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Journal of Fluorine Chemistry 112 (2001) 3–12

JOURNAL OF FLUORINE CHEMISTRY

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Radical telomerisation of vinylidene fluoride with diethyl hydrogenphosphonate Characterisation of the first telomeric adducts and assessment of the transfer constants

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Abstract

The radical telomerisation of vinylidene fluoride (VDF) with diethyl hydrogenphosphonate (DEHP) was investigated to synthesize fluorinated telomers bearing a phosphonate end-group, as $H(VDF)_nP(O)(OEt)_2$. Di-*t*-butyl peroxide was the most effective radical initiator A minute structural study of typical VDF–DEHP telomers was performed by ^1H, ^{13}C, ^{19}F, ^{31}P NMR spectroscopies. These analytical methods allowed us to prove the selective addition of the phosphonyl radical onto the hydrogenated side of VDF, while the telomers containing more than two VDF units were composed of isomers. The kinetics of telomerisation led to the assessment of the six first order transfer constants giving an infinite transfer constant of 0.38 at 140°C for DEHP.

Keywords: Vinylidene fluoride; Radical telomerisation; Diethyl hydrogenphosphonate; Transfer constant; Nuclear magnetic resonance

1. Introduction

Fluorinated derivatives bearing phosphorous 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 [5,6] and electrolytes [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 [10–33]. Among them, the telomerisation reaction has evidenced an easy method to prepare such derivatives. First, the redox telomerisation of vinyl or allyl phosphonate with chlorofluorinated chains bearing a CCl_3 end-group led to original phosphonic acids [30].

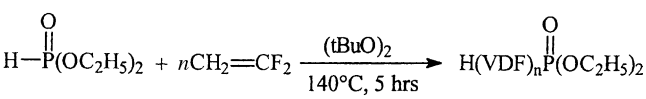
It is also the case for the radical telomerisation of either fluoroalkenes (chlorotrifluoroethylene [27,34] or tetrafluoroethylene [21–23]) with phosphonate-containing transfer agents (e.g. dialkyl hydrogenphosphonates) or of monomers bearing phosphonate function (e.g. vinyl or allyl phosphonates) with fluorinated telogens (mercaptans [31–33] or perfluoroalkyl iodides [29]).

However, to our knowledge, the radical telomerisation of VDF with diethyl hydrogenphosphonate (DEHP) was investigated once [24] and it was found interesting to study this reaction more deeply by an accurate characterisation of the first four adducts. In addition, this work did not take into account the kinetics of telomerisation and we have found it worthwhile to determine the transfer constants of the first order-telomers, goal of the present paper.

2. Results and discussion

2.1. Synthesis and characterisation of the first adducts of the telomerisation of VDF with DEHP

The first adducts of the telomerisation of VDF with DEHP were synthesised in a one-litre autoclave by using di-*t*-butyl peroxide as the initiator (1% in mol as ratio to VDF: $C_0 = [(t\mathrm{BuO})_2]_0/[\mathrm{VDF}]_0 = 0.01$) and acetonitrile as the solvent.



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PII: S0022-1139(01)00475-4

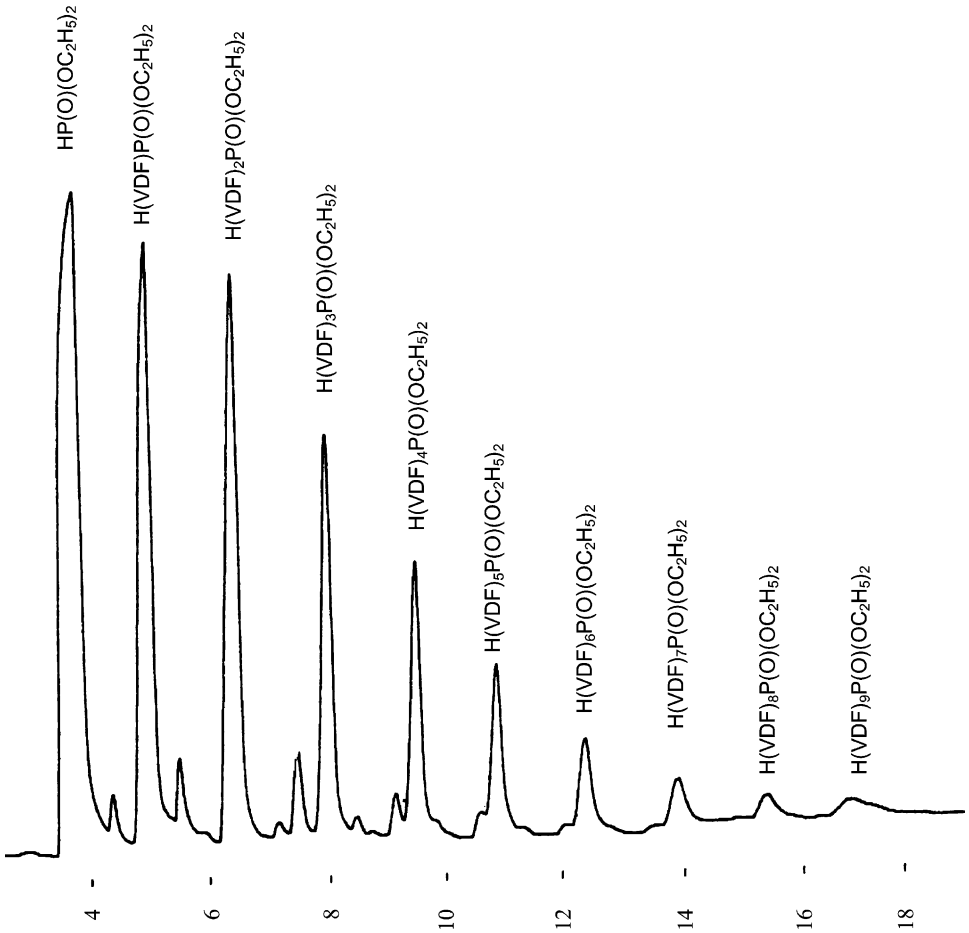


Fig. 1. Gas chromatogram of the total product mixture of the telomerisation of VDF with DEHP after elimination of the solvent ($R_0 = 1$; $C_0 = 1\%$; initiator: $(t\text{BuO})_2$; $T_R = 140^\circ\text{C}$, $t_R = 5$ h). R_0 and C_0 stand for the initial $[\text{DEHP}]_0/[\text{VDF}]_0$ and $[\text{initiator}]_0/[\text{VDF}]_0$ molar ratios.

