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TELOMERIZATION OF TETRAFLUOROETHYLENE AND HEXAFLUOROPROPENE: SYNTHESIS OF DIIODOPERFLUOROALKANES

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SUMMARY

Linear diiodoperfluoroalkanes are easily synthesized by thermal telomerization of tetrafluoroethylene with iodine. When hexafluoropropene reacts with $I(C_2F_4)_nI$ n=2,3,4 as telogen, new diiodocompounds of formula $I(C_3F_6)_m(C_2F_4)_n(C_3F_6)_pI$ n=2,3,4 m=0,1,2 p=1,2 are obtained. In both cases there are high yields, based both on iodine and on olefin.

INTRODUCTION

Perfluoroalkyl iodides are versatile starting materials in the synthesis of a wide range of fluorocarbon derivatives. For example they are starting materials for perfluoroalkyl organometallic and organometalloid systems which have aroused industrial as well as academic interest [1]. Their synthesis and reactivity as telogens have been extensively studied [2-10].

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Literature citations differ in experimental conditions, particularly initiation (U.V., metal/amine catalysis, peroxides, γ-rays, thermal). However, α, ω diiodoperfluoro alkanes, described for the first time by Haszeldine in 1951 [11], have received less attention, especially with regard to experimental details. Knunyants et al. [12] attempted to repeat the earlier work but obtained only a mixture of telomers with very low yields. Subsequently catalysts for the reaction were reported in literature [13] as well as other indirect routes [14-15] : but all of these methods have not appeared to be generally applicable and easy to use for laboratory-scale preparations. Recently a paper on the thermal telomerization of tetrafluoroethylene with iodine [16] reported better but still low yields (67% maximum based on iodine, < 25% on C_2F_4) while other work [17] deals with the synthesis of diiodides using C_2F_4 derived from polytetrafluoroethylene waste (41.4% maximum yield).

Overall it appears that α, ω diiodoperfluoroalkanes are not readily accessible intermediates formed in high yield reactions.

The current work provides a convenient method of synthesizing linear (from C_2F_4) and branched (from C_3F_6) diiodoperfluoroalkanes in high yields. Perfluoroalkylene diiodides are starting materials for a wide variety of bifunctional derivatives, e.g. diols, diolefins, diacids, dihalo-compounds, that show both interesting and uncommon properties [18].

RESULTS AND DISCUSSION

Thermal telomerization of tetrafluoroethylene and hexafluoropropene respectively with iodine and $I(C_2F_4)_nI$ n=2,3,4 were studied. The qualitative influence of various parameters on yields and reaction rate was examined, especially the effect of temperature, telogen/olefin ratio, reaction time, loading level of reactor, kind and rate of stirring.

C_2F_4 telomerization

Telomerization of C_2F_4 with iodine is a typical radical chain reaction [19]. A brief examination of the reaction scheme sheds light on the possible reasons for the reported low yields.

$$I_2 \rightleftharpoons 2I^{\cdot} \qquad \text{Initiation} \tag{1}$$

$$C_2F_4 + I^{\cdot} \rightleftharpoons IC_2F_4^{\cdot} \qquad \text{Propagation} \tag{2}$$

$$IC_2F_4^{\cdot} + nC_2F_4 \longrightarrow I(C_2F_4)^{\cdot}_{n+1} \tag{3}$$

$$I(C_2F_4)^{\cdot}_{n+1} + I_2 \longrightarrow I(C_2F_4)_{n+1}I + I^{\cdot} \qquad \text{Chain transfer} \tag{4}$$

$$I(C_2F_4)^{\cdot}_{n+1} + I(C_2F_4)_mI \longrightarrow I(C_2F_4)_{n+1}I + I(C_2F_4)^{\cdot}_m \tag{5}$$

$$I(C_2F_4)^{\cdot}_{n+1} + I^{\cdot} \longrightarrow I(C_2F_4)_{n+1}I \qquad \text{Termination} \tag{6}$$

$$2I(C_2F_4)^{\cdot}_{n+1} \longrightarrow I(C_2F_4)_{2n+2}I \tag{7}$$

Scheme 1 . Thermal telomerization of C_2F_4 with iodine.

The addition of I_2 to C_2F_4 is an equilibrium [11] :

$$I_2 + C_2F_4 \rightleftharpoons IC_2F_4I \tag{8}$$

At high temperature the equilibrium is completely shifted towards the left and yield based on C_2F_4 declines because the olefine mainly cyclodimerizes [20] :

2 $C_2F_4 \longrightarrow$  Perfluorocyclobutane (9)

Proper choice of reaction conditions can minimize the undesired reactions (7) (widening molecular weight distribution) and (9) (loss of monomer). This has been achieved by working at a temperature as low as possible (180-200°) and by minimizing the concentration of C_2F_4 in the gas phase through successive additions during the reaction (see Experimental).

