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Journal of Fluorine Chemistry 107 (2001) 5–12

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Synthesis of new phosphonic derivatives bearing fluorinated chains

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Accepted 31 July 2000

Abstract

We describe various radical telomerization reactions of chlorotrifluoroethylene (CTFE) and dialkyl hydrogenphosphonates ($HP(O)(OR)_2$ R = Me, Et). Characterization by ^1H, ^{19}F and ^{31}P NMR of the resulting telomers are detailed. For the heaviest telomers, we used MALDI-TOF analyses to give the mass values. Parameters such as pressure, solvent, R_0, C_0, temperature and nature of initiator have been studied in order to optimize this reaction. Some products have been prepared in large quantities using special high-pressure reactors. We also succeeded in the cleavage of phosphonic esters in order to obtain acidic structures well-known for their adhesive properties on metals.

Keywords: Radical telomerization of chlorotrifluoroethylene; Dialkyl hydrogen-phosphonates; Phosphonic esters cleavage; MALDI-TOF analyses; Adhesion; Lubrication

1. Introduction

In our first part [1], we described four methods of synthesis of phosphonic derivatives bearing fluorinated chains used in the literature. Previously, we described the addition of fluorinated thiols onto allylic monomers bearing a phosphonic group [2]. Our researches deal with the telomerization of fluorinated monomers, chlorotrifluoroethylene and difluoroethylene (VDF) with dialkyl hydrogenphosphonates. The present paper gives details of the CTFE monomer.

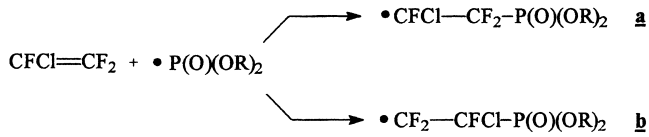
Several authors [3–7] have studied these telomerizations as indicated in Table 1. However, these old studies mainly concern the synthesis and some chemical characterizations of telomers, but neither kinetic studies nor optimizations had been investigated. In order to study applications of this kind of product, we decided to complete these researches.

2. Results and discussion

2.1. Structural analyses

We used benzoyl peroxide as initiator and dimethyl and diethyl hydrogenphosphonates (DMHP and DEHP, respectively) as telogen agents. The various reactions were carried out in sealed tubes over 6 h at 100°C. Gas chromatography analyses of crude products reveal the formation of series of telomers **1,n** and **2,n** with DMHP and DEHP, respectively.

Using tetrafluoroethylene, a symmetric olefin, the direction of addition of telogen onto monomer is not ambiguous. With CTFE, the determination of the structure of our telomers is more complex because two possibilities of addition are possible.



Obviously, during propagation, head–head and head–tail additions of monomer onto the growing radical are possible [8]. In order to determine the exact structure of chlorofluorinated telomers, we isolated by distillation under vacuum the monoadducts (**1,1** and **2,1**) of each series. Elementary analyses and mass spectra of **1,1** and **2,1** lead, respectively, to the formulae $C_4H_7ClF_3O_3P$ and $C_6H_{11}ClF_3O_3P$. IR spectroscopy and ^{31}P NMR confirm the presence of dialkyl phosphonate groups.

From the ^1H, ^{19}F and ^{31}P NMR, we clearly determined the structure of these compounds, and specified the direction of addition of telogen onto monomer.

^1H NMR spectrum (Fig. 1) reveals the presence of a CFClH group α to a CF_2 group. At 6.35 ppm, the terminal proton signal appears as a doublet ($^2J_{cd}$ = 45.5 Hz), typical of a geminal H–F coupling, coupled ($^3J_{ad}$ = 12 Hz) and

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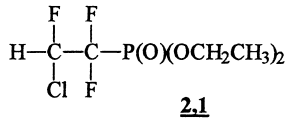
0022-1139/01/$ – see front matter
PII: S0022-1139(00)00336-5

Table 1
Fluorophosphonated compounds obtained by telomerization and radical addition