The initial mixture was composed of an equimolar amount of VDF and DEHP (defined as $R_0 = (\text{DEHP})_0/(\text{VDF})_0 = 1.0$). The use of a solvent was required to improve the homogeneity of the liquid phase and the VDF disolution in that meduim. Acetonitrile was found to be the best solvent and also because of its poor transfer activity in the presence of VDF. Thus, at 140°C, the initial pressure in the autoclave did not exceed 36.0 bars for 108.0 g of VDF, in the presence of 200.0 g of acetonitrile. The reaction was shown to be rather quick as evidenced by a drop of pressure (15.4 bar, after 5 h) and a slight exotherm ($\Delta T \sim +20^\circ\text{C}$) at the beginning of the reaction. The overall VDF conversion was ca. 91%, according to the released VDF, after reaction.

After evaporation of the solvent, the total product mixture was analysed by gas chromatography that evidences the formation of a classical telomeric distribution. The gas chromatogram (Fig. 1) allowed us to identify the first nine adducts produced by such a telomerisation. The higher adducts were in negligible concentrations. The average cumulated degree of the polymerisation in number $\overline{\text{DP}}_{n\,\text{cum}}$ of these telomers has been determined to 2.9, corresponding to an average cumulated molecular weight $\overline{M}_{n\,\text{cum}}$ of about 320, assuming that each adduct has the following formulae $\text{H(VDF)}_n\text{P(O)(OEt)}_2$. Table 1 lists the relative amount (in GC area) of these adducts versus their order. Chromatograms GPC or SEC of the total product mixture (Fig. 2) also shows a telomeric distribution with a difference between each adduct of about 70 (in polystyrene equivalent) in molecular weight. The sensitivity of the apparatus and the resolution of the chromatogram limit

Table 1
Proportions of VDF–DEHP adducts (in %GC) of the telomeric mixture versus their order

Adducts (n)	Amounts (%GC)
1	27.9
2	26.9
3	15.6
4	11.1
5	7.1
6	4.9
7	2.6
8	1.5
9	2.1

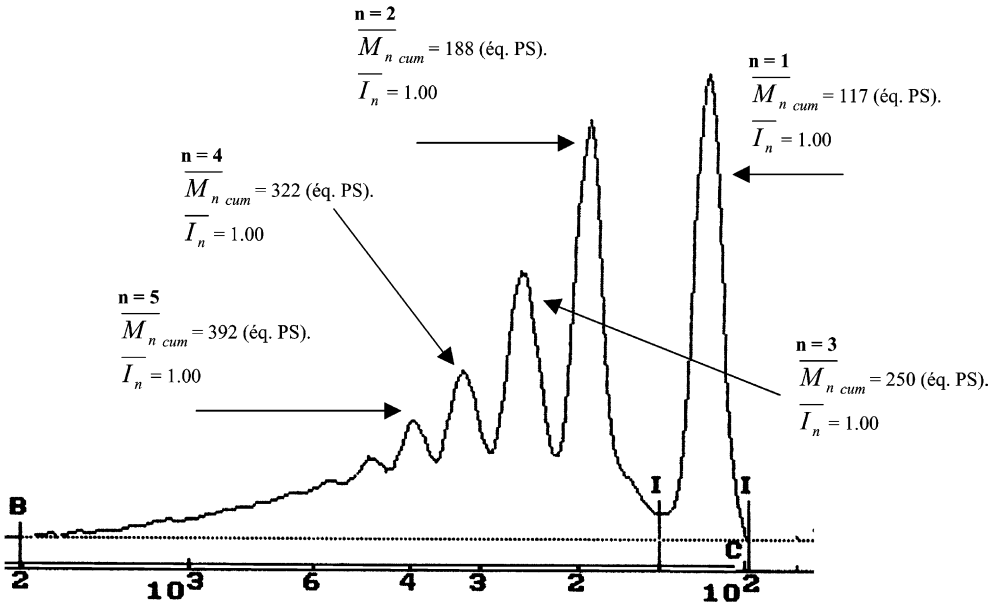


Fig. 2. GPC (or SEC) chromatogram of the total product mixture of the telomerisation of VDF with DEHP after elimination of the solvent ($R_0 = 1$; $C_0 = 1\%$; initiator: $(t\text{BuO})_2$).

the detection of telomers to the sixth adduct. Finally, coupled GC–MS spectrometry has shown that each adduct was characterised by mass of $138 + 64n$ (n being the order of the adduct).

The first four adducts of the telomerisation of VDF with DEHP were isolated by distillation under reduced pressure. Although, the mono and diadduct could be easily purified, the higher order adducts, the boiling points of which were rather high, required a stronger vacuum to obtain pure fractions (however, their purity was higher than 65%).

Centesimal analyses of these four fractions and their boiling points are given in the experimental part and confirm their general formulae $H(VDF)_nP(O)(OC_2H_5)_2$. These are liquid in normal conditions of temperature pressure and soluble in common organic solvents.

The microstructure of the first adducts was performed by means of ^1H, ^{19}F, ^{13}C and ^{31}P spectroscopies (Section 3).

2.1.1. Structure of the monoadduct

The ^1H NMR spectrum of the monoadduct shows the exclusive formulae:

$$HCF_2—CH_2—\overset{\overset{O}{\|}}{P}(OCH_2CH_3)_2 \qquad (1,1)$$

as evidenced by a triplet of doublets ($^2J_{HF} = 56.0$ Hz) of triplets, centred at 5.98 ppm, assigned to difluoromethyl HCF_2 end-group for which the hydrogen is coupled to the phosphorous atom in γ position ($^3J_{HP} = 3.8$ Hz), linked to a methylene group ($^3J_{HH} = 4.9$ Hz) in β position. The doublet of doublets of triplets centred at 2.32 ppm., characteristic of methylene group adjacent to phosphorous atom ($^2J_{HP} = 19.2$ Hz) and linked to the difluoromethyl end-group ($^3J_{HH} = 4.9$ Hz; $^3J_{HF} = 16.3$ Hz) confirms that this telomer arises from the addition of a phosphonate radical toward the non-substituted carbon atom of VDF.

The diethyl phosphonate function is identifiable by a quartet ($^3J_{HH} = 7.2$ Hz) of doublets ($^3J_{HP} = 8.3$ Hz) at 4.05 ppm for $–OCH_2$-groups and a triplet ($^3J_{HH} = 7.1$ Hz) of doublets ($^4J_{HP} = 0.3$ Hz) at 1.23 ppm assigned to the methyl groups.