It is well known that in chain telomerization, even at very low conversion, telomers with n (number of monomer units) > 1 are always present in the crude mixture. We synthesized in high yield telomers with restricted weight distribution by working : a) at the beginning with high ratio I_2/C_2F_4 (> 4) to favour reactions (2) and (4); b) later, when $[I_2] \longrightarrow 0$, through subsequent additions of C_2F_4 keeping a high ratio $I(C_2F_4)_nI/C_2F_4$ n=1,2 to favour chain transfer (5) and propagation (3) reactions, so leading to short telomeric chains (mostly n=2,3). Figures 1 and 2 show the weight telomeric distribution at different C_2F_4/I_2 ratios and loading levels. The importance of the effective stirring is shown in Fig. 3. There is a sharp decrease on C_2F_4 yield on changing from magnetic stirring to rocking reactors and by reducing the rate of stirring. This may be attributed to inefficient gas-liquid exchange.

By following the above guidelines , diiodoperfluoro alkanes now can be synthesized in very high yields, > 96% based on I_2 (the most expensive reagent) and > 80% based on C_2F_4 (Table 1).

The average molecular weight of the reaction mixture was determined satisfactorily by g.l.c. in conjunction with ^{19}F n.m.r. analysis. The physical properties of the products obtained are summarized in Table 2.

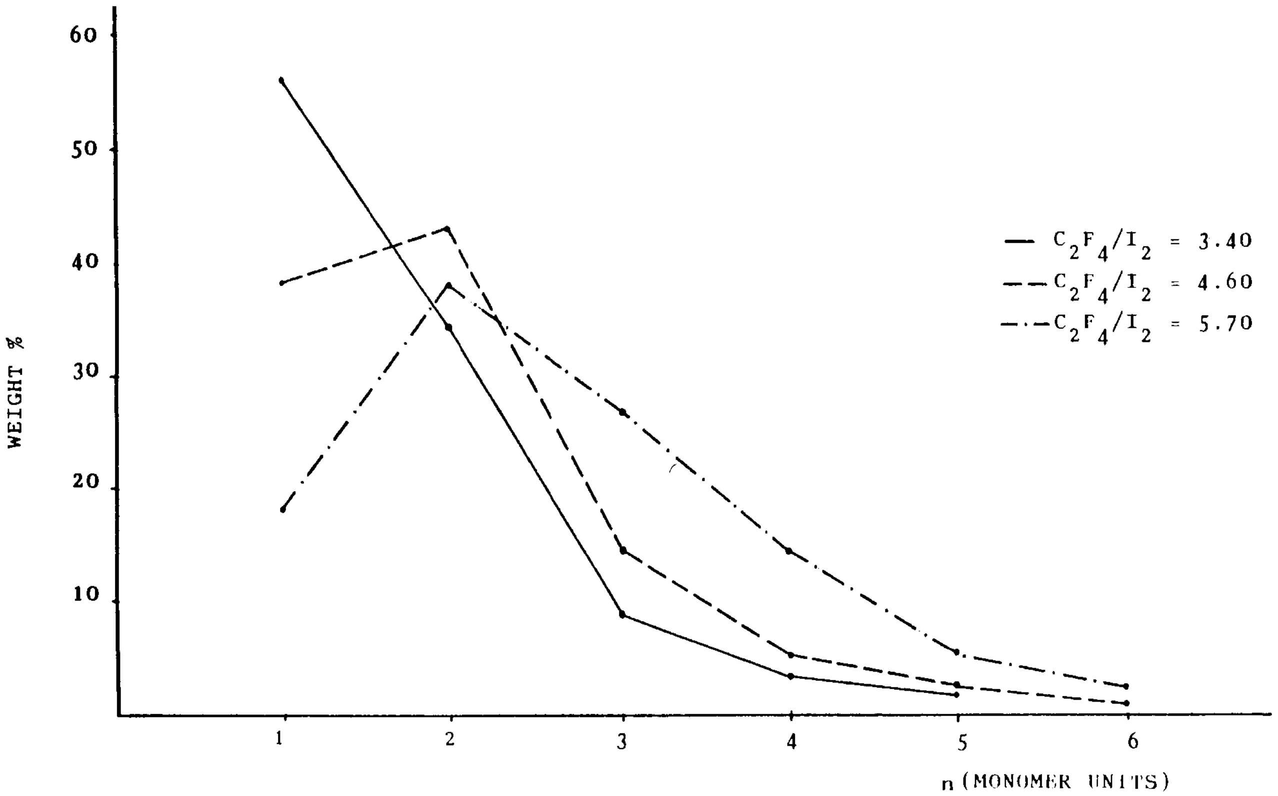


Fig. 1. Telomeric distribution at different C_2F_4/I_2 ratio.
Temperature: 180-200°C, Time: 10 hours, Loading level: 10%.