Monomer	Telogen	Catalysis	Telomers	References
CF_2=CF_2	$HP(O)(OR)_2$	Radical	$H–(CF_2–CF_2)_n–P(O)(OR)_2$	[3,4]
CF_2=CF_2	$HP(O)(OEt)_2$	γ-Ray	$H–(CF_2–CF_2)_n–P(O)(OEt)_2$	[4,5]
CFCl=CF_2	$HP(O)(OR)_2$ (R = Me, Et, nBu)	Radical	$H–(CFCl–CF_2)_n–P(O)(OR)_2$	[6]
CFX=CX_2 (X = Cl, F)	$HP(O)(OR)_2$ (R = Me, iBu)	γ-Ray	$H–(CX_2–CFX)_n–P(O)(OR)_2$	[5]
$CF_3–(CF_2)_n–CH$=CH_2 (n = 5, 7, 9)	$HP(O)(OR)_2$ (R = Me, Et, nBu)	Radical	$CF_3–(CF_2)_n–CH_2–CH_2–P(O)(OR)_2$	[7]

coupled again ($^3J_{bd}$ = 4 Hz) by Fa and Fb vicinal fluorine atoms. Furthermore, the broadening of this signal clearly shows a coupling ($^3J_{dP}$ = 0.8 Hz) with the phosphorus atom.

The ^{31}P NMR spectrum (Fig. 1) shows a CF_2 group attached to the phosphorus atom. Actually, we observe a triplet with coupling constant 94.3 Hz, typical of $^2J_{PF}$ [9]. If the addition of phosphonate group took place onto the CFCl group of monomer, we would have the structure **b** H–CF_2–CFCl–$P(O)(OCH_2CH_3)_2$ and in this case, we should observe a triplet ($^2J_{HF} \approx 45$ Hz) coupled ($^3J_{HF} \approx 10$ Hz) by ^{1}H NMR, and the ^{31}P NMR spectrum should show a doublet ($^2J_{PF} \approx 95$ Hz). So, the telomer **2,1** obviously has the following structure.



2,1

This structure is confirmed by the detailed ^{19}F NMR analysis (Fig. 1). In Table 2, we collect the spectroscopic characteristics of telomer **2,1**. The two fluorine atoms of the difluoromethylene group are anisochronous because of the α asymmetric carbon. They appear as a AB part of an ABX system (J_{AX} = 291 Hz). This AB part is coupled by the phosphorus atom and coupled again by the Hd proton (see Table 2).

The telomer **1,1** of CTFE with DMHP was the subject of such study and it has the following structure **a** HCFCl–CF_2–$P(O)(OCH_3)_2$. The spectra are nearly the same as compound **2,1** except the ^{1}H NMR spectrum where the CH_3 groups appear as a doublet ($^3J_{HP}$ = 11,2 Hz) at 3.96 ppm.

The spectroscopic study of the higher homologues **1,n** and **2,n** also shows the presence of CFClH and CF_2 groups. These results are the characteristic of a selective 'head–tail'

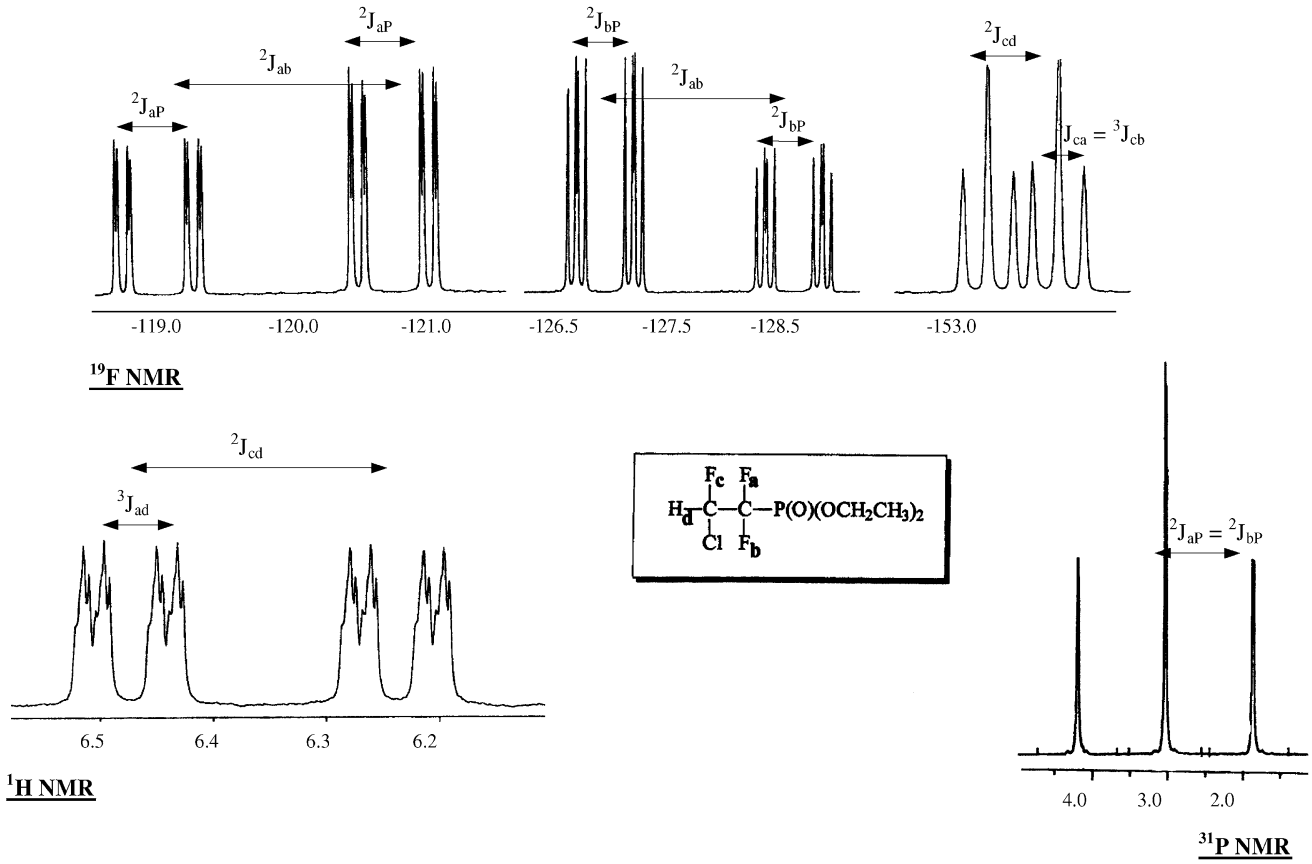
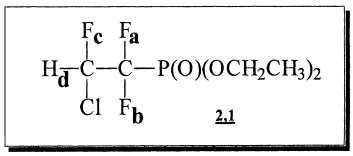


