

## Synthesis of fluorinated telomers. Part 4. Telomerization of vinylidene fluoride with commercially available $\alpha,\omega$ -diiodoperfluoroalkanes

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Received 16 September 1994; accepted 24 December 1994

### Abstract

The synthesis of a new fluorinated  $\alpha,\omega$ -diiodo telomer  $I[(TFE)_x(VDF)_y]_n(A)$ , where TFE and VDF represent tetrafluoroethylene and vinylidene fluoride respectively, has been carried out by telomerization of VDF with  $\alpha,\omega$ -diiodoperfluoroalkanes. The thermal telomerization of VDF with 1,2-diiodoperfluoroethane  $IC_2F_4I$  led to good yields of the monoadduct  $IC_2F_4CH_2CF_2I$  and of the diadduct which was composed of an almost equimolar ratio of  $ICF_2CH_2C_2F_4CH_2CF_2I$  and  $IC_2F_4(CH_2CF_2)_2I$ , together with a small amount of  $IC_2F_4CH_2CF_2CF_2CH_2I$  and a triadduct containing  $I(VDF)C_2F_4(VDF)_2I$  and  $IC_2F_4(VDF)_3I$ . This procedure has been applied successfully to  $\alpha,\omega$ -diiodo-*n*-perfluorobutane and  $\alpha,\omega$ -diiodo-*n*-perfluorohexane. The reactivity of VDF relative to the fluorinated  $\alpha,\omega$ -diiodo telogens has been studied from which it is shown that the environment of the terminal group of the telogen is a major factor affecting the reactivity.

**Keywords:** Telomerization; Vinylidene fluoride; Thermal initiation; Diiodoperfluoroalkane; NMR spectroscopy; Mass spectrometry

### 1. Introduction

Despite their difficulty of synthesis and their corresponding price,  $\alpha,\omega$ -diiodoperfluoroalkanes are useful precursors for fluorinated telechelic oligomers such as diols [1,2], diepoxides [3], diamines or diisocyanates [1,4], dicarboxylic acids or dinitriles [5]. Such reactions have been reviewed previously [6,7]. The major interesting applications of these compounds include fluorinated elastomers [1,8,9] or rubbers [10], block copolymers [9], silicon-containing polymers [5,11] or monomer precursors of membranes as produced by Asahi Glass [12].

Several ways of synthesizing  $\alpha,\omega$ -diiodoperfluoroalkanes are described in the literature and we have commented briefly on the same in a recent paper [13].

Chemical companies have employed the synthesis of novel  $\alpha,\omega$ -diiodoperfluoroalkanes as a means for obtaining elastomers for specific applications. Such products have been obtained

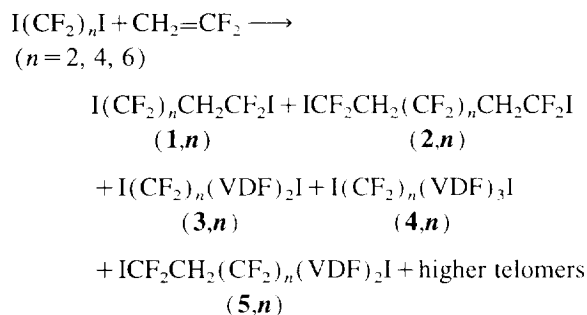
mainly by direct batch cotelomerization of vinylidene fluoride (VDF) and hexafluoropropene (HFP) with  $IC_4F_8I$  [10], of VDF and chlorotrifluoroethylene (CTFE) [10], of HFP and tetrafluoroethylene (TFE) [2], of VDF/HFP/TFE with  $IC_4F_8I$  [10] or  $IC_6F_{12}I$  [5], or of TFE and perfluoro(propylvinyl ether) with  $IC_4F_8I$  [5]. However, the various authors have not specified the regiochemistry of the attack of the  $IC_nF_{2n}CF_2CF_2$  radicals on the fluorinated olefins and few spectroscopic data were provided for the characterization of these cotelomers. The same is true for Rice and coworkers who performed an interesting synthesis of the VDF/HFP diblock copolymer  $ROCOR_F-[(VDF)_{0.65}(HFP)_{0.35}]_nR_FCO_2R$ , produced by the radical polymerization of VDF and HFP from fluorinated telechelic diacids [4] or diesters [14] initiators.

Thus, the object of the present work is a study of the telomerization of VDF using commercially available  $\alpha,\omega$ -diiodoperfluoroalkanes, and the characterization by  $^1H$  and  $^{19}F$  NMR spectroscopy of the different telomers produced.

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## 2. Results and discussion

The telomerization of VDF with the  $\alpha,\omega$ -diiodoperfluoroalkanes is in accordance with the following equation:



The telomerization of VDF with perfluoroalkyl iodides has been investigated by numerous authors [15–18]. In recent work [19], redox catalysis in the presence of ferric salts was described as being very selective to give modest yields, whereas thermal initiation above 180 °C gave the best yields and results, with quantitative conversion of perfluoroalkyl iodides.

However, it is well known that 1,2-diiodoperfluoroethane undergoes a  $\beta$ -elimination of iodine on heating to regenerate TFE. Such behaviour of an  $\alpha,\omega$ -diiodoperfluoroalkane with temperature seemed worthwhile investigating with a view to determining the quantities and nature of the compounds produced.

### 2.1. The thermal behaviour of 1,2-diiodoperfluoroethane

1,2-Diiodoperfluoroethane was heated at different temperatures for 16 h with the liquid phase of the total product mixture being monitored by gas chromatography. For example, the GC chromatogram of the crude product obtained after 16 h at 250 °C showed the formation of higher boiling point telomers which were confirmed by co-injection with  $\text{IC}_n\text{F}_{2n}\text{I}$  standards. These products arise from the addition of  $\text{IC}_n\text{F}_{2n}\text{I}$  to the TFE formed by  $\beta$ -elimination or by recombination of  $\text{IC}_n\text{F}_{2n}\cdot$  radicals, according to the following scheme:

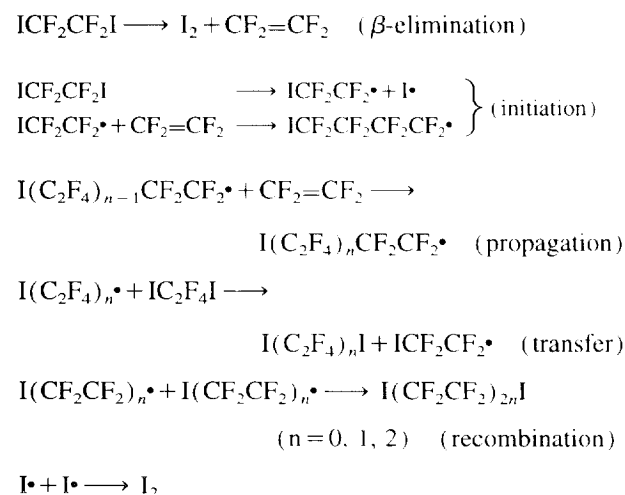


Table 1  
Preparation of TFE oligomers at various temperatures <sup>a</sup>

Products formed reactant remaining (%) <sup>b</sup>	Temperature (°C)			
	180	205	225	250
$\text{IC}_2\text{F}_4\text{I}$ remaining	98	52	40	15
$\text{IC}_4\text{F}_8\text{I}$ formed	2	20	25	19
$\text{IC}_6\text{F}_{12}\text{I}$ formed	0	5	8	11
Higher boiling telomers	0	0	2	5

<sup>a</sup> Preparative conditions: 15 g of 1,2-diiodoperfluoroethane heated at different temperatures for 18 h.

<sup>b</sup> Relative amounts determined from gas chromatography of the liquid phase of the total product mixture.

The areas of the peaks assigned to the remaining  $\text{IC}_2\text{F}_4\text{I}$  and to the higher telomeric diiodides formed at each temperature in the 180–250 °C range have been determined (Table 1), and plots of their different percentages versus temperature are shown in Fig. 1. Obviously, the higher the temperature, the higher the decomposition or transformation of  $\text{IC}_2\text{F}_4\text{I}$  into higher telomers. Thus, at 180 °C, only 3% of the  $\text{IC}_2\text{F}_4\text{I}$  reacted, whereas at 250 °C, 85% was converted. Hence, the formation of  $\text{IC}_4\text{F}_8\text{I}$  and  $\text{IC}_6\text{F}_{12}\text{I}$  increases with temperature, reaching a maximum at 225 °C for  $\text{IC}_4\text{F}_8\text{I}$ . After this point, reaction with TFE becomes important. The formation of perfluorocyclobutane was also observed.

### 2.2. The telomerization of VDF with $\text{IC}_2\text{F}_4\text{I}$

Because of the good thermal stability of  $\text{IC}_2\text{F}_4\text{I}$  at 180 °C and the excellent reactivity of VDF at such temperatures, thermal telomerization of this olefin with 1,2-diiodoperfluoroethane was performed in the 180–200 °C range for 16 h using a 200 or a 500 ml autoclave and employing different initial [diiodide]/[VDF] molar ratio ( $R_0$ ).

In each experiment, the pressure in the autoclave after introduction of the monomer was 20 bar. During reaction, however, the pressure increased up to a maximum of 40 bar and then decreased to 4 bar. After venting and opening the autoclave, a significant quantity of solid iodine was observed in the bottom of the vessel. The liquid phase of the total product mixture was analyzed by gas chromatography.

The results obtained are listed in Table 2, the percentages of diiodide remaining or of telomers produced being determined from the peak areas of the GC chromatograms, taking the coefficient of response into account.

These reactions are satisfactory since the conversion rate of the telogen was in the 75%–86% range. Surprisingly, under similar experimental conditions, the volume of the autoclave seemed to influence the yield since this was greater for a larger volume. However, using a significant excess of VDF, a quantitative yield was obtained in 24 h when the 200 ml vessel was employed. The GC chromatogram showed that the reaction was clean, that almost all of the 1,2-diiodoperfluoroethane had reacted and that a telomeric distribution was

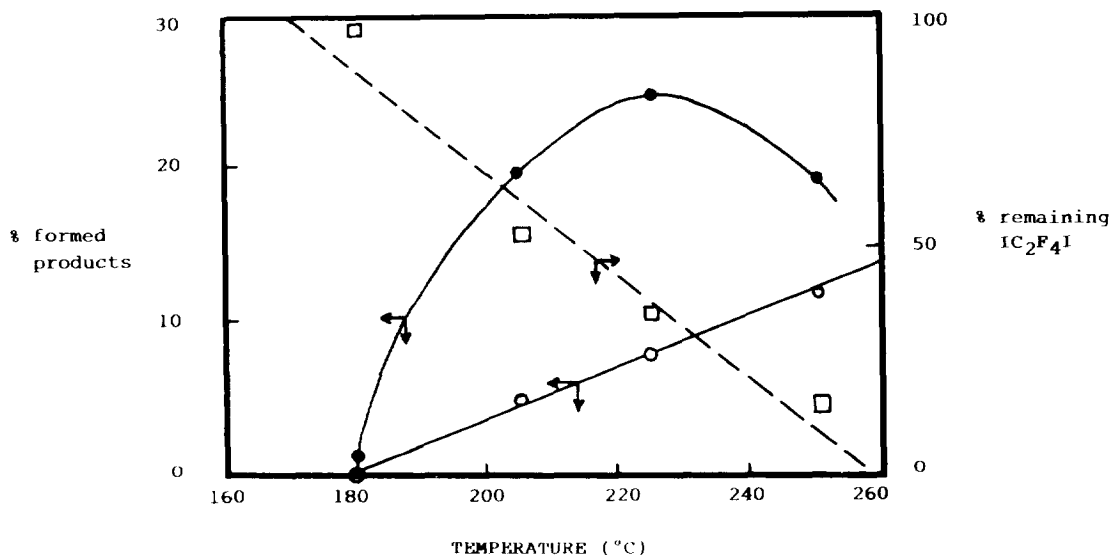


Fig. 1. Percentages of IC<sub>2</sub>F<sub>4</sub>I unconverted (dotted line and open squares), IC<sub>4</sub>F<sub>8</sub>I formed (●) and IC<sub>6</sub>F<sub>12</sub>I formed (○) versus temperature.

produced with a high amount of monoadduct but lower proportions of diadduct and triadduct.

Distillation led to three pure fractions with a 96%–98% purity by GC characterized by <sup>19</sup>F and <sup>1</sup>H NMR, and by mass spectrometry. Formation of telomers **1.2**–**5.2** could be anticipated in such a reaction.

### 2.2.1. Characterization of the first fraction

The <sup>19</sup>F NMR spectrum of the low boiling fraction (86 °C/20 mmHg), i.e. the monoadduct **1.2** contained no peak at δ –53.3 ppm characteristic of the CF<sub>2</sub>I end-group of IC<sub>2</sub>F<sub>4</sub>I, but exhibited the presence of signals centred at δ –38 (quintuplet), –62 (wide triplet) and –106 ppm (multiplet) assigned to CH<sub>2</sub>CF<sub>2</sub>I, ICF<sub>2</sub>CF<sub>2</sub> and ICF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub> groups, respectively.