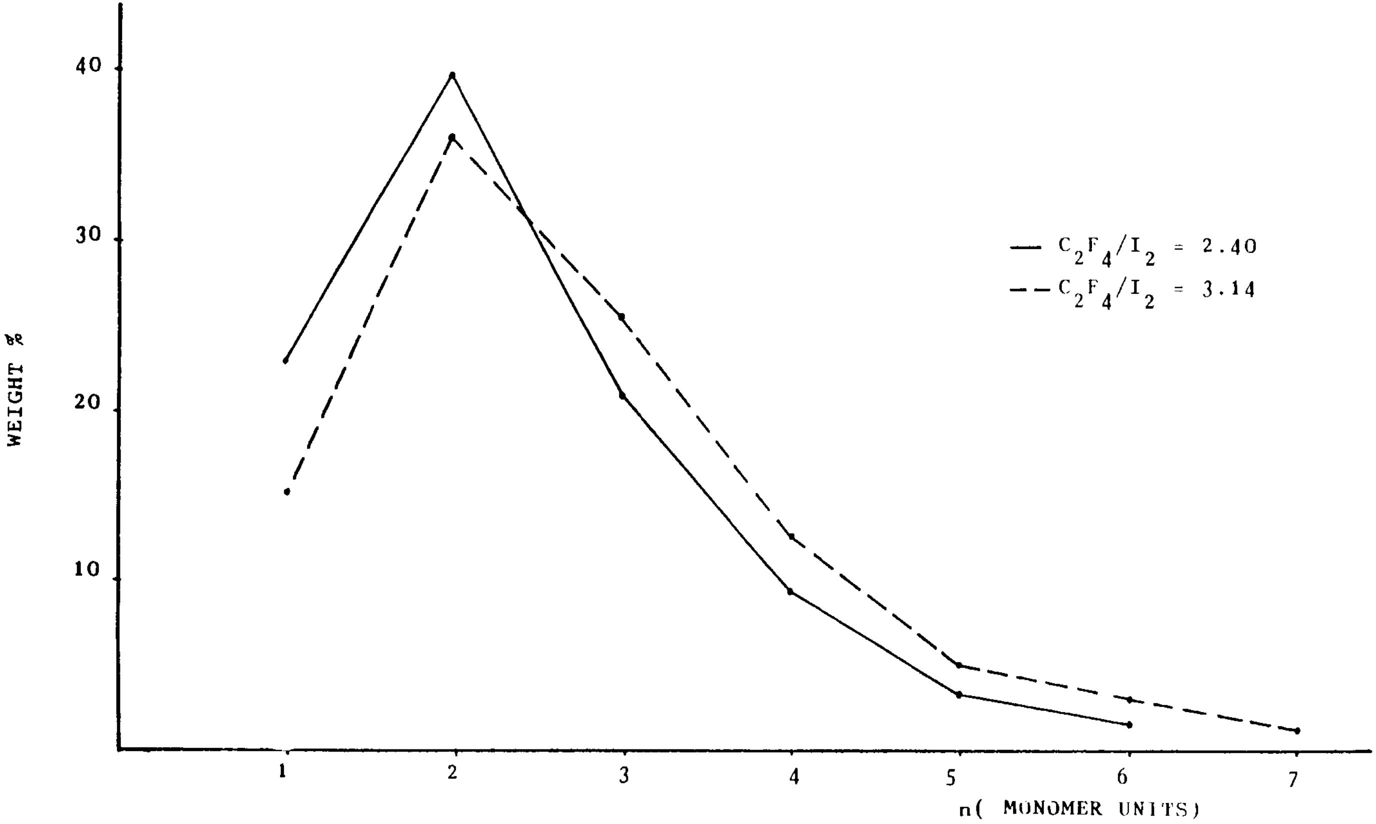


Fig. 2. Telomeric distribution at different C_2F_4/I_2 ratio.
Temperature: 180-200°C, Time: 8 hours, Loading level: 35-50%.