Fig. 1. NMR spectra of telomer **2,1**.

Table 2
NMR characteristics of telomer **2,1**



Nuclei	Fa	Fb	Fc	Hd	CH_2	CH_3	P
δ (ppm)	−119.8	−127.5	−153.1	6.35	4.20	1.28	3
Patterns	AB, dd	AB, dd	X, dd	X, dddt	qd	*t*	*t*
Coupling Constants (Hz)	$^3J_{Fa-Fb} = 291$ $^3J_{Fa-Fc} = 12.8$ $^3J_{Fa-Hd} = 12$ $^2J_{Fa-P} = 94.3$	$^2J_{Fb-Fa} = 291$ $^3J_{Fb-Fc} = 3.4$ $^3J_{Fb-Hd} = 4$ $^2J_{Fb-P} = 94.3$	$^3J_{Fc-Fa} = 12.8$ $^3J_{Fc-Fb} = 3.4$ $^2J_{Fc-Hd} = 45.5$ $^3J_{Fc-P} = 0.5$	$^3J_{Hd-Fa} = 12$ $^3J_{Hd-Fb} = 4$ $^2J_{Hd-Fc} = 45.5$ $^3J_{Hd-P} = 0.8$	$^3J_{CH_2-CH_3} = 7.2$ $^3J_{CH_2-P} = 7.2$	$^3J_{CH_3-CH_2} = 7.2$	$^2J_{P-Fa} = {}^2J_{P-Fb} = 94.3$

addition of the monomer. The general formulae of our two series of telomers are thus:

$$H-(CFCl-CF_2)_n-P(O)(OCH_3)_2 \quad \mathbf{1,n}$$

$$H-(CFCl-CF_2)_n-P(O)(OCH_2CH_3)_2 \quad \mathbf{2,n}$$

2.2. Optimization

In order to use this kind of products as surfactants or reactive lubricants, we carried out the preparation of the chlorofluorinated phosphonates in larger scale. For such applications, a minimum of a six-carbon-chain is necessary. That is, therefore, we studied the variation of the number average degree of polymerization (DP_n) and yields according to several parameters before carrying out reactions in 1 or 5 l capacity reactors. Table 3 sums up these preliminary trials.