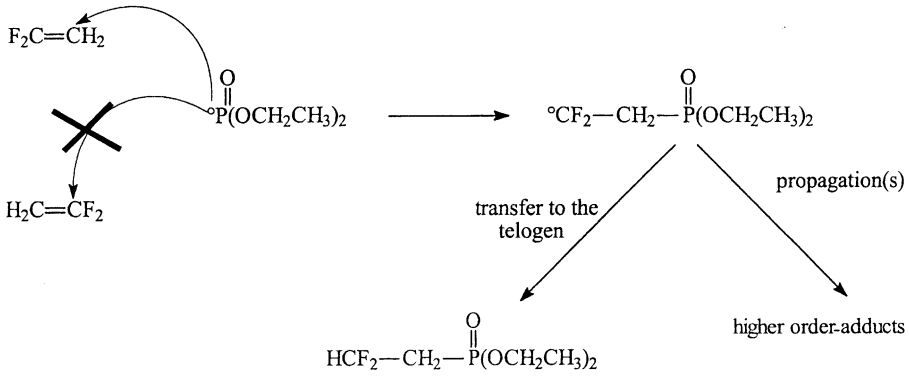
That structure was also evidenced by ^{13}C, ^{19}F and ^{31}P NMR spectroscopies (see experimental session).

The ^{19}F NMR spectrum exhibits a doublet ($^2J_{FH} = 56.0$ Hz) of doublets ($^3J_{FP} = 29.7$ Hz) of triplets ($^3J_{FH} = 16.3$ Hz) centred at -110.55 ppm., while ^{31}P NMR spectrum shows after P–C and P–H couplings a unique triplet centred at 20.9 ppm., with a coupling constant $^3J_{FP} = 29.7$ Hz.

This structural study brings up the evidence of the selectivity of the addition of diethyl phosphonate radicals onto the non-fluorinated carbon atom of VDF. It is noted, the absence of a triplet centred at ca. 1.8 ppm assigned to the monoadduct of formula $H_3C–CF_2P(O)(OEt)_2$ as shown in VDF/method telomers [35].

2.1.2. Structure of the diadduct

It is interesting to analyse the diadduct obtained by telomerisation of VDF with DEHP, in terms of the regioselectivity of the VDF chaining. Indeed, if elemental analyses are consistent with the expected gross formula, i.e. $H(VDF)_2P(O)(OEt)_2$, it is observed the existence of two types of diadducts, resulting from VDF propagations, as follows:



The presence of both isomers was evidenced by ^{1}H and ^{19}F NMR. As in the case of the monoadduct, was noted the normal (2,1) diadduct bearing the $-CF_2H$ end-group, as a triplet ($^{2}J_{HF} = 55.3$ Hz) of triplets ($^{3}J_{HH} = 4.6$ Hz) centred at 6.00 ppm. Both VDF units were shown by a complex structure ranging between 2.2 and 2.9 ppm, as an overlapping of a doublet ($^{2}J_{HP} = 19.7$ Hz) of triplets ($^{3}J_{HF} = 15.7$ Hz) centred at 2.47 ppm and a quintet ($^{3}J_{HF} = 15.7$ Hz) of doublets ($^{3}J_{HH} = 4.6$ Hz) centred at 2.66 ppm corresponding to methylene groups of VDF located in α and γ positions, respectively about the phosphorous atom. The characteristic structures of diethylphosphonate functions are unchanged about that of monoadduct.

Isomer (2,2) exhibits a methyl end-group resulting from a reversed addition of a VDF unit as evidenced by the presence of a triplet characterised by a high coupling constant ($^{3}J_{HF} = 17.3$ Hz) and centred at 1.65 ppm.

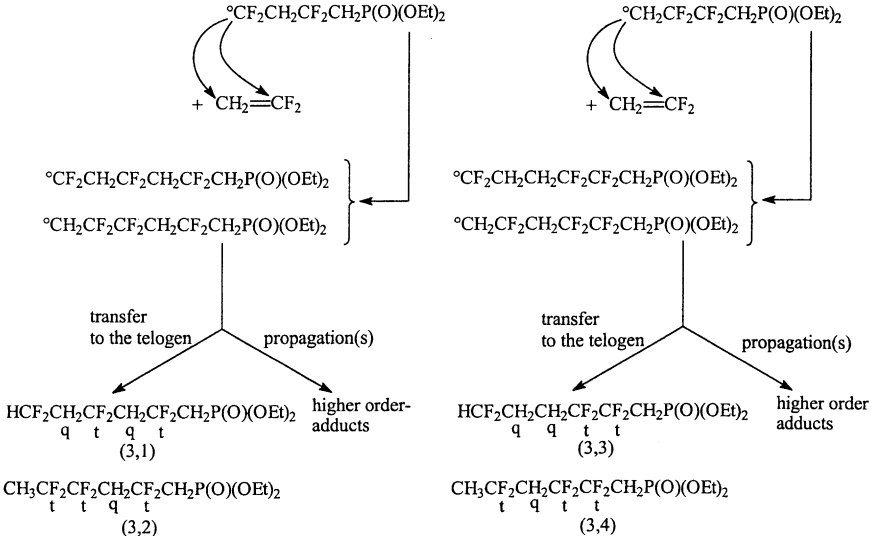
The amount of these defects of chaining (head to head), assessed by the corresponding integrals, were evaluated to 14.2% that represents a high value. This was also noted on the ^{19}F NMR as the presence of a doublet of multiplets centred at -115.5 ppm and a multiplet centred at -87.2 ppm (assigned to a difluoromethylene in β about the phosphorous atom) corresponding to isomers (2,2) and (2,1), respectively: their ratio of integrals enabled us to deduce the amount of reversed addition as 13.5%.

The triplet ($^{3}J_{PF} = 29.5$ Hz) noted on the ^{31}P NMR spectrum has undergone a high field shift of 1 ppm about that of the monoadduct, from 20.9 to 19.9 ppm.

2.1.3. Structure of triadduct

The formation of the triadduct from the telomerisation of VDF with DEHP supposes a high amount of possibilities of inversions of VDF chaining. Beside, the expected major head to tail chaining, head to head and tail to tail additions may occur.

The ^{1}H NMR spectrum of that triadduct shows similar structures as those of the diadduct. The major difference, except the integrals, concerns the characteristic structures of methylene groups brought by VDF. The relative proportion of triadduct with methyl extremity can be determined by the integral assigned methyl ($\delta \sim 1.6$ ppm) and difluoromethyl ($\delta \sim 6.0$ ppm), respectively. This amount assessed to 6.7%, is twice lower than that of the diadduct.