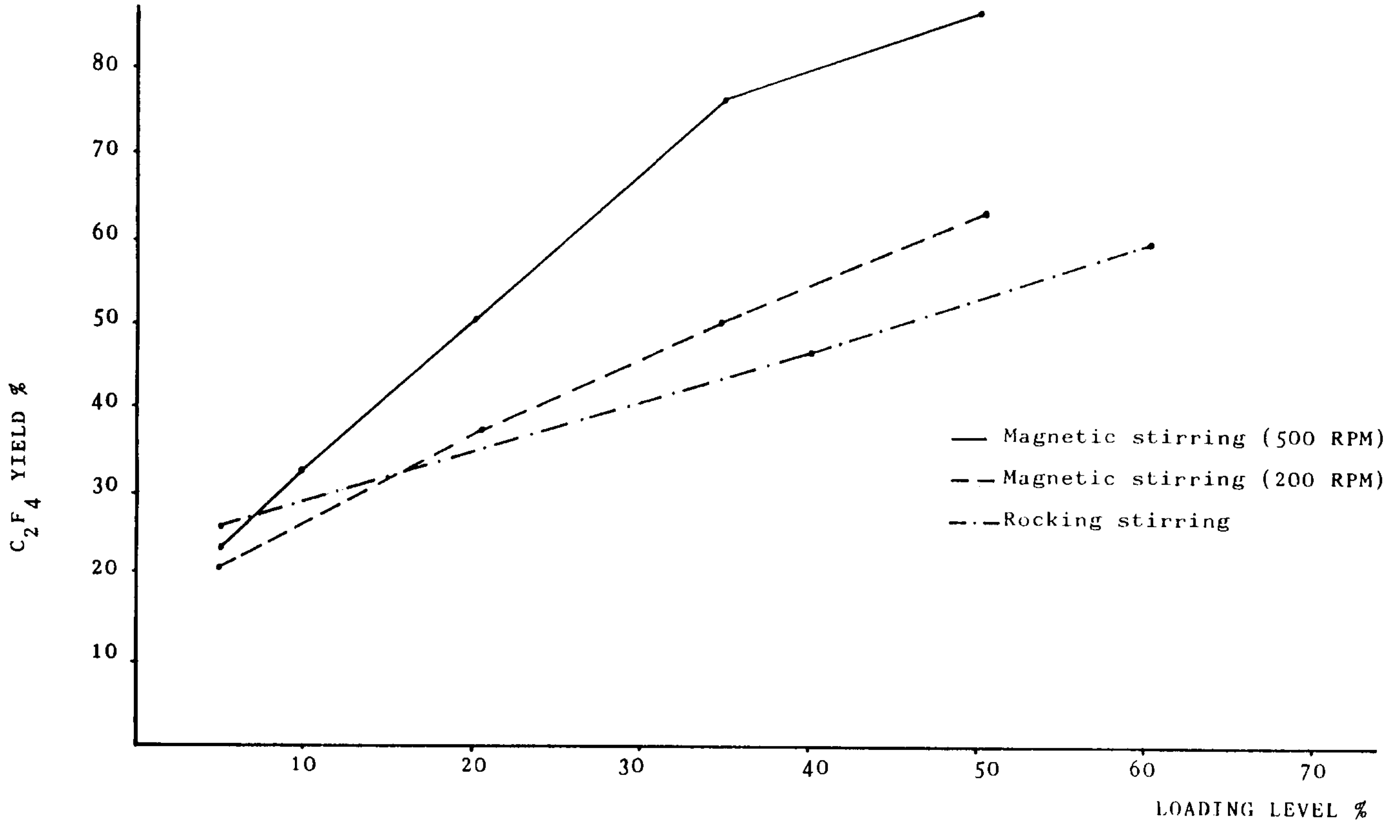


Fig. 3. Influence of loading level on C_2F_4 yield for different types of stirring at C_2F_4/I_2 = 3.14.