R designates the nature of the phosphonic ester $P(O)(OR)_2$. R_0 is the molar ratio of telogen to monomer, and C_0 the molar ratio of initiator to telogen.

$$R_0 = \frac{\text{telogen}}{\text{monomer}} \qquad C_0 = \frac{\text{initiator}}{\text{telogen}}$$

where telogen is $HP(O)(OR)_2$ and monomer is $CFCl{=}CF_2$. Experiments are stopped after 4 h (there is no significant evolution after that time). The reaction temperature is fixed at 100°C except with di-*tert*-butyl peroxide when it is 140°C. Thus, we notice:

- there is no difference between $R = Me$ and $R = Et$ whereas yields are lower with $R = Bu$;
- results are better without solvent and R113 is better than acetonitrile. However, R113 is not advisable for environmental reasons, and pressures will be higher without any solvent;
- the best initiator we used is di-*tert*-butyl peroxide, but a higher temperature and a higher pressure are necessary;
- copper and stainless steel inhibit the reaction.

In order to evaluate the internal pressure and obtain larger yields of products, we used two different metallic reactors: a glazed steel PFAUDLER-type reactor (5 l capacity) for which the maximum pressure is 30 bar, and a Hastelloy PARR-type reactor (1 l capacity) for which the maximum pressure is 70 bar.

From vapor pressure values given in the literature [10], we represented the theoretical curve of total pressure with temperature in order to compare it with the experimental ones. Fig. 2 represents the variations of vapor pressure of solvent and reactants with temperature, and also, the

Table 3
Preliminary studies of CTFE telomerization

Number	*R*	Initiator	Solvent	R_0	C_0 (10^{-2})	DP_n	Yield (%)	
1	CH_3	Bz_2O_2	R113	3	0.5	1.6	43	
2	C_2H_5	Bz_2O_2	R113	3	0.5	1.5	41	
3	nC_4H_9	Bz_2O_2	R113	3	0.5	1.5	19	
4	C_2H_5	AIBN	R113	3	0.5	1.7	25	
5	C_2H_5	Bz_2O_2	CH_3CN	3	0.5	1.6	30	
6	C_2H_5	Bz_2O_2	–	3	0.5	1.6	46	
7	C_2H_5	Bz_2O_2	R113	3	0.23	2.0	37	
8	C_2H_5	Bz_2O_2	R113	1	0.5	–	0	Presence of copper
9	C_2H_5	Bz_2O_2	R113	1	0.5	–	0	Presence of stainless steel
10	C_2H_5	$(tBuO)_2$	CH_3CN	2	5	1.5	60	
11	C_2H_5	$(tBuO)_2$	CH_3CN	1	5	2.0	51	

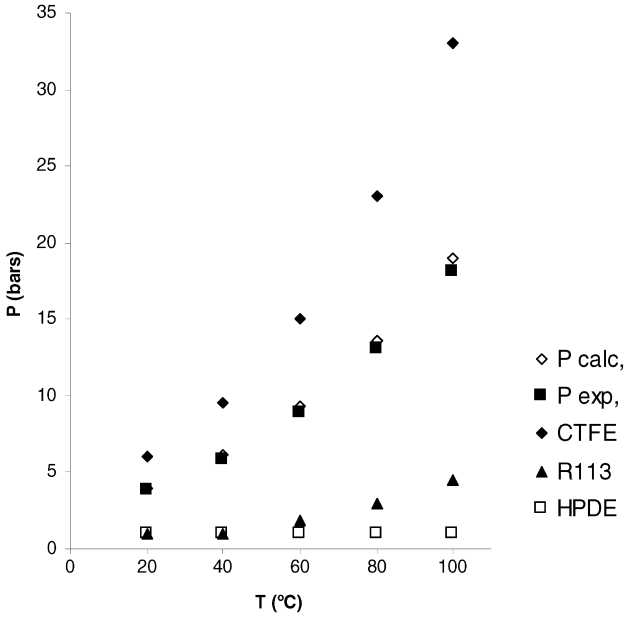


Fig. 2. Pressure variations with temperature.

theoretical and experimental curves for the mixtures with composition specified in Table 4. The total pressure was calculated from Raoult and Dalton laws:

$$P = \sum x_i P_i + \text{Pair}$$

where x_i and P_i represent the molar fraction and the vapor pressure of a component at the considered temperature. We note that experimental and theoretical curves are very similar. As for experimental errors (manometer precision, thermometer), these results show that our reaction systems behave as an ideal mixture.

In order to obtain better yields and families of telomers characterized by various DP_n, we used the second reactor. It allowed us to perform the reaction with di-*tert*-butyl peroxide at 140°C in acetonitrile. The Table 5 summarizes the various experiments carried out under these conditions. We monitored the reaction by following the pressure, which decreases with the consumption of monomer, and we stopped the reaction when the pressure was stable (after about 4 h).