The coupling constants are in good agreement with those observed in the <sup>19</sup>F NMR spectrum of ICF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I [20] which exhibited a triplet at δ –60.4 ppm (<sup>3</sup>J<sub>FF</sub> = 4.7 Hz) broadened by the methylene group (<sup>4</sup>J<sub>FH</sub> = 1 Hz) assigned to the CF<sub>2</sub>I end-group. The other CF<sub>2</sub> group is represented by a triplet (<sup>3</sup>J<sub>IF</sub> = 4.9 Hz) broadened by the adjacent CH<sub>2</sub> group (<sup>3</sup>J<sub>FH</sub> = 15 Hz).

The <sup>1</sup>H NMR spectrum of **1.2** exhibited a quintet centred at δ 3.4 ppm characteristic of the methylene group adjacent to two CF<sub>2</sub> groups (typical A<sub>4</sub>X system with a coupling constant J<sub>HIF</sub> of 16 Hz).

These NMR chemical shifts confirm that the ICF<sub>2</sub> radical reacts selectively on the CH<sub>2</sub> side of VDF as described in the literature [15–19], being consistent with the anticipated regiochemistry of attack of a highly electrophilic radical on VDF.

Table 2

Experimental conditions and amounts (in wt %) of telomers obtained in the thermal telomerization of vinylidene fluoride with 1,2-diiodoperfluoroethane <sup>a</sup>

Volume of autoclave (ml)	200	200	200	200	500	500
IC <sub>2</sub> F <sub>4</sub> I (mol)	0.35	0.28	0.35	0.42	0.37	0.45
[IC <sub>2</sub> F <sub>4</sub> I] / [VDF]	0.4	1.0	1.0	1.2	0.9	1.0
Temperature (°C)	200	205	205	205	200	190
Time (h)	24	16	18	18	15	18
Volatile compounds (%)	1.6	8.9	8.3	14.6	5.8	1.7
IC <sub>2</sub> F <sub>4</sub> I (%)	0.5	14.2	7.7	16.3	16.2	1.1
	99.3 <sup>b</sup>	84.4 <sup>b</sup>	91.50 <sup>b</sup>	83.70 <sup>b</sup>	81.3 <sup>b</sup>	98.7 <sup>b</sup>
IC <sub>4</sub> F <sub>8</sub> I (%)	0.1	1.8	5.1	4.1	2.3	0.9
IC <sub>2</sub> F <sub>4</sub> (VDF)I (%)	26.2	59.2	51.4	52.4	65.0	41.3
	31.2 <sup>c</sup>	55.1 <sup>c</sup>	48.3 <sup>c</sup>	44.3 <sup>c</sup>	63.4 <sup>c</sup>	40.8 <sup>c</sup>
IC <sub>6</sub> F <sub>12</sub> I (%)	0	0.3	1.2	0.7	0.5	0
IC <sub>4</sub> F <sub>8</sub> (VDF)I (%)	1.3	2.6	2.5	6.1	5.1	1.5
I(VDF)C <sub>2</sub> F <sub>4</sub> (VDF)I (%)	47.2	11.2	19.2	5.3	4.6	43.0
IC <sub>2</sub> F <sub>4</sub> (VDF) <sub>2</sub> I (%)	49.1 <sup>c</sup>	9.4 <sup>c</sup>	16.2 <sup>c</sup>	4.1 <sup>c</sup>	5.3 <sup>c</sup>	37.5 <sup>c</sup>
I(VDF) <sub>2</sub> C <sub>2</sub> F <sub>4</sub> (VDF)I (%)	22.3	1.1	4.4	0	0	10.1
IC <sub>2</sub> F <sub>4</sub> (VDF) <sub>3</sub> I (%)	21.0 <sup>c</sup>	1.1 <sup>c</sup>	3.1 <sup>c</sup>			8.4 <sup>c</sup>
Overall yield (%)	99	66	67	48	69	86

<sup>a</sup> Amounts determined by GC methods.

<sup>b</sup> Conversion of IC<sub>2</sub>F<sub>4</sub>I (%).

<sup>c</sup> Yield relative to IC<sub>2</sub>F<sub>4</sub>I (%).



mechanism is favoured, probably due to transfer of the telogen occurring faster than the propagation step.

### 2.2.3. Study of the third fraction

The triadduct was also isolated by distillation (124–127 °C/19 mmHg), the  $^1\text{H}$  and  $^{19}\text{F}$  NMR characteristics of all such telomers being listed in Table 3. The  $^{19}\text{F}$  NMR spectrum of the  $\text{IC}_2\text{F}_4\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  isomer (**4,2**) exhibits similar chemical shifts to those of  $\text{IC}_2\text{F}_4(\text{VDF})_2\text{I}$  but with different integrated areas. Such a triadduct also contained the reverse isomer  $\text{IC}_2\text{F}_4\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$  (**4,2'**) at ca. 10% extent as shown by the presence of signals at  $\delta -113$  and  $-108$  ppm, assigned to the  $\text{CF}_2$  groups in the  $\beta$  and  $\gamma$  positions relative to the iodine atom. Similarly,  $\text{I}(\text{VDF})\text{C}_2\text{F}_4(\text{VDF})_2\text{I}$  is composed of 90%  $\text{ICF}_2\text{CH}_2\text{C}_2\text{F}_4\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  (**5,2**) and 10%  $\text{ICF}_2\text{CH}_2\text{C}_2\text{F}_4\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$  (**5,2'**). Finally the triadduct consisted of 45% of **4,2**, 45% of **5,2**, 5% of **4,2'** and 5% of **5,2'**.

To synthesize new fluorinated  $\alpha,\omega$ -diiodoalkanes with a higher TFE base unit number, the telomerization of vinylidene fluoride with longer  $\alpha,\omega$ -diiodoperfluoroalkanes was performed in a similar manner to that above (thermal initiation at 190 °C).

### 2.3. The telomerization of vinylidene fluoride with 1,4-diiodoperfluorobutane

As listed in Table 4, several attempts have been made to effect this telomerization using different initial  $[\text{VDF}]_0/[\text{IC}_4\text{F}_8\text{I}]_0$  molar ratios for various reaction times and with two different capacity Hastelloy autoclaves (200 ml and 500 ml). In each case, the initial pressure after introduction of the reactants was 25 bar and after several hours at 190 °C reached a maximum of 35–38 bar and then decreased to 3 bar. The deposit of solid iodine observed in the bottom of the autoclave was less significant than that noted for the telomerization described above.