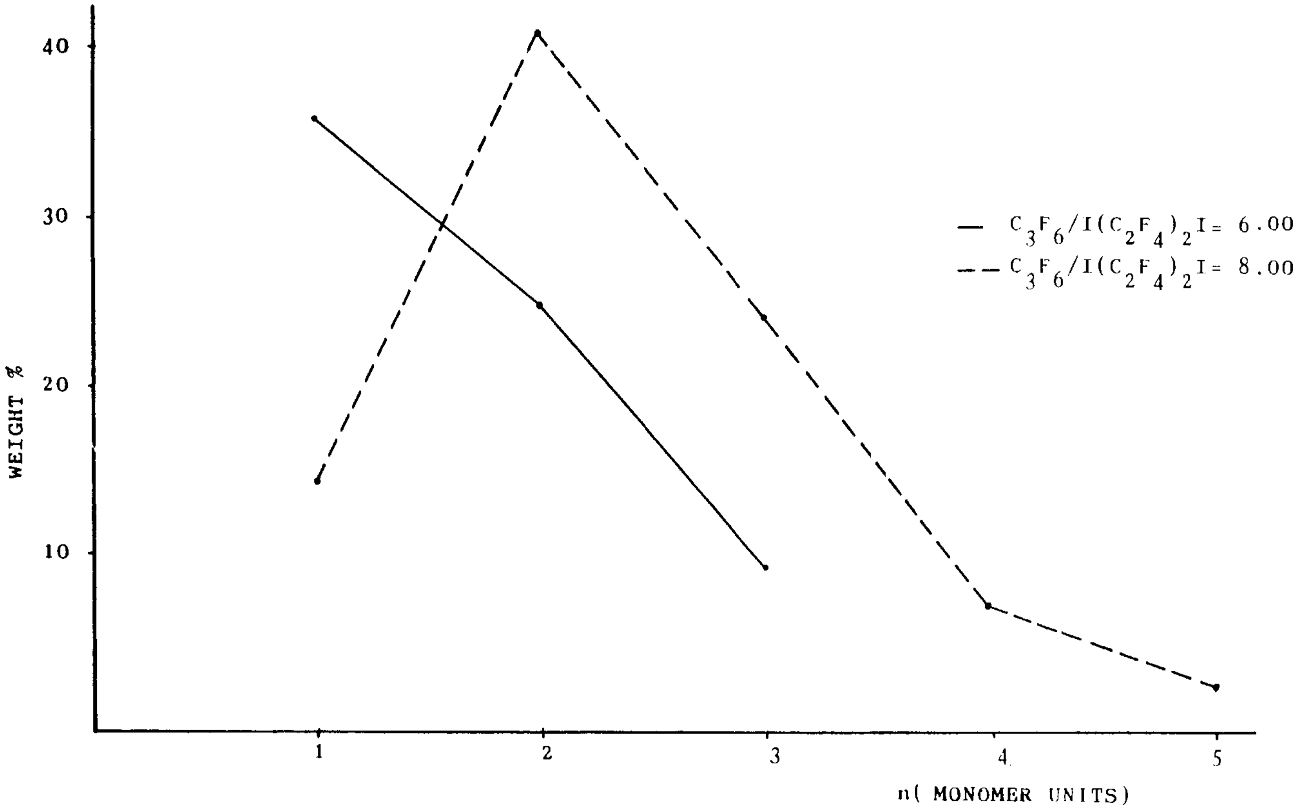


Fig. 4. Telomeric distribution at different $C_3F_6/I(C_2F_4)_2I$ ratio
Temperature: 210°C, Time: 18 hours.

TABLE 1

Telomerization of tetrafluoroethylene with iodine

Run	I_2 (moles)	C_2F_4/I_2 (moles/mole)	Time (hours)	Final Loading level	Yield (%) based on I_2	C_2F_4	Product composition % weight $I(C_2F_4)_nI$ n=1	n=2	n=3	n=4	higher
1	2.81	2.41	8	50	98.0	84.0	23.5	37.3	23.9	9.6	3.6
2	1.85	2.41	8	35	99.0	76.0	16.5	34.7	26.0	13.0	5.5
3	1.85	3.40	10	10	99.0	50.0	54.1	33.7	8.4	1.8	0.3
4	1.85	4.60	10	10	99.0	42.0	38.1	41.7	13.1	3.8	1.0
5	1.85	5.70	10	10	99.0	35.0	18.2	37.4	23.7	12.0	6.0
6	0.20	12.5	5	5	99.0	23.5	9.9	20.8	31.2	17.6	18.6

TABLE 2

Physical properties of α,ω diiodoperfluoroalkanes

Product	Mw	d_{25}	bp (°)	(mmHg)	m.p. (°)
IC_2F_4I	354	2.706	47	(35)	-
$I(C_2F_4)_2I$	454	2.487	63	(35)	-3
$I(C_2F_4)_3I$	554	2.357	72-75	(10)	29
$I(C_2F_4)_4I$	654	-	90	(8-10)	74

C_3F_6 telomerization

Telomerization of hexafluoropropene with perfluoroalkyliodides is a stepwise (and not a chain) process [10]. Radical reaction proceeds through consecutive insertions of C_3F_6 into the telogen's carbon-iodine bonds. At low conversion with telogens of formula $I(C_2F_4)_nI$ n=2,3,4 the scheme of reaction is the following :

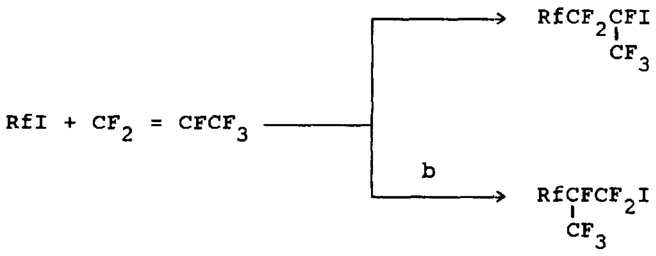
$$I(C_2F_4)_nI + C_3F_6 \longrightarrow I(C_2F_4)_nC_3F_6I \tag{10}$$

$$IC_3F_6(C_2F_4)_nI + C_3F_6 \longrightarrow IC_3F_6(C_2F_4)_nC_3F_6I \tag{11a}$$

$$I(C_2F_4)_nC_3F_6I + C_3F_6 \longrightarrow I(C_2F_4)_n(C_3F_6)_2I \tag{11b}$$

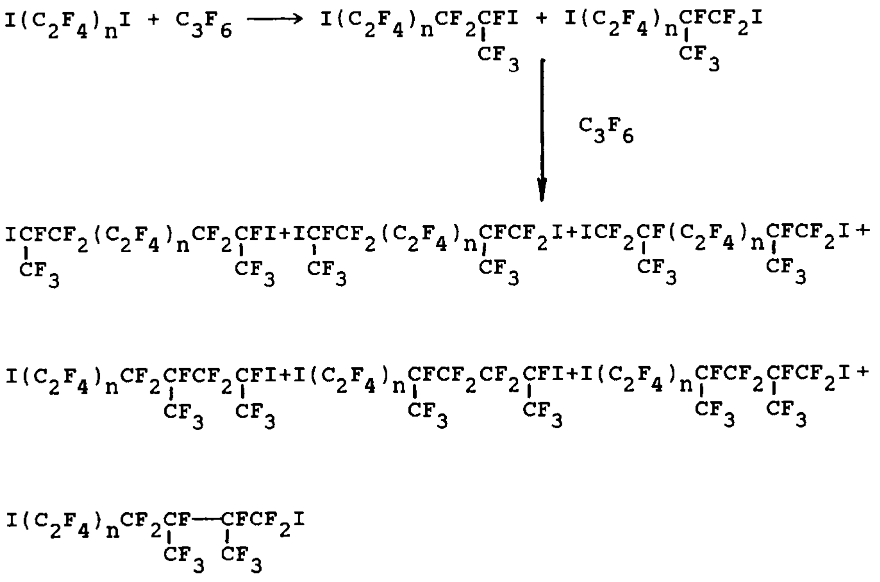
Scheme 2. Thermal telomerization of C_3F_6 with $I(C_2F_4)_nI$ n=2,3,4.