The ^{19}F NMR spectrum of that fraction shows three structures of the same intensity representing the fluorine atoms of difluomeythylene groups and the fluorine of the difluoromethyl end-group, characterised by a doublet

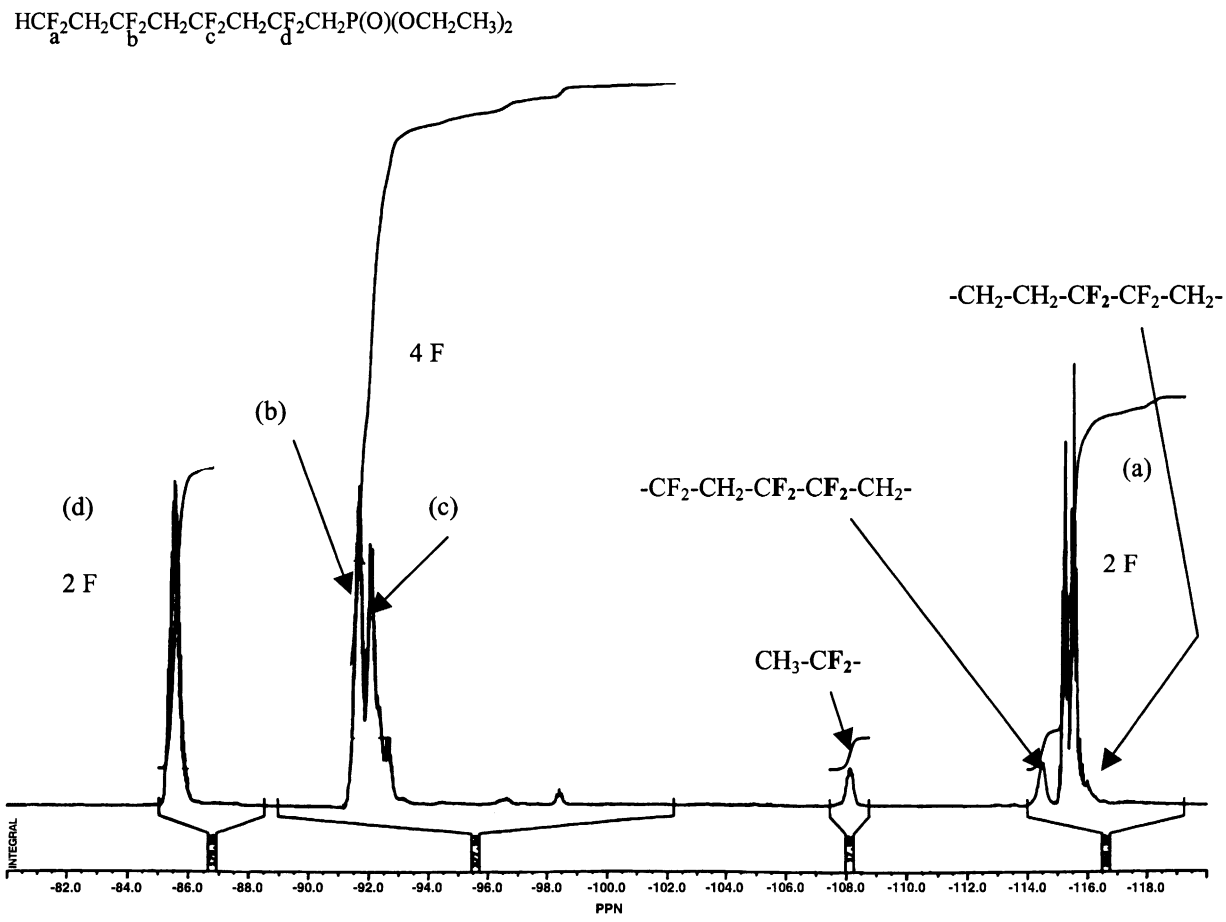


Fig. 3. ^{19}F NMR spectrum of tetradduct $H(VDF)_4P(O)(OEt)_2$ from the telomerisation of VDF with DEHP.

($^2J_{FH} = 56.0$ Hz) of multiplets centred at −115.7 ppm. Certain minor structures (−108.0 and −114.5 ppm) evidence the presence of telomers bearing methyl end-group.

As above, the proportion of reversed adduct was assessed from the ratio of integral of the characteristic signals centred at −108.0 and −115.7 ppm, as 9.2%.

2.1.4. Structure of tetraadduct

As for lower order adducts, NMR analyses of the tetra-adduct evidence $H(VDF)_4P(O)(OEt)_2$ general structure. The increasing VDF units hence involved more complex structures, especially from the methylene groups in ^{1}H and ^{13}C NMR, leading to broad multiplets centred at 2.8 and 42.4 ppm, respectively. Only the ^{19}F NMR spectrum (Fig. 3) clearly shows the incorporation of a fourth unit by the presence of a fourth multiplet centred at −91.8 ppm that identifies without ambiguity the fluorine atoms of the difluoromethylene group, in β of the difluoromethyl group, surrounding by two methylene groups. The amount of methyl end-group formed by transfer with a reversed radical adduct was assessed to 9.3%.

The phosphorous atom of this tetraadduct appears as a unique triplet ($^3J_{PH} = 29.7$ Hz) at 19.7 ppm.

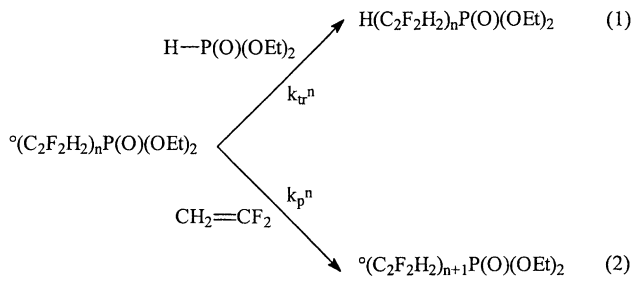
2.2. Kinetic study of the telomerisation reaction of diethyl phosphite (or DEHP): assessment of the transfer constants of first orders C_T^n

2.2.1. Assessment of transfer constants of first orders

The activity of transfer of diethylphosphite (or DEHP) in the presence of vinylidene fluoride (VDF) is characterised 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:

$$C_T^n = \frac{k_{tr}^n}{k_p^n}$$

These rate constants characterise 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. The produced telomers are unable to participate to new radical reaction, especially as transfer agents. Indeed, we have checked that the phosphonates produced by this telomerisation could not act as new transfer agents when they were involved in reaction in the presence of organic initiator and VDF, as it is the case of perfluoroalkyl iodides with TFE [36] or VDF [37].