We noted that yields are far better than in sealed tubes. The concentration of gaseous monomer in the liquid phase is directly linked to its conversion. So, the higher the pressure and the more important the liquid phase, the better the conversion rate of CTFE. Besides, increasing the amount of solvent, the solubility of gaseous monomer is improved.

Table 4
Study of vapour pressures with temperature: initial mixture characteristics

Compounds	Weight (g)	
CTFE	1850	R_0 = HPDE/CTFE = 0.47
HPDE	1035	
R113	1720	C_0 = Bz_2O_2/HPDE = 0.1
Bz_2O_2	21.8	

Table 5
CTFE telomerization with a Hastelloy PARR-type reactor

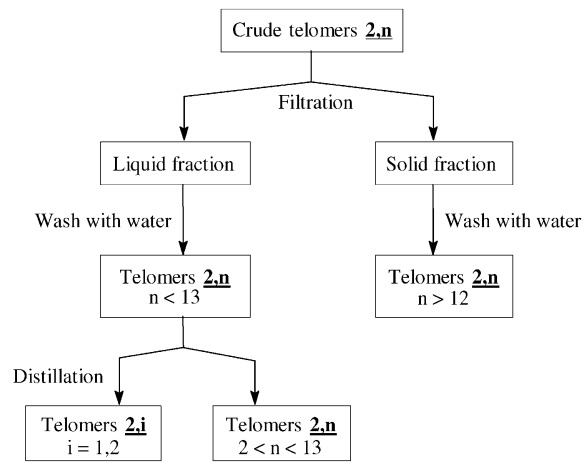
Number	R_0	DP_n	Yields (%)
1	2	1.5	95.5
2	1	2	77.2
3	0.5	Not determined	56.3
4	0.25	Not determined	45.8

Although we obtained liquid telomers with $R_0 > 1$, the fluorophosphonated compounds became solid telomers with $R_0 < 1$. This shift of physical characteristics suggests that as we lengthen the chlorofluorinated chains so we increased the degree of telomerization.

Scheme 1 describes the way to purify our crude products after evaporation by vacuum distillation the solvent. After separation of liquid and solid telomers by filtration, we characterized each fraction by MALDI-TOF analysis.

For the liquid fraction (Fig. 3(a)), we observe series of mass peaks spaced about 116 corresponding to the mass of CTFE unit. For each telomer **2,n**, we see its parent peak of formula is H–$(CFCl–CF_2)_n$–P(O)$(OC_2H_5)(O^-)$. We note a decreasing shape of intensity from peak 341 to 1271. The values 341 and 1271 correspond, respectively, to the parent peaks of telomers **2,2** and **2,10**. These results give information on the average molar mass values, and especially on their relative values according to parameters as R_0. Thus, we estimate the DP_n of this fraction at 4,5.

Fig. 3(b) is an expansion of spectrum 3(a) for the peak 573 corresponding to the parent peak of telomer **2,4**. Taking account of the chlorine isotopes, the main peak M [573 (82), 575 (100), 577 (51), 579 (11), 581 (1)] is the characteristic of a fragment containing four chlorine atoms. We also observe an equivalent peak (4 Cl) corresponding to the fragment M + H.



Scheme 1. Splitting of telomers **2,n**.

