFP, in the presence of 35.0 g of acetonitrile. The reaction was shown to be rather quick as evidenced by a drop of pressure (5 bar after 7 h) and a slight exotherm ($\Delta T \sim +15$ °C) at the beginning of the reaction. After reaction, the overall TFP conversion was ca. 58%, according to the recovered TFP. After cooling down to room temperature, the autoclave was chilled in an ice bath. The unreacted TFP was then vented to a weight dry ice trap and the vessel opened. After evaporation of the acetonitrile, the total product mixture was fractionally distilled. The first fraction contained the unreacted DEHP while the other pure fractions were composed of the various TFP telomeric adducts.

4.1.3. Apparatus and analysis of products

After reaction and evaporation of the solvent, the total product mixture was analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, 2 m × 1/8 in. (i.d.). The nitrogen pressure at the entrance to the column was maintained at 1 bar and the detector and injector temperatures were 240 and 235 °C, respectively. The temperature program started from 50 °C and reached 200 °C at a heating rate of 10 °C/min. The GC apparatus was connected to a Hewlett Packard integrator (model 3390). The sensitivity of the apparatus and the resolution of the chromatogram limit the detection of telomers to the sixth adduct.

The structure of the telomers was determined by NMR spectroscopy at room temperature. The ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker AC-200 or Bruker AC-250 instruments using deuterated chloroform, and tetramethyl silane or $CFCl_3$, as the solvent and internal references, respectively. Coupling constants and chemical shifts are given in hertz (Hz) and in part per million (ppm). The experimental conditions for recording ^1H (or ^{19}F) NMR spectra were the following: flip angle 90° (30°); acquisition time 4.5 s (0.7 s); pulse delay 2 s (5 s); 36 (64) scans and pulse width of 5 μs for ^{19}F NMR. The letters s, d, t, q and m represent singlet, doublet, triplet, quartet and multiplet, respectively.

4.1.4. Characteristics of the telomers

4.1.4.1. Monoadduct. 1,1,1-Trifluoro-2-diethyl phosphonate propane $CF_3CH(CH_3)–P(O)(OCH_2CH_3)_2$ (**1.1**), 3,3,3-trifluoro-1-diethyl phosphonate propane, $CF_3CH_2CH_2–P(O)(OC_2H_5)_2$ (**1.2**): b.p. 73–75 °C/20 mmHg. ^1H NMR ($CDCl_3$) δ, ppm: 3.3 (m, $^3J_{HP} = 8.5$; $^3J_{HF} = 12.5$, $^3J_{HH} = 5.7$, 2H, $CF_3–CH_2–$, isomer **1.2**); 2.1 (dt, $^2J_{HP} = 15.3$, $^3J_{HH} = 5.7$, 2H, $–CH_2P–$, isomer **1.2**); 2.9 ($^2J_{HP} = 19.1$, 1H, $C^*H(CF_3)$, isomer **1.1**); 1.8 (t, $^3J_{HH} = 4.8$, $^3J_{HP} = 3.8$, 3H, $CH_3–$, isomer **1.1**); 3.8 (qd, $^3J_{HH} = 7.1$, $^3J_{HP} = 8.1$, 2H, $–OCH_2$); 1.05 (td, $^3J_{HH} = 6.9$, $^4J_{HP} = 0.4$, 3H, $CH_3CH_2–$). ^{19}F NMR ($CDCl_3$) δ, ppm: centered at −68.0 (td, $^3J_{FH} = 10.7$, $^3J_{FH} = 16.3$, 3F, $CF_3–CH_2$, isomer **1.2**); −70.8 to −72.7 (td, $^3J_{FH} = 16.3$, $^3J_{FP} = 2.2$, 3F, $(CF_3)C^*H–$, isomer **1.1**). ^{31}P NMR ($CDCl_3$) δ, ppm: for normal adduct (85%), 28 (t, $^3J_{PF} = 8.5$, $^2J_{PH} = 15.3$); for reversed isomer (15%), 32.0 (tt, $^3J_{PF} = 29.3$, $^2J_{PH} = 15.2$ Hz, $^3J_{PF} = 29.5$).

4.1.4.2. Diadducts. $CF_3CH_2CH_2–CH(CF_3)CH_2–P(O)(OCH_2CH_3)_2$ (5,5,5-trifluoro-2-trifluoromethyl-1-diethyl phosphonate pentane) (**2.1**), $CH_3CH(CF_3)–CH(CF_3)CH_2–P(O)(OCH_2CH_3)_2$ (2,3-bis-trifluoromethyl-1-diethyl phosphonate butane) (**2.2**), $CH_3CH(CF_3)CH_2CH(CF_3)P(O)(OCH_2CH_3)_2$ (1,3-bis-trifluoromethyl-1-diethyl phosphonate butane) (**2.3**), $CF_3CH_2CH_2CH_2CH(CF_3)P(O)(OCH_2CH_3)_2$ (5,5,5-tri-