We have also shown that the telomerisation in solution of VDF with diethylhydrogenphosphonate, from equimolar amounts of these reactants, led to a mixture composed of the first adducts of the telomerisation, $H(VDF)_nP(O)(OEt)_2$, for which the average cumulated degree of telomerisation in number $\overline{DP}_{n\,\mathrm{cum}}$ did not exceed 3. Besides, studies performed in our laboratory by Boutevin et al. [38] evidenced the requirement to differentiate the rates constants characterising each step of the telomerisation, when it produces low $\overline{DP}_{n\,\mathrm{cum}}$ (i.e. lower than 10) mainly. Thus,

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

$$k_{\mathrm{p}}^1 \neq k_{\mathrm{p}}^2 \neq k_{\mathrm{p}}^3 \neq \cdots \neq k_{\mathrm{p}}^n, \quad n < 10.$$

Obviously, it is deduced that $C_{\mathrm{T}}^1 \neq C_{\mathrm{T}}^2 \neq C_{\mathrm{T}}^3 \neq \cdots \neq C_{\mathrm{T}}^n$, 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 characterise the 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. Among these investigations, well-summarised by Starks [39], we have chosen the David and Gosselain theory [40], 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:

$$F_n = \frac{C_{\mathrm{T}}^n R'}{\prod_{j=1}^{j=n}(C_{\mathrm{T}}^j R' + 1)} \tag{1}$$

These authors also proposed the following relationship linking the transfer constants of each order:

$$C_{\mathrm{T}}^n = \frac{F_n}{R' \cdot \sum_{j=n+1}^{\infty} F_j} \tag{2}$$

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 characterising each order n, hence give the values C_{T}^n. We performed the kinetics of telomerisation in sealed Carius tubes under stirring. It was possible to use accurate amount of VDF thanks to a special apparatus and to perform simultaneous experiments.

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).

To determine that reaction time for which R is considered as a constant equal to its initial value R_0, we monitored the evolution of the amounts of telogen and VDF versus time (Fig. 4 and Table 2) considering the telomerisation of VDF with an equimolar amount of telogen ($R_0 = 1$) in solution in

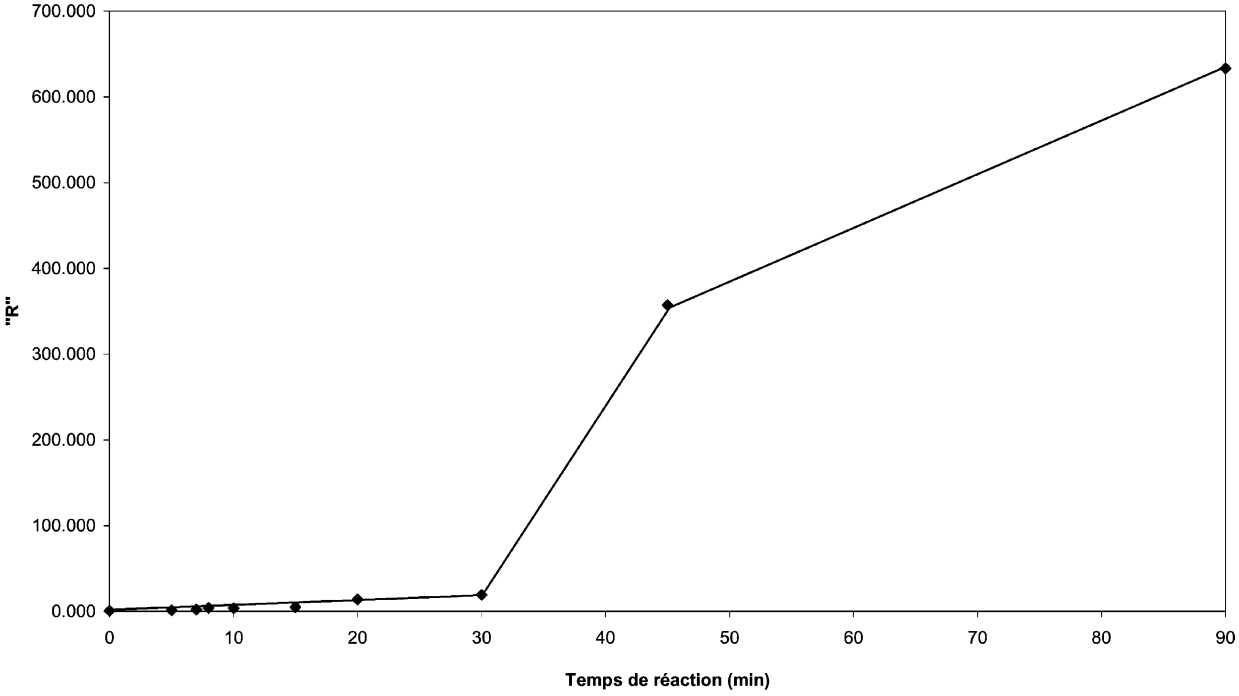


Fig. 4. Evolution of ratio R versus the reaction time.

Table 2
Evolution of ratio R versus the reaction time

Reaction time (min)	R
0	1.000
5	1.109
7	1.922
8	4.180
10	3.828
15	4.860
20	13.804
30	19.420
45	357.366
90	633.280

acetonitrile at 141°C (initiator: di-*t*-butyl peroxide). These amounts were assessed by gas chromatography of the gaseous phase of the residual liquid and of gas phases. It was noted that for the first 7 min of the reaction, the molar ratio R could be assigned to R_0. After this period of time, R highly increases with the reaction time.

The experiments required for the assessment of the C_T^n of the first adducts were investigated involving the following parameters:

- telomerisations initiated by di-*t*-butyl peroxide ($C_0 = ([t\text{BuO}]_2)_0/[\text{VDF}]_0 = 0.01$);
- reaction temperature: 140°C;
- reactions in shaken sealed Carius tubes;
- reaction time: 7 min.

The initial molar R_0 varied for each experiment. The transfer constants up to the six orders were determined from the experimental results and are listed in Table 3. For example, for coefficient C_T^1, the evolution of the ratio $F_1/\sum_{i=2}^{\infty} F_i$ versus R_0 was drawn. The experimental data are located onto a straight line, the slope of which is $C_T^1 \sim 0.26$. The other transfer constants were calculated according to the same procedure (Fig. 5). Table 3 lists the different values of these constants.

From these results, the coefficients of transfer are likely that from order $n = 2$, a constant value was found equal to ca. 0.38. Only the first order constant is slightly different from that value. Such a phenomenom can be explained by the influence of the phosphonate end-function.