GC chromatograms of the liquid phase of the total product mixture showed a small peak at 3.4 min assigned to the telogen and other peaks with higher retention times corresponding to the telomers **1,4** derived from the monoadduct, telomers **2,4** and **3,4** derived from the diadduct and telomers **4,4** and **5,4** derived from the triadduct. The GC chromatogram

also showed that the reaction was clean as for the previous case of telomerization from  $\text{IC}_2\text{F}_4\text{I}$ . The percentages of the products generated were calculated from the areas of the peaks arising in the GC chromatogram.

This reaction led to good yields with high telogen conversion (greater than 90%). After distillation, three main pure fractions were obtained and characterized by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy. Table 5 lists the different chemical shifts observed.

#### 2.3.1. Analysis of the first fraction

As for the characterization of the monoadduct  $\text{IC}_2\text{F}_4\text{CH}_2\text{CF}_2\text{I}$  (**1,2**), the  $^1\text{H}$  NMR spectrum exhibited a quintet centred at  $\delta$  3.4 ppm and assigned to the methylene group that forms an  $\text{A}_4\text{X}$  system.

Five signals were noted in the  $^{19}\text{F}$  NMR spectrum. Those centred at  $\delta -38$  and  $-59$  ppm were similar to those of **1,2** assigned to the  $\text{ICF}_2\text{CH}_2$  and  $\text{ICF}_2\text{CF}_2$  groups, whereas that centred at  $\delta -123$  ppm corresponded to the difluoromethylene of a  $\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  group with a characteristic highfield shift compared to that of **1,2**. Finally, the last two multiplets centred at ca.  $\delta -113$  ppm correspond to internal  $\text{CF}_2$  groups.

As for the homologous monoadduct **1,2**, the first fraction contained  $\text{IC}_4\text{F}_8\text{CH}_2\text{CF}_2\text{I}$  selectively.

#### 2.3.2. Study of the second fraction

The  $^{19}\text{F}$  NMR spectrum exhibited seven peaks. Three of these were very intense with similar intensities. Those at  $\delta -38.3$  and  $-112.9$  ppm were assigned to the  $\text{ICF}_2\text{CH}_2$  and internal  $\text{CF}_2$  groups, respectively, whereas the third centred at  $\delta -123.6$  ppm corresponded to the fluorine atoms adjacent to the methylene groups of the  $\alpha,\omega$ -diadduct  $\text{ICF}_2\text{CH}_2\text{CF}_2\text{C}_2\text{F}_4\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  (**2,4**).

The signal that exhibited the smallest intensity centred at  $\delta -107.5$  ppm corresponded to a  $\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$  group resulting from the 'reverse' addition of VDF as observed in the previous series.

Integration of the signals indicated that three isomers,  $\text{ICF}_2\text{CH}_2(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{I}$ ,  $\text{I}(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  and  $\text{I}(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$ , had been produced in 90%, 8% and 2% yield, respectively. Interestingly, the symmetrical telomer  $\text{I}(\text{VDF})\text{C}_4\text{F}_8(\text{VDF})\text{I}$  was obtained in a higher proportion than the non-symmetrical **3,4**, in contrast to the preparation of their homologues from  $\text{IC}_2\text{F}_4\text{I}$  which produced equimolar amounts of both isomers. This can be explained by the electrophilicity of the difluoromethylene end-group of the  $\text{ICF}_2\text{CH}_2\text{C}_3\text{F}_6\text{CF}_2\cdot$  radical being greater than that of the  $\text{CF}_2$  group of the  $\cdot\text{CF}_2\text{CH}_2\text{C}_4\text{F}_8\text{I}$  radical, because of the presence of the electron-withdrawing  $\text{C}_3\text{F}_6$  group in the fluorinated chain.

#### 2.3.3. Characterization of the third fraction

The triadduct was also purified by distillation and analyzed by  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectroscopy. It was mainly composed of the  $\text{ICF}_2\text{CH}_2\text{CF}_2\text{CH}_2(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{I}$  isomer (96%) whose chemical shifts were similar to those of  $\text{I}(\text{VDF})-$

Table 4

Experimental conditions employed and amounts (in wt.%) of telomers obtained from the telomerization of VDF with 1,4-diiodoperfluorobutane

$R_0 = [\text{IC}_4\text{F}_8\text{I}]_0/[\text{VDF}_2]_0$	0.4	0.8	1.1
Conversion of $\text{IC}_4\text{F}_8\text{I}$ (%)	99	99	95
$\text{IC}_4\text{F}_8(\text{VDF}_2)\text{I}$ (%)	8	12	48
$\text{IC}_4\text{F}_8(\text{VDF}_2)_2\text{I} + \text{I}(\text{VDF}_2)\text{C}_4\text{F}_8(\text{VDF}_2)\text{I}$ (%)	37	53	32
$\text{IC}_4\text{F}_8(\text{VDF}_2)_3\text{I} + \text{I}(\text{VDF}_2)_3\text{C}_4\text{F}_8(\text{VDF}_2)_2\text{I}$ (%)	44	28	17
Higher homologues (%)	9	6	2
$\overline{\text{DP}}_n$	2.55	2.28	1.70

Table 5

<sup>19</sup>F and <sup>1</sup>H NMR parameters of telomers obtained from the telomerization of VDF with 1,4-diiodoperfluorobutane