The stepwise process differs from the chain one (C_2F_4 telomerization) mainly because termination in the former case, e.g. $Rf^{\cdot} + I^{\cdot} \longrightarrow RfI$, is greatly faster than propagation, e.g. $Rf^{\cdot} + nC_3F_6 \longrightarrow Rf(C_3F_6)^{\cdot}_n$. Thus only the monoaddition product is observed at short reaction time. The telomer's molecular weight at the same telomerization conversion and telogen/olefin ratio is much more limited than in C_2F_4 telomerization. Loading level is less important because C_3F_6 does not cyclodimerize appreciably below 350° [21]. Telogen mainly adds to difluoromethylene terminated alkenes at the $=CF_2$ end due to both steric and electronic factors.



a/b = 11.5 at 200° (Experimental, example 1)

Moreover reaction 11a is faster than 11b for steric reasons (Scheme 3). Isolated products are consistent with the following scheme :



$$I(C_2F_4)_nI + C_3F_6 \longrightarrow I(C_2F_4)_nCF_2\underset{CF_3}{\underset{|}{C}}FI + I(C_2F_4)_n\underset{CF_3}{\underset{|}{C}}FCF_2I$$

$$\Big\downarrow C_3F_6$$

$$I\underset{CF_3}{\underset{|}{C}}FCF_2(C_2F_4)_nCF_2\underset{CF_3}{\underset{|}{C}}FI + I\underset{CF_3}{\underset{|}{C}}FCF_2(C_2F_4)_n\underset{CF_3}{\underset{|}{C}}FCF_2I + ICF_2\underset{CF_3}{\underset{|}{C}}F(C_2F_4)_n\underset{CF_3}{\underset{|}{C}}FCF_2I +$$

$$I(C_2F_4)_nCF_2\underset{CF_3}{\underset{|}{C}}FCF_2\underset{CF_3}{\underset{|}{C}}FI + I(C_2F_4)_n\underset{CF_3}{\underset{|}{C}}FCF_2CF_2\underset{CF_3}{\underset{|}{C}}FI + I(C_2F_4)_n\underset{CF_3}{\underset{|}{C}}FCF_2\underset{CF_3}{\underset{|}{C}}FCF_2I +$$

$$I(C_2F_4)_nCF_2\underset{CF_3}{\underset{|}{C}}F - \underset{CF_3}{\underset{|}{C}}FCF_2I$$

Scheme 3. Product distribution of C_3F_4 telomerization with $I(C_2F_4)_nI$ n=2,3,4.

Increasing the reaction time and rising the olefin/telogen ratio affords compounds containing more than 2 units of C_3F_6 (Experimental, example 2). Typical molecular weight distribution/(C_3F_6/telogen) plots are shown in Fig. 4.

EXPERIMENTAL

Analytical g.l.c. was performed with a 4200 Carlo Erba instrument equipped with a thermal conductivity detector (columns : 2 m packed with silicon rubber 5% (SE 52) on acid washed Chromosorb W, 80-100 Mesh; 8 m packed with ethyl-hexyl sebacate on acid-washed Chromosorb W, 80-100 Mesh; carrier helium).

Peak areas were determined with a Hewlett Packard 3350 A integrator. ^{19}F n.m.r. spectra recorded on 60 Mhz and 200 MHz Varian Spectrometers ($CFCl_3$ as internal standard, $CDCl_3/CHCl_3$ as solvent).

Chemical shifts of products are summarized in Table 7.

Reagents : doubly sublimed iodine was a commercial sample (Carlo Erba RPE); C_2F_4 and C_3F_6 are Montefluos products (polymerization grade).

C_2F_4 telomerization. General procedure

Iodine was introduced under nitrogen in 1l reactor of Hastelloy C (to avoid iodine corrosion at high temperature) equipped with magnetic stirring.

0.7 moles of C_2F_4 were charged through a membrane Corblin compressor. Temperature was increased while stirring up to 180°C : a fast decrease of pressure was readily observed. Then, at this temperature a further 0.7 moles of C_2F_4 were charged.

The temperature was raised to 200° to have an appreciable rate of reaction and maintained there until the pressure dropped and stabilized at a lower value. Then, at 200°C and in the same way as outlined before, more C_2F_4 was added in portions of 0.5-0.7 moles each. Details of reaction parameters are given in Table 1.

Finally after cooling at room temperature, gases were vented and the crude telomeric mixture was collected and analyzed by g.l.c. and ^{19}F n.m.r.