Nevertheless, the results obtained allow us to define a value of C_T^∞, assigned to the limit value of calculated C_T^n, as:

$$C_{T\,(\text{H–P(O)(OEt)}_2/\text{VDF})}^{\infty} = 0.38 \quad \text{at} \quad 140^\circ\text{C}$$

These transfer constants, all lower than 1.0, evidence the preponderance of the propagation toward the transfer at each step of the telomerisation. It is also observed that the value of the constant C_T^∞, characteristic of the reactivity of the transfer of DEHP in the presence of VDF, is overall of

Table 3
Values of transfer constants C_T^n of DEHP with VDF for 1–6 orders

n	1	2	3	4	5	6
C_T^n	0.256	0.375	0.375	0.376	0.378	0.378

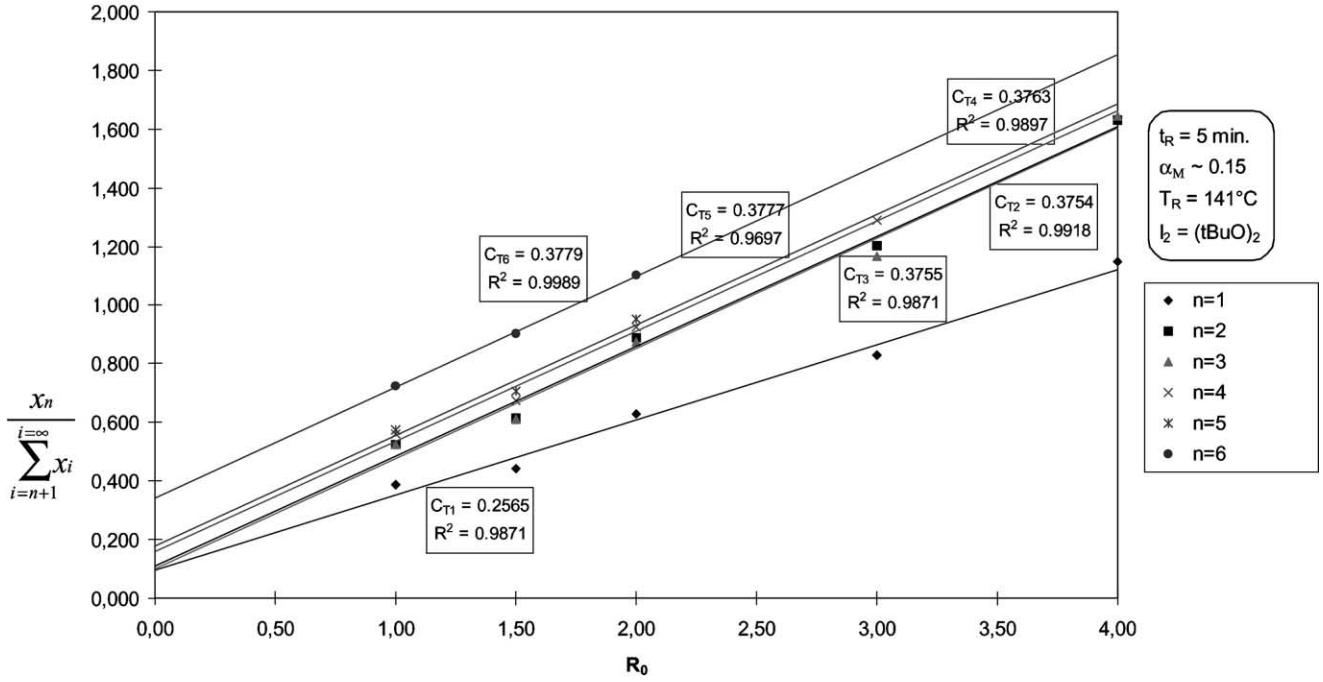


Fig. 5. Assessment of first order transfer constants C_T^n, characteristic of the radical telomerisation of VDF with DEHP, in solution in acetonitrile, at 140°C.

the same order than those reported in the literature and obtained in the presence of TFE ($C_T^{\infty} = 0.2$ [21,22,41]) or CTFE ($C_T^{\infty} = 0.37$ [34]).

3. Experimental details

3.1. General comments

3.1.1. Reactants

VDF was kindly supplied by Elf Atochem (Pierre Benite, France); acetonitrile from SDS, DEHP and di-*t*-butyl peroxide, were supplied by Aldrich, and were used as recieved.

3.1.2. Reactions

For obtaining a high amount of VDF telomers, the telomerisation occured in a one-liter Parr Hastelloy Autoclave equipped with a manometer, a rupture disk, inner and outlet valves using 2.5 g (0.017 mol) of di-*t*-butyl peroxide, 234.2 g (1.69 mol) of DEHP and 200 g (4.93 mol) of acetonitrile. Then, the autoclave was closed and saturated of nitrogen. After cooling in a liquid nitrogen/acetone mixture, the medium was evacuated and 108.1 g (1.69 mol) of VDF were introduced by double weighing. Then, the mixture was heated up to 140°C for 5 h and after cooling down to room temperature, the autoclave was cooled into an ice bath. The unreacted VDF was then released and the vessel opened. After evaporation of the acetonitrile, the total product mixture was distilled.

The first fraction contained the unreacted DEHP while the other pure fractions were composed of the various adducts.

3.1.3. Apparatus

After reaction and evaporation of the solvent, the total product mixture was analysed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, 3 m × 1/8 in. (i.d.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260 and 255°C, respectively. The temperature programme started from 50°C and reached 250°C at a heating rate of 15°C/min. The GC apparatus was connected to a Hewlett-Packard integrator (model 3390).

The structure of the telomers was determined by NMR spectroscopy at room temperature. The ^{1}H, ^{19}F, ^{13}C 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. The experimental conditions for recording ^{1}H (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); 64 (128) scans and pulse width of 5 μs for ^{19}F NMR. The letters s, t, q and m represent singlet, triplet, quintet and multiplet, respectively. State, purity and boiling point of the first four telomers are listed in Table 4.

3.1.4. Characteristics of the telomers

3.1.4.1. 2,2-Difluoro diethyl phosphonate (1,1) HCF_2-$CH_2P(O)(OC_2H_5)_2$ b.p. 83–84°C/5 mmHg. ^{1}H NMR ($CDCl_3$) δ: 5.98 (tdt, $^2J_{FH} = 56.0$ Hz, $^3J_{HP} = 8.3$ Hz, $^3J_{HH} = 4.9$ Hz, HCF_2,1H); 4.05 (qd, $^3J_{HH} = 7.2$ Hz, $^3J_{HP} = 8.3$ Hz, OCH_2); 2.32 (ddt, $^2J_{HP} = 19.2$ Hz, $^3J_{HH} = 4.9$ Hz, $^3J_{FH} = 16.3$ Hz, CH_2CF_2); 1.23 (td, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.3$ Hz, CH_3).