Telomer	Chemical shifts, $\delta$ (ppm)									
	a	b	c	d	e	f	g	$\alpha$	$\beta$	$\omega$
I $\overset{a}{\text{CF}_2} \overset{b}{\text{CF}_2} \text{CF}_2 \text{CF}_2 \text{I}$	-59.0	-112.0								
I $\overset{a}{\text{CF}_2} \overset{b}{\text{CF}_2} \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} (\overset{e}{\text{CH}_2} \overset{f}{\text{CF}_2}) \text{I}$	-59.2	-113.0	-112.9	-123	-38.3			3.4		
I $(\overset{a}{\text{CF}_2} \overset{b}{\text{CH}_2}) \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} \overset{e}{\text{CF}_2} \overset{f}{\text{CF}_2} (\overset{g}{\text{CH}_2} \overset{h}{\text{CF}_2}) \text{I}$	-38.3	-123.6	-112.9					3.4		
I $\overset{a}{\text{CF}_2} \overset{b}{\text{CF}_2} \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} (\overset{e}{\text{CH}_2} \overset{f}{\text{CF}_2}) (\overset{g}{\text{CH}_2} \overset{h}{\text{CF}_2}) \text{I}$	-59.2	-112.9	-112.9	-123	-88.6	-39.0		3.4	2.8	
I $\overset{a}{\text{CF}_2} \overset{b}{\text{CF}_2} \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} (\overset{e}{\text{CH}_2} \overset{f}{\text{CF}_2}) (\overset{g}{\text{CF}_2} \overset{h}{\text{CH}_2}) \text{I}$	-59.2	-112.9	-112.9	-123	-113.0	-108.0			2.8	3.6
I $(\overset{a}{\text{CF}_2} \overset{b}{\text{CH}_2}) \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} \overset{e}{\text{CF}_2} \overset{f}{\text{CF}_2} (\overset{g}{\text{CH}_2} \overset{h}{\text{CF}_2}) (\overset{i}{\text{CH}_2} \overset{j}{\text{CF}_2}) \text{I}$	-38.5	-123.0	-113.0	-113	-123.0	-88.0	-39.5	3.4	2.8	
I $\overset{a}{\text{CF}_2} \overset{b}{\text{CF}_2} \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} (\overset{e}{\text{CH}_2} \overset{f}{\text{CF}_2}) (\overset{g}{\text{CH}_2} \overset{h}{\text{CF}_2}) (\overset{i}{\text{CH}_2} \overset{j}{\text{CF}_2}) \text{I}$	-59.2	-112.9	-112.9	-123	-88	-88.0	-39.5	3.4	2.8	
I $(\overset{a}{\text{CF}_2} \overset{b}{\text{CH}_2}) \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} \overset{e}{\text{CF}_2} \overset{f}{\text{CF}_2} (\overset{g}{\text{CH}_2} \overset{h}{\text{CF}_2}) (\overset{i}{\text{CF}_2} \overset{j}{\text{CH}_2}) \text{I}$	-38.5	-123.0	-113.0	-113	-123.0	-113	-108.0	3.4	2.8	3.6
I $\overset{a}{\text{CF}_2} \overset{b}{\text{CF}_2} \overset{c}{\text{CF}_2} \overset{d}{\text{CF}_2} (\overset{e}{\text{CH}_2} \overset{f}{\text{CF}_2}) (\overset{g}{\text{CH}_2} \overset{h}{\text{CF}_2}) (\overset{i}{\text{CF}_2} \overset{j}{\text{CH}_2}) \text{I}$	-59.2	-112.9	-112.9	-123	-88	-113	-108.0	3.6	2.8	

$\text{C}_4\text{F}_8(\text{VDF})\text{I}$ , except for the presence of the multiplet at  $\delta$  -88 ppm assigned to the difluoromethylene group of the  $\text{ICF}_2\text{CH}_2\text{CF}_2\text{CH}_2$  segment. The isomers  $\text{I}(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$ ,  $\text{I}(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$  and  $\text{ICH}_2\text{CF}_2\text{CF}_2\text{CH}_2(\text{C}_4\text{F}_8)\text{CH}_2\text{CF}_2\text{I}$  were produced in 2%, 1% and 1% yield, respectively.

Table 5 summarizes the chemical shifts for the characterized telomers.

#### 2.4. The telomerization of vinylidene fluoride with 1,6-diiodoperfluorohexane

Similar reactions to the above were performed using thermal initiation and starting from two different  $[\text{VDF}]_0/[\text{IC}_6\text{F}_{12}\text{I}]_0$  initial molar ratios (Table 6) to produce a crude product mixture containing mainly the monoadduct or having a higher amount of di- and tri-adducts.

The monoadduct contained  $\text{IC}_6\text{F}_{12}\text{CH}_2\text{CF}_2\text{I}$  exclusively whereas the diadduct was composed of 95% of  $\text{ICF}_2\text{CH}_2\text{C}_6\text{F}_{12}\text{CH}_2\text{CF}_2\text{I}$  (**2,6**) and 5% of  $\text{IC}_6\text{F}_{12}\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  (**3,6**) with a very small amount of isomer **3,6'**. This could suggest, as in the previous example, that the telomerization occurred by stepwise monoaddition and not by propagation. The triadduct consisted of four different isomers,

Table 6

Experimental conditions employed and amounts (in wt.%) of telomers obtained from the telomerization of VDF with 1,6-diiodoperfluorohexane

$R_0 = [\text{IC}_6\text{F}_{12}\text{I}]_0/[\text{VDF}_2]_0$	0.2	1.0
Conversion of $\text{IC}_6\text{F}_{12}\text{I}$ (%)	99	97
$n = 1$ (%)	4	44
$n = 2$ (%)	39	35
$n = 3$ (%)	45	18
$n > 3$ (%)	11	2
$\overline{\text{DP}}_n$	2.63	1.77

$\text{IC}_6\text{F}_{12}(\text{VDF})_3\text{I}$  (**4,6** and **4,6'**) and  $\text{ICF}_2\text{CH}_2\text{C}_6\text{F}_{12}(\text{VDF})_2\text{I}$  (**5,6** and **5,6'**) which were characterized by <sup>19</sup>F and <sup>1</sup>H NMR spectroscopy (Table 7 and Experimental details).

### 3. Experimental details

#### 3.1. Starting materials

Vinylidene fluoride (VDF) was kindly supplied by Elf Atochem.  $\alpha,\omega$ -Diiodoperfluoroalkanes were supplied by the Mihama Co., Japan, and were washed with sodium thiosulphate solution, dried over  $\text{MgSO}_4$  and distilled.

Reactions were conducted using a 200 or 500 ml Hastelloy C276 autoclave (Vinci Technologies). After introduction of the non-volatile reactants, the vessel was closed, frozen in an acetone/liquid nitrogen mixture and then evacuated for several minutes. The required amounts of VDF were then introduced.

After the reaction was completed, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE 30 column, 1 m  $\times$  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 °C and 255 °C, respectively. The temperature program commenced at 50 °C and attained 250 °C at a heating rate of 15 °C min<sup>-1</sup>. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

The products were characterized by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy, all undertaken at room temperature. The <sup>19</sup>F and <sup>1</sup>H NMR spectra were recorded on Bruker AC-200, -250 or WM-360 instruments, using deuterated chloroform as the solvent.