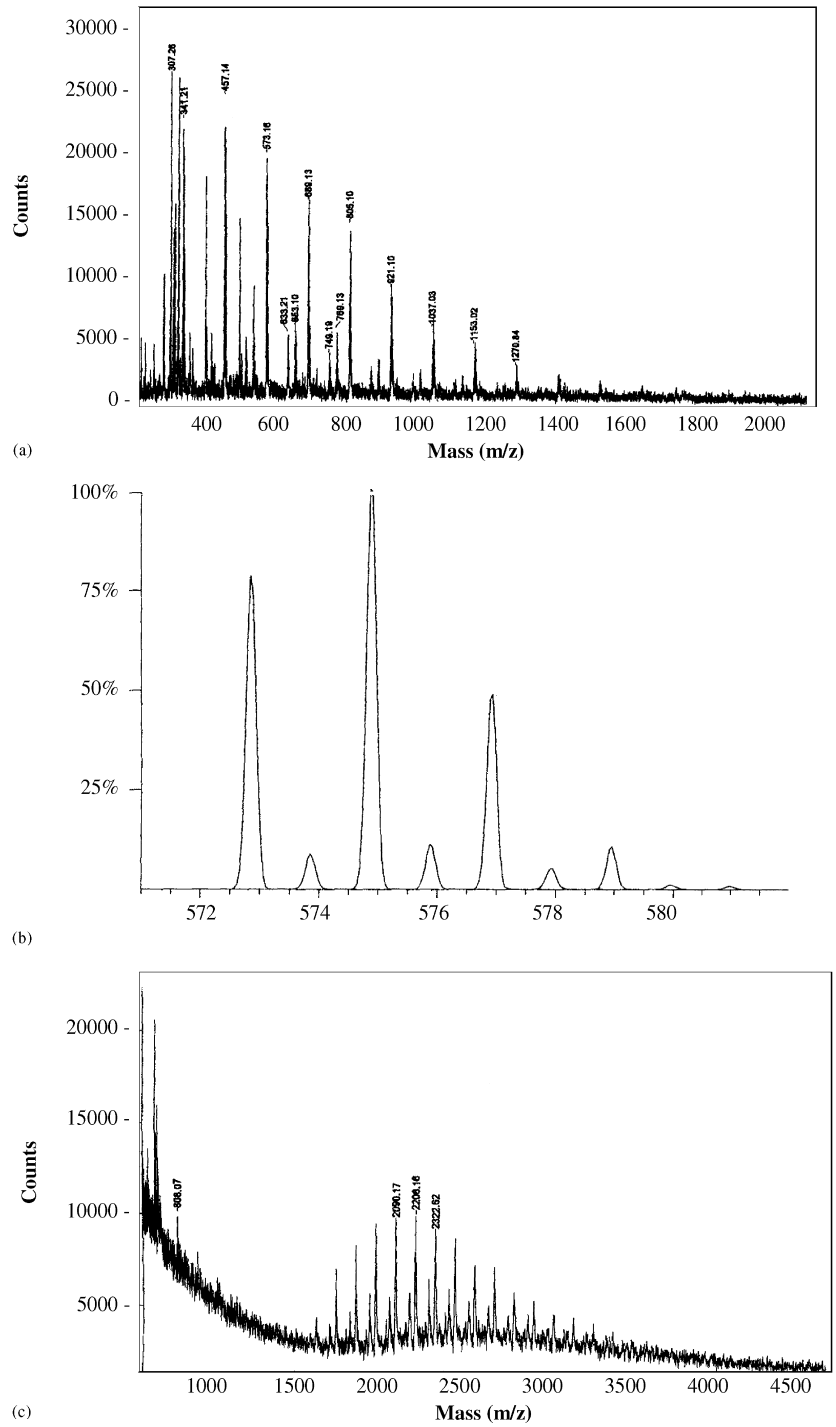


Fig. 3. MALDI-TOF spectra of telomer **2,n**: (a) liquid fraction; (b) parent peak massive of telomer **2,4** ($M = 573$); (c) solid fraction.

The Fig. 3(c) shows the MALDI-TOF spectrum of a solid fraction **2,n**. The parent peaks masses vary from about 1600 to 3500 corresponding to DP between 13 and 30. An approximate calculation of DP_n leads to 19. Because of the poor solubility of these solid telomers, other analytical methods do not allow us to measure these average mass values.

2.3. Cleavage of phosphonic esters

The cleavage of phosphonic esters can be performed by several methods. The chemical change was generally accomplished by heating in concentrated acidic solution (HCl or HBr) [4,11], or in alkaline solution [12–15], by using silylating reagents [1,16–19] or inorganic halides

Table 6
Cleavage of phosphonic esters of telomer **2,1**

Number	Reagent	Cure conditions				Diester (%)	Monoacid (%)	Diacid (%) **3,1**
		Molar ratio (substrate/reagent)	Solvent	Temperature (°C)	Time (h)			
1	HCl 12N	1/10	Toluene	110	12	18	22	60
2	HCl 12N	1/10	Toluene	110	24	–	–	100
3	NaOH	1/10	Water/dioxane (1/4)	65	12	50	50[a]	–
4	$BrSiMe_3$	1/3	Acetonitrile	rt[b]	4	59	41	–
5	$BrSiMe_3$	1/3	Acetonitrile	65	4	12	56	32
6	$BrSiMe_3$	1/3	Acetonitrile	65	24	–	–	100

[a] Partial cleavage of CF_2–P bond.
[b] Room temperature.

[20–23], but in this latter case, lead only to monoacid structures.