^{19}F NMR ($CDCl_3$) δ: −110.6 (ddt, $^2J_{FH} = 56.0$ Hz, $^3J_{PF} = 29.7$ Hz, $^3J_{FH} = 16.3$ Hz, HCF_2), 80 MHz multiplicity ^{13}C NMR ($CDCl_3$) δ: 113.3 (negative triplet of doublets, $^1J_{CF} = 241.1$ Hz, $^2J_{CP} = 1.6$ Hz, HCF_2); 62.3 (positive d, $^2J_{CP} = 6.3$ Hz CH_2–O,1C); 32.6 (positive dt, $^1J_{CP} = 141.6$ Hz, $^2J_{CF} = 23.1$ Hz, CH_2,1C); 16.2 (positive d, $^3J_{CP} = 6.1$ Hz,CH_3,1C).

^{31}P NMR ($CDCl_3$) δ: 20.9 (t, $^3J_{PF} = 29.7$ Hz).

Elemental analysis $C_6F_2H_{13}PO_3$ (202.06 g/mol).

%C, calc. 35.7 (found 35.6); H, calc. 6.5 (found 6.4); F calc. 18.8 (found 15.4).

3.1.4.2. 2,2,4,4-Tetrafluoro butane diethyl phosphonate $HCF_2CH_2CF_2CH_2P(O)(OC_2H_5)_2$ (2,1) and CH_3CF_2-$CF_2CH_2P(O)(OC_2H_5)_2$ (2,2) b.p. 93–94°C/1 mmHg. ^{1}H NMR ($CDCl_3$) δ: 6.00 (tt, $^2J_{FH} = 55.3$ Hz, $^3J_{HH} = 4.6$ Hz, HCF_2,1H); 4.05 (qd, $^3J_{HH} = 7.2$ Hz, $^3J_{HP} = 8.3$ Hz, OCH_2); 2.66 (qd, $^3J_{FH} = 15.7$ Hz, $^3J_{HH} = 4.6$ Hz, $HCF_2C\underline{H}_2$ of (2,1)); 2.47 (dt, $^2J_{HP} = 19.7$ Hz, $^3J_{FH} = 15.7$ Hz, PCH_2CF_2); 1.65 (t, $^3J_{FH} = 17.3$ Hz, CH3 of (2,2)), 1.23 (td, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.3$ Hz, $C\underline{H}_3CH_2$).

^{19}F NMR ($CDCl_3$) δ: −115.6 (dm, $^2J_{FH} = 55.3$ Hz, HCF_2), −114.8 (m, $CH_3CF_2CF_2$ of (2,2)); −108.1 (m, $CH_3C\underline{F}_2$ of (2,2)),−87.2 (m, $CH_2C\underline{F}_2CH_2$ of (2,1)).

The multiplicity of 80 MHz ^{13}C NMR ($CDCl_3$) δ: 119.3 (negative tt, $^1J_{CF} = 239.3$ Hz,$^3J_{CF} = 7.4$ Hz, CF_2CH_2P);

Table 4
Description of fractions of distillation corresponding to the first adducts of the telomerisation of VDF with DEHP[a]

Fraction (*n*)	Purity (GC%)	Boiling point	State
1	81	B.p. = 83–84°C (5 mbars)	Colourless liquid
2	75	B.p. = 93–94°C (1 mbar)	Colourless liquid
3	63	B.p. = 103–104°C (0,3 mbar)	Clear yellow liquid
4	51	B.p. = 118–119°C (0.8 mbar)	Yellow viscous liquid

[a] The purity of the adducts is given assuming the GC response factors of the species.

113.0 (negative triplet of doublets, $^1J_{CF} = 243.5$ Hz, $^3J_{CF} = 6.4$ Hz, HCF_2); 62.3 (positive d, $^2J_{CP} = 6.3$ Hz CH_2–O,1C); 41.4 (positive q,$^2J_{CF} = 24.0$ Hz); 34.9 (positive dt, $^1J_{CP} = 142.1$ Hz,$^2J_{CF} = 26.9$ Hz, CH_2,1C); 16.2 (positive d, $^3J_{CP} = 6.1$ Hz,CH_3,1C); 16.2(positive t, $^2J_{CF} = 24$ Hz,CH_3CF_2 of 2,2).

^{31}P NMR ($CDCl_3$) δ: 19.9 (t, $^3J_{PF} = 29.5$ Hz).

Elemental analysis $C_8F_4H_{15}PO_3$ (266.06 g/mol).

%C, calc. 36.1 (found 33.2); H, calc. 5.7 (found 5.5); F calc. 28.6 (found 25.9).

3.1.4.3. 2,2,4,4,6,6-Hexafluoro hexane diethyl phosphonate $HCF_2CH_2CF_2CH_2CF_2CH_2P(O)(OC_2H_5)_2$ *(3,1)* $CH_3CF_2CF_2CH_2CF_2CH_2P(O)(OC_2H_5)_2$ *(3,2) and* CH_3CF_2 CH_2CF_2 $CF_2CH_2P(O)$ $(OC_2H_5)_2$ *(3,3) b.p 103–104°C/0.3 mmHg.* ^{1}H NMR ($CDCl_3$) δ: 6.00 (tt, $^2J_{FH} = 55.3$ Hz, $^3J_{HH} = 4.6$ Hz, HCF_2, 1H); 4.05 (qd, $^3J_{HH} = 7.2$ Hz, $^3J_{HP} = 8.3$ Hz, OCH_2); 2.78 (qi, $^3J_{FH} = 15.7$ Hz, $CH_2CF_2C\underline{H}_2$ of (3,1)); 2.50 (qi, $^3J_{FH} = 15.7$ Hz, $^3J_{HH} = 4.6$ Hz, $HCF_2C\underline{H}_2CF_2$ of (3,1)), 2.47 (dt, $^2J_{HP} = 19.7$ Hz, $^3J_{FH} = 15.7$ Hz, PCH_2CF_2); 1.65 (t, $^3J_{FH} = 17.3$ Hz, CH3 of (3,2) and (3,3)), 1.23 (td, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.3$ Hz, CH_3CH_2).