Table 7  
 $^{19}\text{F}$  and  $^1\text{H}$  parameters of telomers obtained from the telomerization of VDF with 1,6-diiodoperfluorohexane

Telomers	Chemical shifts, $\delta$ (ppm)										
	a	b	c	d	e	f	g	h	$\alpha$	$\beta$	$\omega$
$\text{I CF}_2^a \text{CF}_2^b \text{CF}_2^c \text{CF}_2 \text{CF}_2 \text{CF}_2 \text{I}$	-59.5	113.5	-121.3								
$\text{I CF}_2^a \text{CF}_2^b \text{C}_2\text{F}_4^c \text{CF}_2^d \text{CF}_2^e (\text{CH}_2^f \text{CF}_2^g) \text{I}$	-59.5	-113.5	-122.0	-113.5	-123.5	-38.5				3.4	
$\text{I} (\text{CF}_2^a \text{CH}_2^b) \text{CF}_2^c \text{CF}_2^d \text{C}_2\text{F}_4^e \text{CF}_2^f \text{CF}_2^g (\text{CH}_2^h \text{CF}_2^i) \text{I}$	-38.5	-123.0	-113.5	-122.0						3.4	
$\text{I CF}_2^a \text{CF}_2^b \text{C}_2\text{F}_4^c \text{CF}_2^d \text{CF}_2^e (\text{CH}_2^f \text{CF}_2^g) (\text{CH}_2^h \text{CF}_2^i) \text{I}$	-59.5	-113.5	-122.0	-113.5	-123.0	-88.6	-38.5			3.4	2.8
$\text{I CF}_2^a \text{CF}_2^b \text{C}_2\text{F}_4^c \text{CF}_2^d \text{CF}_2^e (\text{CH}_2^f \text{CF}_2^g) (\text{CF}_2^h \text{CCH}_2^i) \text{I}$	-59.5	113.5	-122.0	-113.0	-123.0	-113.0	-108.0				2.8 3.6
$\text{I} (\text{CF}_2^a \text{CH}_2^b) \text{CF}_2^c \text{CF}_2^d \text{C}_2\text{F}_4^e \text{CF}_2^f \text{CF}_2^g (\text{CH}_2^h \text{CF}_2^i) (\text{CH}_2^j \text{CF}_2^k) \text{I}$	-38.5	123.0	-113.5	-122.0	-113.5	-123.0	-88.6	-38.5	3.4	2.8	
$\text{I CF}_2^a \text{CF}_2^b \text{C}_2\text{F}_4^c \text{CF}_2^d \text{CF}_2^e (\text{CH}_2^f \text{CF}_2^g) (\text{CH}_2^h \text{CF}_2^i) (\text{CH}_2^j \text{CF}_2^k) \text{I}$	-59.5	-113.5	-122.0	-113.5	-123.0	-88.6	-88.6	-38.5	3.4	2.8	
$\text{I} (\text{CF}_2^a \text{CH}_2^b) \text{CF}_2^c \text{CF}_2^d \text{C}_2\text{F}_4^e \text{CF}_2^f \text{CF}_2^g (\text{CH}_2^h \text{CF}_2^i) (\text{CF}_2^j \text{CH}_2^k) \text{I}$	-38.5	-123.0	-113.5	-122.0	-113.5	-123.0	-113.0	-108.0	3.4	2.8	3.6
$\text{I CF}_2^a \text{CF}_2^b \text{C}_2\text{F}_4^c \text{CF}_2^d \text{CF}_2^e (\text{CH}_2^f \text{CF}_2^g) (\text{CH}_2^h \text{CF}_2^i) (\text{CF}_2^j \text{CH}_2^k) \text{I}$	-59.5	-113.5	-122.0	-113.5	-123.0	-88.6	-113.0	-108.0		2.8	3.6

TMS and  $\text{CFCl}_3$  were employed as respective internal references. The letters s, d, t, q, and m designate singlet, doublet, triplet, quintet and multiplet, respectively.

The various compounds were analyzed chemically at the Laboratory of Microanalysis (CNRS) of ENSCM (the figures indicated below for the elemental analyses designate the content of carbon, hydrogen or fluorine in  $\text{g} (100 \text{ g})^{-1}$  of pure product).

### 3.2. Synthesis of higher tetrafluoroethylene oligomers from 1,2-diiodotetrafluoroethane

1,2-Diiodotetrafluoroethane (15 g, 0.042 mol) was introduced into the autoclave (200 ml) and heated at  $205^\circ\text{C}$  for 18 h. After the reaction was completed, the volatile derivatives were removed and the crude product worked-up with alkaline sodium thiosulphate solution, dried over magnesium sulphate, filtered and distilled. Unreacted  $\text{IC}_2\text{F}_4\text{I}$  (7.7 g, 0.022 mol) was recovered (conversion, 52%) as a reddish liquid, b.p.  $112^\circ\text{C}$  (lit. value [23]:  $45^\circ\text{C}/35 \text{ mmHg}$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-53$  (s, 4F) ppm.

The oligomer  $\text{IC}_4\text{F}_8\text{I}$  (3.7 g, 0.008 mol, 18%) was purified by distillation, b.p.,  $85^\circ\text{C}/100 \text{ mmHg}$  (lit. value [23]:  $63^\circ\text{C}/35 \text{ mmHg}$ ). Analysis: Found: C, 10.8; F, 33.2%.  $\text{C}_4\text{F}_8\text{I}_2$  requires: C, 10.6; F, 33.5%; M, 454.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-59$  (t,  $\text{ICF}_2$ , 4F,  $J=10.3 \text{ Hz}$ );  $-112$  (m,  $\text{ICF}_2\text{CF}_2$ , 4F) ppm.

Another TFE oligomer,  $\text{IC}_6\text{F}_{12}\text{I}$  (1.2 g, 0.002 mol, 5%), was also purified by distillation, b.p.  $115^\circ\text{C}/100 \text{ mmHg}$  (lit. value [23]:  $107^\circ\text{C}/62 \text{ mmHg}$ ). Analysis: Found: C, 13.3; F, 41.1%.  $\text{C}_6\text{F}_{12}\text{I}_2$  requires: C, 13.0; F, 41.2%; M, 554.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-59.5$  (t,  $\text{ICF}_2$ , 4F,  $J=43 \text{ Hz}$ );  $-113.5$  (m,  $\text{ICF}_2\text{CF}_2$ , 4F);  $-121.4$  (m,  $\text{IC}_2\text{F}_4\text{CF}_2$ , 4F) ppm.