To obtain diacid structures, we did not study the last method. Table 6 sums up the various experiments we conducted with telomer **2,1**. The cleavage was monitored by NMR. For ^{1}H NMR, we observed the disappearance of ethyl esters, and ^{31}P NMR showed the formation of acidic structures: the monoacid product is characterized by a triplet at 2 ppm whereas the diacid product by a triplet at 1 ppm. We isolated the last one as a very hygroscopic white solid with the following formula.

$$H-CFCl-CF_2-P(O)(OH)_2 \quad \mathbf{3,1}$$

We noted that the cleavage of phosphonic esters of fluorinated chain was more difficult than for an hydrocarbon chain. For cleavage using a silylating reagent, although 2 h at room temperature is usually sufficient, we had to heat the mixture reaction at 65°C for 48 h to complete the total conversion to disilyl ester structures in the case of telomer **2,1**. The poor reactivity to silylation is probably linked to the strong inductive effects of fluorine atoms α to the phosphonic group which weaken the P=O bond.

For all these conditions (Table 6), the best way of cleavage of phosphonic esters seems to be acidic hydrolysis. Thus, we prepared the family **3,n** by hydrolysis with 12N HCl in refluxing toluene during 24 h.

3. Conclusions

This paper deals with the synthesis of phosphonic derivatives bearing chlorofluorinated chains. These were prepared by telomerization of chlorotrifluoroethylene with dialkyl hydrogenphosphonates in the presence of peroxide initiators. From a detailed study of experimental parameters, we optimized the reaction to obtain several telomer mixtures with various chlorofluorinated chain lengths.

In this study we carried out a full structural characterization of these telomers showing a selective 'head–tail' addition of the monomer by studying telomers **1,1** and **2,1**. Furthermore, MALDI-TOF analyses allowed us to determine the average true masses of mixtures of high polymerization degree telomers. Cleavage of the phosphonic esters gave acidic structures well-known for their adhesion properties. Now, we are studying the lubrication performances of chlorofluorinated chains and adhesion properties of phosphonic acids towards metal substrates, and these results will be described in a further paper.

4. Experimental details

4.1. General comments

Most starting materials were purchased from Aldrich and did not require purification prior to use. Benzoyl peroxide was precipitated from its chloroform solution by methanol and dried in vacuo. The authors thank Elf-Atochem Company for the gift of CTFE.

Most telomerizations were carried out in Carius tubes. The tubes were filled with reactants, saturated with nitrogen (or argon), cooled in a liquid nitrogen/acetone mixture, sealed and placed into a shaken oven equipped with a thermoregulator. At the end of the reaction, the tubes were left at room temperature, then cooled in liquid nitrogen and opened before analyses.

Other telomerizations have been performed in special high-pressure reactors of capacity are either 1 or 5 l (detail in text). The reactor was filled with liquid reactants, saturated with nitrogen and then closed. It was cooled in liquid nitrogen/acetone mixture, filled with gaseous monomer and placed in a thermoregulated oven. At the end of the reaction, the reactor is degased under vacuum. The telomers mixture is purified as specified in Scheme 1.

The different pure telomers were characterized by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy at 20°C. Spectra were recorded on Brüker AC 200 or 250 instruments, using deuterated chloroform as solvent and TMS as reference for ^{1}H. References for ^{19}F and ^{31}P NMR were $CFCl_3$ and H_3PO_4, respectively. The letters s, d, t, q and m stand for singlet, doublet, triplet, quadruplet and multiplet, respectively.

IR spectra were recorded with a FT-IR NIWLET 510 P spectrophotometer using KBr discs. The position of the bands is given per cm^{-1} with an error of $\pm 2.5\ cm^{-1}$. The

letters vs, s, m and w designate very strong, strong, medium and weak intensities.

Mass spectra were obtained on a CEC 21–110C double beam apparatus equipped with a flame ionization source and a system of direct introduction. The *m/z* values are given for main peaks with their abundances relative to the base peak in brackets. The formulae of some important fragment ions are also given (*M* is the mass peak).

MALDI-TOF measurements were conduced with a Voyager Elite MALDI-TOF mass spectrometer (Perspective Biosystems, Framingham, MA, USA). All analyses were recorded by negative ions in reflectron mode with delayed extraction. For all experiments, the matrix was 2,5-dihydroxybenzoic acid. The telomer sample was dissolved in tetrahydrofuran (THF) at a concentration of 2 g l^{-1} and 10 μl of this solution was mixed with 50 μl of a 15 g l^{-1} matrix solution in THF. A fraction of 1 μl of the resulting stock solution was placed on the multistage target and airdried. The ions were accelerated by a potential of 20 kV and the reflectron voltage was 29 kV.

Gas chromatography analyses have been obtained on a Delsi F30 apparatus, using a OV1 column 1 m in length. The Central Microanalysis Service of CNRS, Division of ENSCM, performed elementary analyses.