^{19}F NMR ($CDCl_3$) δ: −115.7 (dm, $^2J_{FH} = 55.3$ Hz, HCF_2), −115.2 (m, $CH_3CF_2CF_2$ of (3,2)); −108.1 (m, $CH_3CF_2CF_2$ of (3,2)), −92.7 (m, $CH_2C\underline{F}_2CH_2$ of (3,1)); −85.7 (m, $CH_2CF_2CH_2P(O)(OC_2H_5)_2$ of (3,1)).

The multiplicity of 80 MHz ^{13}C NMR ($CDCl_3$) δ: 119.3 (negative tt, $^1J_{CF} = 239.3$ Hz,$^3J_{CF} = 7.4$ Hz,$\underline{C}F_2CH_2P$); 113.06 (negative triplet of doublets, $^1J_{CF} = 243.5$ Hz, $^3J_{CF} = 6.4$ Hz, HCF_2); 62.3 (positive d, $^2J_{CP} = 6.3$ Hz CH_2–O,1C); 42.7 (positive q,$^2J_{CF} = 24.0$ Hz); 41.7 (positive q, $^2J_{CF} = 24.0$ Hz); 34.9 (positive dt, $^1J_{CP} = 142.1$ Hz,$^2J_{CF} = 26.9$ Hz, CH_2,1C); 16.2 (positive d,$^3J_{CP} = 6.1$ Hz,CH_3CH_2,1C); 16.2 (positive t, $^2J_{CF}$= 24.1 Hz,$\underline{C}H_3CF_2$ of 3,2 and 3,3).

^{31}P NMR ($CDCl_3$) δ: 19.7 (t, $^3J_{PF} = 29.5$ Hz).

Elemental analysis $C_{10}F_6H_{17}PO_3$ (330.08 g/mol).

%C, calc. 36.4 (found 36.0); H, calc. 5.2 (found 5.3); F calc. 34.5 (found 34.4).

3.1.4.4. 2,2,4,4,6,6,8,8-Octafluorooctane diethyl phosphonate $HCF_2CH_2CF_2CH_2CF_2CH_2CF_2CH_2P(O)(OC_2H_5)_2$ *(4,1) and* $CH_3CF_2(VDF)_3P(O)(OC_2H_5)_2$ *(4,2) b.p. 118–119°C/0.08 mmHg.* ^{1}H NMR ($CDCl_3$) δ: 6.00 (tt, $^2J_{FH} = 55.2$ Hz, $^3J_{HH} = 4.6$ Hz, HCF_2,1H); 4.05 (qd, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 8.3$ Hz, OCH_2); 2.3–3.0 (overlapping of complex structures); 1.65 (t, $^3J_{FH} = 17.3$ Hz, CH3 of (4,2) and (3,3)), 1.23 (td, $^3J_{HH} = 7.2$ Hz, $^4J_{HP} = 0.3$ Hz, $\underline{C}H_3CH_2$).

^{19}F NMR ($CDCl_3$) δ: −115.7 (dm, $^2J_{FH} = 55.3$ Hz, HCF_2), −108.1 (m, $CH_3\underline{C}F_2CF_2$ of (4,2)), −91.8 (m, $CH_2CF_2CH_2$ of (4,1)); −86.7 (m, $CH_2CF_2CH_2P(O)(OC_2H_5)_2$ of (4,1)).

The multiplicity of 80 MHz ^{13}C NMR ($CDCl_3$) δ: 119.3 (negative tt, $^1J_{CF} = 239.3$ Hz,$^3J_{CF} = 7.4$ Hz, $\underline{C}F_2CH_2P$); 113.0 (negative triplet of doublets, $^1J_{CF} = 243.5$ Hz, $^3J_{CF} = 6.4$ Hz, HCF_2); 62.3 (positive d, $^2J_{CP} = 6.3$ Hz CH_2–O,1C); 42.3 (m, HCF_2CH_2 and $(CF_2CH_2)_2CF_2CH_2P$); 34.9 (positive dt, $^1J_{CP} = 142.1$ Hz,$^2J_{CF} = 26.9$ Hz, CH_2,1C); 16.2 (positive d, $\underline{C}H_3CH_2$,1C); 16.1 (t,$^2J_{CF} = 24.0$ Hz, CH_3CF_2 of 4.2).

^{31}P NMR ($CDCl_3$) δ: 19.7 (t, $^3J_{PF} = 29.4$ Hz).

Elemental analysis $C_{12}F_8H_{19}PO_3$ (394.09 g/mol).

%C, calc. 36.6 (found 36.2); H, calc. 4.9 (found 4.6); F calc. 38.6 (found 33.7).

The kinetics of telomerisations of VDF with DEHP were performed in thick borosilicate Carius tubes in a batch process (length: 130 mm, i.d.: 10 mm, thickness: 2.5 mm, for a total volume of 8 cm^3). After having placed the initiator (ca. 1 mol% 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 6 thaw-freeze cycles performed to remove oxygen, VDF was trapped under vacuum in the tube frozen in liquid nitrogen, after a release in an intermediate metallic container calibrated in pressure. The required amount of VDF (from 0.147 to 1.324 ± 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 VDF (Table 3). A beforehand calibration curve weight of trapped VDF (in gram) versus drop of pressure (in bar) was consulted (for 1.324 g of VDF, a difference of pressure of 0.90 bar was required). The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed into a shaking oven at 141°C for 7 min.

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

4. Conclusion

The radical telomerisation of VDF with DEHP allowed us to synthesise original oligo-VDF bearing a phosphonate end-group. The first four adducts described above exhibit a major structure as $H(VDF)_nP(O)(OEt)_2$ where n represents the order of the considered adduct. Except the monoadduct, the first VDF–DEHP telomers contain a rather high amount of defects of the VDF block close to 10% (i.e. reversed additions). Further, these compounds are liquid at room temperature and have an excellent solubility in common organic solvents such as acetone, chloroform, acetonitrile, or DMF. These properties enable them to be used as original hydrofluorinated solvents. In addition, we did not note any degradation of these compounds for a long time (higher than one year) even when they were stored under air. Moreover, it was observed that the C–P bond appeared stable even at 150°C, without any further reinitiation as evidenced by a total inefficiency of the telomers in the telomerisation of VDF involving a peroxidic initiator at 140°C. The kinetics of this telomerisation allowed us to determine the transfer constants of the first six telomers with an infinite value of 0.38 at 140°C for DEHP, showing that medium to high

telomers can be produced. The optimisation of that reaction (choice of cosolvents, nature and amounts of initiators, use of various dialkyl phosphonates and initial molar of transfer agent to VDF) is under investigation and will be published in a further paper.

Acknowledgements

The authors thank the Elf Atochem (now Atofina) Company for sponsoring this work and for the gift of VDF.

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