### 3.3. Telomerization of VDF with 1,2-diiodoperfluoroethane

Into a 500 ml Hastelloy autoclave was introduced 1,2-diiodoperfluoroethane (150 g, 0.423 mol) and vinylidene fluoride (27 g, 0.421 mol). The mixture was stirred at  $190^\circ\text{C}$  for 18 h and, after cooling, the vessel was degassed and opened. It was noted that a large amount of solid iodine had been produced, the liquid phase being worked-up as previously and distilled.

The first fraction consisted 1,4-diiodo-1,1,2,2,4,4-hexafluorobutane (**1,2**) (132 g, 0.32 mol, 75% yield) which distilled as a reddish liquid b.p.  $86^\circ\text{C}/20 \text{ mmHg}$ . Analysis: Found: C, 12.1; H, 0.2; F, 29.5%.  $\text{C}_4\text{H}_2\text{F}_6\text{I}_2$  requires: C, 11.5; H, 0.5; F, 27.3%, M, 418.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-38.0$  (q,  $\text{ICF}_2\text{CH}_2$ , 2F,  $^3J_{\text{FH}} = ^4J_{\text{FF}} = 13.6 \text{ Hz}$ );  $-62.0$  (tt,  $\text{ICF}_2\text{CF}_2$ , 2F,  $^3J_{\text{FF}} = 4.3 \text{ Hz}$ ,  $^4J_{\text{FH}} = 1 \text{ Hz}$ );  $-106.0$  (m,  $\text{ICF}_2\text{CF}_2$ , 2F,  $^3J_{\text{FF}} = 4.3 \text{ Hz}$ ,  $^3J_{\text{FH}} = 16 \text{ Hz}$ ,  $^4J_{\text{FF}} = 16 \text{ Hz}$ ) ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.4 (q, 2H,  $J=16 \text{ Hz}$ ) ppm. MS  $m/z^+$ : 50 ( $\text{CF}_2^+$ ); 100 ( $\text{CF}_2\text{CF}_2^+$ ); 127 ( $\text{I}^+$ ); 177 ( $\text{CF}_2\text{I}^+$ ); 227 ( $\text{CF}_2\text{CF}_2\text{I}^+$ ); 254 ( $\text{M}^+ - 2\text{I}$ ); 291 ( $\text{M}^+ - \text{I}$ ); 418 ( $\text{M}^+$ ).

Another reddish fraction (19.3 g, 40 mmol, 9.5%) was also distilled, b.p.  $107^\circ\text{C}/20 \text{ mmHg}$ . This consisted of three isomers,  $\text{ICF}_2\text{CH}_2\text{C}_2\text{F}_4\text{CH}_2\text{CF}_2\text{I}$  (**2,2**),  $\text{IC}_2\text{F}_4\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$  (**3,2**) and  $\text{IC}_2\text{F}_4\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$  (**3,2'**) which were produced in 50%, 45% and 5% yield, respectively. Analysis: Found: C, 15.1; H, 0.8; F, 32.6%.  $\text{C}_6\text{H}_4\text{F}_8\text{I}_2$  requires: C, 14.9; H, 0.8; F, 31.5%; M, 482. The  $^{19}\text{F}$  NMR chemical shifts are listed in Table 3.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (Table 3)  $\delta$ : 2.8 (q,  $^3J_{\text{HF}} = 15.5 \text{ Hz}$ ,  $\text{CF}_2\text{CH}_2\text{CF}_2$  of **3,2**, 2H); 3.4 (q,  $^3J_{\text{HF}} = 15.5 \text{ Hz}$ ,  $\text{ICF}_2\text{CH}_2$  of **2,2** and **3,2**, 6H); 3.6 (tt,  $\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$  of **3,2'**) ppm.

The next pure fraction arising from the distillation consisted of 6.5 g (12 mmol, 2.8%) of a red liquid, b.p.  $124\text{--}127^\circ\text{C}/19 \text{ mmHg}$ . Analysis: Found: C, 18.2; H, 1.0; F,

35.5%.  $C_8H_6F_{10}I_2$  requires: C, 17.6; H, 1.1; F, 34.8%; M, 546. This fraction consisted of four different isomers, viz.  $ICF_2CH_2(C_2F_4)(CH_2CF_2)_2I$  (**5,2**) (45%),  $I(C_2F_4)CH_2CF_2CH_2CF_2CH_2CF_2I$  (**4,2**) (45%),  $ICF_2CH_2(C_2F_4)CH_2CF_2CF_2CH_2I$  (**5,2'**) (5%) and  $I(C_2F_4)CH_2CF_2CH_2CF_2CF_2CH_2I$  (**4,2'**) (5%), respectively. The  $^1H$  and  $^{19}F$  NMR chemical shifts for these isomers are listed in Table 3.

Another similar experiment was conducted using 1,2-diiiodoperfluoroethane (150 g, 0.423 mol), and vinylidene fluoride (140 g, 0.58 mol). The monoadduct **1,2** was produced in 10% yield whereas the mixture of **2,2**, **3,2** and **3,2'** was obtained in 60% yield. The triadduct was formed in 8% yield and higher VDF oligomers were produced in ca. 7% yield.

### 3.4. Telomerization of VDF with 1,4-diiiodoperfluorobutane

As in the previous experiment, 1,4-diiiodoperfluorobutane (150 g, 0.33 mol) and VDF (30 g, 0.47 mol) were stirred at 190 °C for 18 h. After reaction, the autoclave was cooled, degassed and opened. The solid iodine was filtered off and the total product mixture was distilled.

The first fraction consisted of 1,6-diiiodo-1,1,2,2,3,3,4,4,6,6-decafluorohexane (**1,4**) (65 g, 0.13 mol, 38%) which existed as a pink liquid, b.p. 36–38 °C/0.08 mmHg. Analysis: Found: C, 14.2; H, 0.7; F, 36.1%.  $C_6F_{10}H_2I_2$  requires: C, 13.8; H, 0.3; F, 36.6%; M, 518.  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$ : -38.3 (q,  $J_{FH} = J_{FF} = 13.6$  Hz,  $CH_2CF_2I$ , 2F); -59.2 (tt,  $^3J_{FF} = 4.3$  Hz,  $ICF_2CF_2$ , 2F); -113 (m,  $ICF_2CF_2CF_2$ , 4F); -123 (m,  $CF_2CH_2CF_2I$ , 2F) ppm.  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.4 (q,  $A_X$  system,  $J = 15.5$  Hz, 2H) ppm.