4.2. Synthesis of dimethyl 2-chloro-1,1,2-trifluoroethylphosphonate **1,1**

- $Eb_{20\ mm} = 105^{\circ}C$
  - IR (CS_2): 2970(m), 2920(w), 1280(vs), 1200(m), 1180(m), 1110(s), 1070(vs), 1040(vs), 975(m), 850(s), 785(w), 740(m), 550(m).
  - ^1H NMR ($CDCl_3$)δ: 4.0 (d, 6H, CH_3); 6.6 (dddt, 1H, $^2J_{Hd-Fc} = 45.5$ Hz, $^3J_{Hd-Fa} = 12$ Hz, $^3J_{Hd-Fb} = 4$ Hz, $^3J_{Hd-P} = 0.8$ Hz) ppm. ^{19}F NMR ($CDCl_3$) similar to compound **2,1** (see Table 2). ^{31}P NMR ($CDCl_3$)δ: 4.0 (t, 1P) ppm.
  - Mass spectroscopy: 198(1.6), 196(4.2), 191(4.5), 147(20), 145(62), 140(6), 129(28), 117(6), 116(5), 114(6), 113(5), 110(43), 109(100), 105(9), 100(15), 98(48), 97(29), 95(22), 94(4), 93(14), 82(33), 81(8), 80(37), 79(85), 77(7), 69(6), 67(16), 65(6), 63(8), 47(37), 45(42).
  - Elementary analysis found: C, 20.30; H, 3.50; F, 24.46; P, 13.80%. $C_4H_7ClF_3O_3P$ requires: C, 21.19; H, 3.09; F, 25.17; P, 13.69%.

4.3. Synthesis of dimethyl 2,4-dichloro-1,1,2,3,3,4-hexafluorobutylphosphonate **1,2**

- $Eb_{0.1\ mm} = 106^{\circ}C$
  - IR (CS_2): similar to compound **1,1** but we noticed a decrease of 1280, 1040, 975 and 785 bands.
  - ^1H, ^{19}F, ^{31}P NMR ($CDCl_3$) similar to compound **1,1**.
  - Elementary analysis found: C, 21.32; H, 2.53; Cl, 19.97; P, 8.71%. $C_6H_7Cl_2F_6O_3P$ requires: C, 20.99; H, 2.04; Cl, 20.70; P, 9.04%.

4.4. Synthesis of diethyl 2-chloro-1,1,2-trifluoroethylphosphonate **2,1**

- $Eb_{20\ mm} = 117^{\circ}C$
  - IR (CS_2): 2985(s), 2960(m), 2950(m), 2925(w), 1390(m), 1370(m), 1340(w), 1280(vs), 1200(s), 1160(s), 1115(s), 1065(vs), 1020(vs), 980(s), 845(w), 790(s), 740(s), 600(w), 550(s).
  - ^1H, ^{19}F, ^{31}P NMR ($CDCl_3$) described in results and discussion part (see Table 2).
  - Mass spectroscopy: 229(0.8), 227(2.5), 225(2), 199(15), 198(6), 183(15), 181(14), 178(15), 163(8), 155(14), 137(38), 129(7), 127(9), 119(3), 117(8), 109(100), 99(17), 98(18), 93(12), 91(29), 82(28), 81(77), 65(27), 63(23), 45(85).
  - Elementary analysis found: C, 27.03; H, 4.68; F, 21.37; P, 12.19%. $C_6H_{11}ClF_3O_3P$ requires: C, 28.29; H, 4.32; F, 22.40; P, 12.48%.

4.5. Synthesis of diethyl 2,4-dichloro-1,1,2,3,3,4-hexafluorobutylphosphonate **2,2**

- $Eb_{0.1\ mm} = 112^{\circ}C$
  - IR (CS_2): similar to compound **2,1** but we noticed a decrease of 1280, 1065, 980 and 790 bands.
  - ^1H, ^{19}F, ^{31}P NMR ($CDCl_3$) similar to compound **2,1**.
  - Elementary analysis found: C, 26.29; H, 3.36; F, 30.17; P, 8.02%. $C_8H_{11}Cl_2F_6O_3P$ requires: C, 25.87; H, 2.96; F, 30.73; P, 8.36%.

Acknowledgements

The MALDI-TOF measurements were carried out in the "Laboratoire de Chimie Structurale Organique et Biologique" of Pierre and Marie Curie University (Paris) and the authors thank their staff members and in particular J.C. Blais for their kind assistance.

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