The average molecular weight calculated by these two different ways are always in good agreement. Unreacted iodine (if present) was determined by titration.

The reaction mixture was fractionally distilled (2 m column packed with Rashing rings; 30 plates). A typical g.l.c. analysis of reaction products and their distillation are shown in Tables 3 and 4 (relative to run 1, Table 1).

TABLE 3

Gas chromatography composition of telomeric mixture

Product	Retention time (minute) *	Weight % **
C_2F_4	0.42	1.1
	0.62	1.0
IC_2F_4I	2.44	23.5
$I(C_2F_4)_2I$	4.89	37.3
$I(C_2F_4)_3I$	7.16	23.9
$I(C_2F_4)_4I$	8.95	9.6
$I(C_2F_4)_5I$	10.47	2.8
higher telomers	>11.8	0.8

* SE 52 column; flow : 40 ml/min; program : from 70° to 170° at 10°C/minute

** Based on relative response factors ($I(C_2F_4)_2I=1$)

TABLE 4

Experimental condition of $I(C_2F_4)_nI$ distillation

Fraction	Weight (g)	Head Temp. (°)	Residual Pressure (mmHg)	g.l.c. composition A	B	C	D	E	F	G
1	11	–	60	97	3					
2	14	35	40	6	–	94				
3	278	42-47	35-40	–	–	99				
4	31	47-60	35	–	–	48	52			
5	449	60-63	35-30	–	–	–	99			
6	36	63-72	20-10	–	–	–	57	43		
7	277	72-75	10	–	–	–	1	99		
8	24	75-90	10	–	–	–	–	71	29	
9	111	90	8	–	–	–	–	1	98	
residue	52			–	–	–	–	–	20	80

A = F B = C_2F_4 C = IC_2F_4I D = $I(C_2F_4)_2I$ E = $I(C_2F_4)_3I$

F = $I(C_2F_4)_4I$ G = higher products

C_3F_6 telomerization

1) In a 250 ml rocking Inconel reactor were introduced 60 g of $I(C_2F_4)_2I$ (0.13 moles) under nitrogen and then 98 g of C_3F_6 (0.65 moles) by condensation. The temperature was increased to 210°C and maintained there for 18 hours. The internal pressure decreased from 50 to 35 atm. After cooling to room temperature, unreacted C_3F_6 was degassed and 82.3 g of crude mixture were collected whose gas-chromatographic composition is summarized in Table 5.

TABLE 5

Gas chromatographic composition of $C_3F_6/I(C_2F_4)_2I$ telomeric mixture

Product	Retention time (minute) *	Weight %
$I(C_2F_4)_2I$	3.15	22.3
$I(C_2F_4)_2C_3F_6I$	6.08	38.7
$I(C_2F_4)_4I$	6.30	traces
$IC_3F_6(C_2F_4)_2C_3F_6I$	8.44	27.4
$I(C_2F_4)_2(C_3F_6)_2I$	8.12	
$IC_3F_6(C_2F_4)_2(C_3F_6)_2I$	9.97	9.6
higher telomers	>11.0	2.0

* SE 52 column; flux = 50 ml/min; program : from 70° to 170° at 10°C/minute

Conversion based on $I(C_2F_4)I$: 70%

Yield based on C_3F_6 : 100%

The crude mixture was fractionally distilled (90 cm Spalthror Fisher column; 60 plates) as summarized in Table 6. Products were identified by the ^{19}F n.m.r. analysis (see Table 7) from which was obtained the following distribution:

TABLE 6

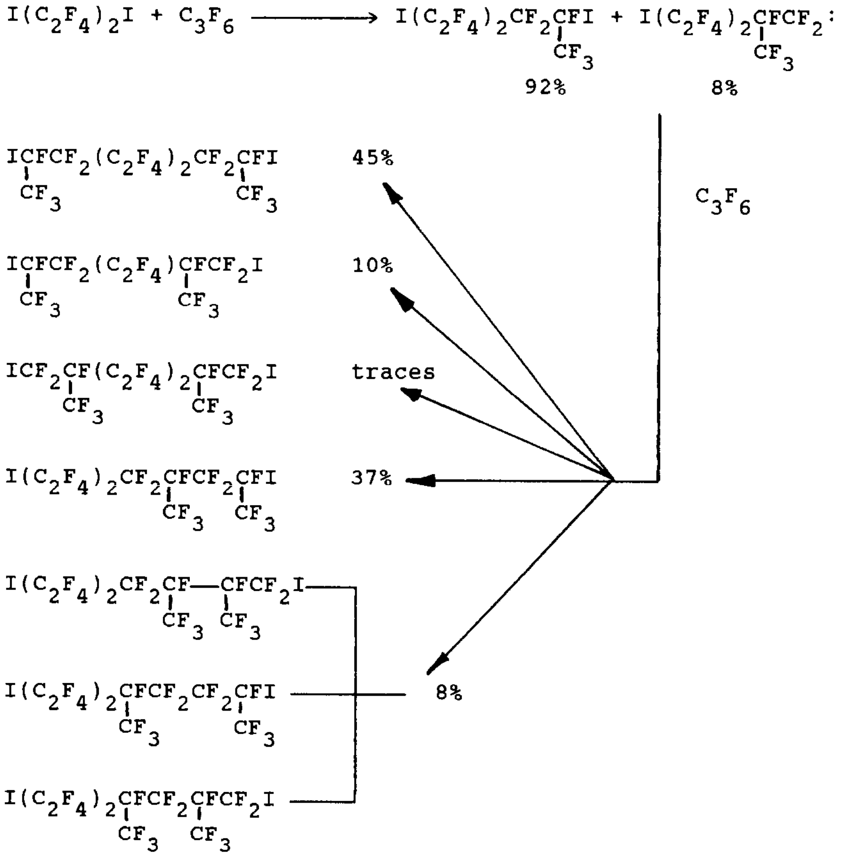
Experimental condition of $C_3F_6/I(C_2F_4)_2I$ telomerix mixture distillation