The second fraction was obtained as a pink solid (76 g, 0.13 mol, 40%), m.p. 37.5 °C, b.p. 56–59 °C/0.005 mmHg. Analysis: Found: C, 17.5; H, 1.2; F, 38.3%.  $C_8F_{12}H_4I_2$  requires: C, 16.5; H, 0.7; F, 39.2%; M, 582. This fraction consisted of three isomers, viz. 1,8-diiiodo-1,1,2,2,3,3,4,4,6,6,8,8-dodecafluorooctane,  $I(C_4F_8)CH_2CF_2CH_2CF_2I$  (**3,4**) (8%), 1,8-diiiodo-1,1,3,3,4,4,5,5,6,6,8,8-dodecafluorooctane,  $ICF_2CH_2(C_4F_8)CH_2CF_2I$  (**2,4**) (90%) and 1,8-diiiodo-1,1,2,2,3,3,4,4,6,6,7,7-dodecafluorooctane,  $I(C_4F_8)CH_2CF_2CF_2CH_2I$  (**3,4'**) (2%). The  $^{19}F$  and  $^1H$  NMR chemical shifts for these isomers are listed in Table 5.

The third fraction, b.p. 75–79 °C/0.005 mmHg, was obtained in 8% yield and consisted of four isomers, viz. 1,10-diiiodo-1,1,2,2,3,3,4,4,6,6,8,8,10,10-tetradecafluorodecane,  $I(C_4F_8)CH_2CF_2CH_2CF_2CH_2CF_2I$  (**4,4**) (2%), 1,10-diiiodo-1,1,3,3,4,4,5,5,6,6,8,8,10,10-tetradecafluorodecane,  $ICF_2CH_2(C_4F_8)CH_2CF_2CH_2CF_2I$  (**5,4**) (96%), 1,10-diiiodo-1,1,2,2,3,3,4,4,6,6,8,8,9,9-tetradecafluorodecane,  $I(C_4F_8)CH_2CF_2CH_2CF_2CF_2CH_2I$  (**4,4'**) (1%) and 1,10-diiiodo-2,2,3,3,4,4,5,5,6,6,8,8,9,9-tetradecafluorodecane,  $ICF_2CH_2(C_4F_8)CH_2CF_2CF_2CH_2I$  (**5,4'**) (1%). The  $^{19}F$  and  $^1H$  NMR chemical shifts of these isomers are also listed in Table 5.

### 3.5. Telomerization of VDF with 1,6-diiiodoperfluorohexane

Similar to the previous experiment, 1,6-diiiodoperfluorohexane (50.0 g, 0.09 mol) and VDF (8.0 g, 0.12 mol) were stirred at 200 °C for 18 h. After the same work-up, the following fractions were distilled.

The first fraction (11 g, 0.018 mol, 20% yield) consisted of 1,8-diiiodo-1,1,2,2,3,3,4,4,5,5,6,6,8,8-tetradecafluorooctane,  $I(C_6F_{12})CH_2CF_2I$  (**1,6**), b.p. 60–64 °C/0.08 mmHg. The  $^{19}F$  and  $^1H$  NMR chemical shifts of this compound are listed in Table 7.

The second fraction (22 g, 0.032 mol, 40% yield), b.p. 80–86 °C/0.005 mmHg, was composed of three isomers, viz. 1,10-diiiodo-1,1,2,2,3,3,4,4,5,5,6,6,8,8,10,10-hexadecafluorodecane,  $I(C_6F_{12})CH_2CF_2CH_2CF_2I$  (**3,6**) (4%), 1,10-diiiodo-1,1,3,3,4,4,5,5,6,6,7,7,8,8,10,10-hexadecafluorodecane,  $ICF_2CH_2(C_6F_{12})CH_2CF_2I$  (**2,6**) (95%) and 1,10-diiiodo-1,1,2,2,3,3,4,4,5,5,6,6,8,8,9,9-hexadecafluorodecane (**3,6'**) (1%). The  $^{19}F$  and  $^1H$  NMR chemical shifts of these isomers are listed in Table 7.

The third fraction (6 g, 8 mmol, 10% yield), b.p. 100–110 °C/0.005 mmHg, consisted of four isomers, viz. 1,12-diiiodo-1,1,3,3,4,4,5,5,6,6,7,7,8,8,10,10,12,12-octadecafluorododecane,  $ICF_2CH_2(C_6F_{12})CH_2CF_2CH_2CF_2I$  (**5,6**) (90%), 1,12-diiiodo-1,1,2,2,3,3,4,4,5,5,6,6,8,8,10,10,12,12-octadecafluorododecane,  $I(C_6F_{12})(CH_2CF_2)(CH_2CF_2)(CH_2CF_2)I$  (**4,6**) (6%), 1,12-diiiodo-1,1,3,3,4,4,5,5,6,6,7,7,8,8,10,10,11,11-octadecafluorododecane,  $ICF_2CH_2(C_6F_{12})CH_2CF_2CF_2CH_2I$  (**5,6'**) (2%) and 1,12-diiiodo-1,1,2,2,3,3,4,4,5,5,6,6,8,8,10,10,11,11-octadecafluorododecane,  $I(C_6F_{12})(CH_2CF_2)(CH_2CF_2)(CF_2CH_2)I$  (**4,6'**) (2%). The  $^{19}F$  and  $^1H$  NMR chemical shifts of these isomers are also listed in Table 7.

## 4. Conclusions

Telomerization of vinylidene fluoride with  $\alpha,\omega$ -diiiodoperfluoroalkanes has been successfully achieved by thermal initiation. For each reaction, the first three adducts have been produced and carefully characterized by  $^1H$  and  $^{19}F$  NMR spectroscopy. These telomers were obtained in very good yield, with quantitative telogen conversions.

Interestingly, the monoadducts were formed by selective addition of  $I(CF_2)_nI$  ( $n = 2, 4, 6$ ) to the  $CH_2$  side of the olefin whereas the other adducts were composed of isomers arising from the normal or reverse addition of VDF, with the former being favoured.

In addition, the generation of  $I(VDF)(CF_2)_n(VDF)I$  was dependent on both the TFE base unit number and the reactivity of the  $\alpha,\omega$ -diiiodoperfluoroalkane telogen, the greater these two factors the higher the proportion of telomer generated.

The mechanism of this reaction mainly involves the stepwise addition of VDF, with the telomer produced acting as the telogen in further steps with VDF. Such a scheme is favoured over a propagation mechanism.



These new fluorinated  $\alpha,\omega$ -diiodoalkanes are particularly interesting since they may be used as potential telogens for future telomerizations of other fluorinated monomers which are under investigation.

### Acknowledgements

The authors thank the Dow Corning Corporation for financial support and Elf Atochem for the gift of vinylidene fluoride.

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