fluoro-1-trifluoromethyl-1-diethyl phosphonate pentane) (**2.4**): b.p. 100–103 °C/20 mmHg. ^{1}H NMR ($CDCl_3$) δ, ppm: 3.8 (qd, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 8.3, 2H, –OCH_2); 3.3 (tq, $^3J_{HF}$ = 19.7, $^3J_{HH}$ = 7.1, 2H, CF_3CH_2–); 2.2 (m, $^3J_{HF}$ = 3.8, $^3J_{HH}$ = 4.9, 1H, (CF_3)C*H–, isomer **2.1**); 1.8 (m, $^3J_{HP}$ = 8.0, $^3J_{HH}$ = 6.7, 2H, C*–CH_2–C*, isomer **2.3**); 1.6 (q, $^3J_{HF}$ = 17.3, $^2J_{HP}$ = 15.3, 2H, –CH_2P– of isomers **2.1** and **2.2**); 1.05 (td, $^3J_{HH}$ = 7.1, 3H, CH_3CH_2–). ^{19}F NMR ($CDCl_3$) δ, ppm: −66.3 to −68.3 (m, $^3J_{FH}$ = 16.8, 3F, CF_3–CH_2– of isomers **2.1** and **2.4**); −69 (s, $^3J_{FH}$ = 17.2, 3F, –CH_2C*H(CF_3)CH_2– of isomer **2.1**); −71.0 to −73.2 (s, (CF_3)C*H– of isomers **2.2**–**2.4**). ^{31}P NMR ($CDCl_3$) δ, ppm: for normal TFP diadduct (2.1, 75%): 28 (s, $^4J_{PF}$ = 4.4; $^2J_{PH}$ = 15.1), for isomers **2.2** (15%): 27.1 (t, $^3J_{PF}$ = 29.7), for isomers **2.3** and **2.4** (10%): 31.7 (s, $^3J_{PF}$ = 29.6).

4.1.4.3. Triadducts. $CF_3CH_2CH_2$–$CH(CF_3)CH_2$–$CH(CF_3)CH_2$–P(O)(OCH_2CH_3)$_2$ (7,7,7-trifluoro-2,4-bis(trifluoromethyl)-1-diethyl phosphonate heptane) (**3.1**), CF_3CH_2–$CH_2CH(CF_3)$–$CH(CF_3)CH_2$–P(O)(OCH_2CH_3)$_2$ (7,7,7-trifluoro-2,3-bis(trifluoromethyl diethyl)-1-phosphonate heptane) (**3.2**), $CH_3CH(CF_3)$–$CH(CF_3)CH_2$–$CH(CF_3)CH_2$–P(O)(OCH_2CH_3)$_2$ (2,4,5-tris(trifluoromethyl diethyl)-1-phosphonate hexane) (**3.3**) (the other isomers change only the position of CF_3– groups): b.p. 84–86 °C/5 mmHg. ^{1}H NMR ($CDCl_3$) δ, ppm: 3.8 (qd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 8.3, 2H, –OCH_2); 3.3 (d, $^3J_{HF}$ = 17.3, $^3J_{HH}$ = 6.8 Hz, 2H, CF_3CH_2–); 2.2 (m, $^3J_{HF}$ = 3.8, $^3J_{HH}$ = 4.9, 1H, (CF_3)C*H); 1.8 (m, $^3J_{HH}$ = 6.8, 2H, C*–CH_2–C*); 1.65 (q, $^3J_{HF}$ = 17.3, 2H, –CH_2P–); 1.04 (m, $^3J_{HH}$ = 7.1, 3H, CH_3CH_2OP). ^{19}F NMR ($CDCl_3$) δ, ppm: −67 to −68 (dm, $^3J_{FH}$ = 16.1, 3F, CF_3CH_2– of isomers **3.1** and **3.2**), −68.5 (s, $^3J_{FH}$ = 16.0, –C*H(CF_3)– of different isomers); −70.2 to −73.4 (compl., $^3J_{HF}$ = 15.8), –C*(CF_3)H–C*(CF_3)–, different isomers. ^{31}P NMR ($CDCl_3$) δ: from 27.1 to 31.7 (m, $^2J_{PH}$ = 19.5, $^3J_{PF}$ = 28.5, 1P, $POCH_2$).

4.1.5. Kinetics of telomerization of TFP with DEHP

Kinetics of telomerization of TFP with DEHP were performed in thick borosilicate Carius tubes in a batch process (length: 130 mm, internal diameter: 10 mm, thickness: 2.5 mm, for a total volume of 8 cm^3). After having placed the initiator (ca. 3 mol% with respect to the monomer mixture), DEHP and acetonitrile in the tube, it was connected to a vacuum line and purged several times by evacuating and flushing with helium. After a minimum of six thaw–freeze cycles performed to remove oxygen, TFP was transferred from an intermediate pressure calibrated metallic container, under vacuum, to the reaction tube, which had been frozen in liquid nitrogen. The required amount of TFP (0.500 or 1.000 ± 0.008 g) introduced into the tube was assessed by the relative drop of pressure in this release container, initially fed from a cylinder of 300 g of TFP. A beforehand calibration curve ''weight of trapped TFP (in g) *versus* drop of pressure (in bar)'' was made and consulted (for 1.0 g of TFP, a difference of pressure of 0.4 bar was required). The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed into a shaking oven at 141 °C for 30 min.

After reaction, the tube was frozen in liquid nitrogen and then opened, and the total product mixture was GC analyzed.

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