Fraction	Weight	B.p.	Residual Pressure	g.l.c. composition					
	(g)	(°)	(mmHg)	A	B	C	D	E	F
1	18.9	40-50	30	5	94				
2	2.0	50-67	30	-	84	12			
3	30.2	67	30	-	2	94			
4	1.7	60	10	-	-	11	80		
5	21.8	80	10	-	-	1	97.5		
residue	7.1	-	-	-	-	-	-	89	11

A = C_3F_6 B = $I(C_2F_4)_2I$ C = $I(C_2F_4)_2C_3F_6I$

D = $IC_3F_6(C_2F_4)_2C_3F_6I$ + $I(C_2F_4)_2(C_3F_6)_2I$

E = $IC_3F_6(C_2F_4)_2(C_3F_6)_2I$ F = higher telomers



2) The reaction was repeated as described in example 1, for 20 hours with $C_3F_6/I(C_2F_4)_2I = 8$.
The final gas chromatographic composition was :

$I(C_2F_4)_2I$	2.7%
$I(C_2F_4)_2C_3F_6I$	16.0%
$IC_3F_6(C_2F_4)_2C_3F_6I$ $I(C_2F_4)_2(C_3F_6)_2I$	41%
$I(C_3F_6)(C_2F_4)_2(C_3F_6)_2I$	26.5%

higher telomers 11%

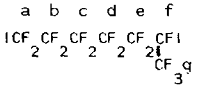
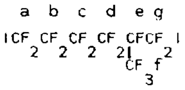
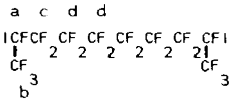
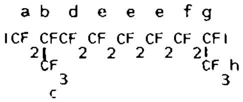
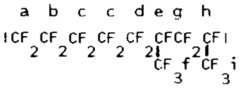
Conversion based on $I(C_2F_4)_2I$: 96%

Selectivity based on $I(C_2F_4)_2I$: 95%

Yield based on C_3F_6 : 100%

TABLE 7

^{19}F n.m.r. chemical shifts of telomeric products $I(CF_2CF_2)_nI$ n=1,2,3,4 and $I(C_3F_6)_m-(C_2F_4)_n-(C_3F_6)_pI$ r=2 m=0,1 p=1,2 (relative to $CFCl_3$)

	a	b	c	d	e	f	g	h	i
$\overset{a}{ICF_2}CF_2I$	-54								
$\overset{a}{ICF_2}\overset{b}{CF_2}CF_2CF_2I$	-59	-112.5							
$\overset{a}{ICF_2}\overset{b}{CF_2}\overset{c}{CF_2}CF_2CF_2CF_2I$	-59	-113.5	-121.5						
$\overset{a}{ICF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}CF_2CF_2CF_2CF_2I$	-59	-113.5	-121.5	-122.5					
 $\overset{a}{ICF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF_2}\overset{f}{CF}(\overset{g}{CF_3})I$	-59	-113	-120.5	-122.0	-108	-145	-73		
 $\overset{a}{ICF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF}(\overset{f}{CF_3})\overset{g}{CF_2}I$	-59	-113	-120.5	-108.0	-162	-70	-50		
 $\overset{a}{ICF}(\overset{b}{CF_3})\overset{c}{CF_2}\overset{d}{CF_2}\overset{d}{CF_2}CF_2CF_2CF_2CF(CF_3)I$	-144	-74	-107	-120/-122					
 $\overset{a}{ICF_2}\overset{b}{CF}(\overset{c}{CF_3})\overset{d}{CF_2}\overset{e}{CF_2}\overset{e}{CF_2}\overset{e}{CF_2}\overset{f}{CF_2}\overset{g}{CF}(\overset{h}{CF_3})I$	-50	-162	-70	-108	-120/-122	-108	-144	-74	
 $\overset{a}{ICF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF}(\overset{f}{CF_3})\overset{g}{CF_2}\overset{h}{CF}(\overset{i}{CF_3})I$	-59	-113	-120/-123	108	185	-71	-105	-143	-74

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