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A new telogen for telechelic oligomers of chlorotrifluoroethylene ☆

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Abstract

Elemental iodine is slightly soluble in liquid chlorotrifluoroethylene (CTFE) under autogenous pressure at room temperature. Exposure of a mixture of no more than 0.22 mol of iodine with 1 mol of CTFE in a borosilicate glass Carius tube to sunlight, an artificial UV source or to γ-radiation resulted in complete conversion of all the solid iodine initially to ICF_2CFClI (**1**), which was isolated and characterised. The reaction is reversible, the equilibrium constant for $I_2 + CTFE_{liq.} \rightleftharpoons$ **1** being ca. 0.22. Thus with light or heat, isolated unconfined **1** reverted to iodine and CTFE. Additional irradiation of **1** confined with excess liquid CTFE led to the irreversible formation of telomers $I(CF_2CFCl)_nI$ (**2**). The average value of n in the distribution of telomers increased with dose giving liquids ($n = 2$–4) or greases ($n = 2$–10) which were much more stable than **1**. Upon bromination, individual telomers in the series $Br(CF_2CFCl)_nBr$ were isolated and characterised.

Keywords: Telogens; Telechelic oligomers; Chlorotrifluoroethylene; NMR spectroscopy; Mass spectrometry; IR spectroscopy

1. Introduction

The simplest example of a fluorolefin-derived telechelic telomer is that which uses as telogen the adduct of the monomer with two halogen atoms which then become the terminating functional units of the telomer. Known examples are listed in Table 1.

$$XZ + CF_2{=}CFY \longrightarrow XCF_2{-}CFYZ \longrightarrow X(CF_2{-}CFY)_nZ \quad (1)$$

Of these, telechelic telomers derived from telogens ICF_2CF_2I and IC_4F_8I with tetrafluoroethylene have received the most industrial interest [20,21]. We now describe the chemistry of the related iodine-functional telogen $ICF_2{-}CFClI$ (**1**) and its telomers with chlorotrifluoroethylene (CTFE), $I(CF_2{-}CFCl)_nI$ (**2**). Such telomers could be useful in forming copolymers with silicone intermediates [22,23].

The existence of **1** has been proposed only in a single early study. An unstable adduct, thought to be 1-chloro-1,2,2-trifluoro-1,2-diiodoethane, was obtained in 30%–35% yield by the distillation of a mixture of equal weights of CTFE and iodine which had been allowed to stand at room temperature for several days sealed in a Pyrex reactor [24]. This material (b.p. 54–55 °C/20 mm Hg with slight decomposition), having a density greater than 2.5, decomposed readily upon standing to yield crystals of iodine but no other residue. Probably because of this instability, no reliable analysis or refractive index was obtained and no attempt was described to form telomers from this material.

A telogen usually forms telomer by an energy-initiated fragmentation to a carbon centred radical which subsequently propagates through a sequence of olefin-addition and atom-transfer steps until radical recombination occurs [25]. Under such conditions the average distribution of molecular weights increases in line with the following factors: (a) as the rate of the olefin-addition step increases; (b) as the rate of the atom-transfer step decreases; (c) as the concentration of olefin increases; and (d) as the concentration of telogen decreases [26]. By an adjustment of these parameters it is often possible to tailor molecular weights to give

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☆ See also Ref. [1].
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Table 1
Known examples of XCF_2CFYZ and derived telomers

	$XZ+CF_2{=}CF_2 \rightarrow XCF_2{-}CF_2Z$	$\rightarrow X(CF_2{-}CF_2)_nZ$	$XZ+CF_2{=}CFCl \rightarrow XCF_2{-}CFClZ$	$\rightarrow X(CF_2{-}CFCl)_nZ$
ICl	[2] [a]	[3] [a]	[4,5] [a]	[6] [a], [7] [b]
Br_2	[8,9] [a]	[10] [c]	[11,12] [a]	[13] [d], [14] [e], [15] [f]
IBr	[16] [a]	[16] [f]	[5] [a]	
I_2	[2] [a], [17] [g]	[18,19] [a]		

[a] Thermal, pressure.
[b] UV, extended irradiation.
[c] Vacuum UV laser, 233–263 nm, gas phase.
[d] UV gives radical-coupled product $BrCF_2CFClCFClCF_2Br$.
[e] Transition metal redox.
[f] Peroxide or AIBN.
[g] UV, minimum irradiation.

liquids, oils, greases or waxes. The examples cited in Table 1 involved a wide range of conditions, and in some cases deviations from the usual mechanism have been proposed.

2. Results

2.1. Synthesis of telogen

Upon UV or γ-irradiation, iodine added almost quantitatively to liquified CTFE to give $ICF_2{-}CFClI$ (**1**) and telomers $I(CF_2{-}CFCl)_nI$ (**2**).

$$I_2+CF_2{=}CFCl \rightleftharpoons \underset{(\mathbf{1})}{ICF_2{-}CFClI} \qquad (2)$$

$$ICF_2{-}CFClI+nCF_2{=}CFCl \longrightarrow \underset{(\mathbf{2})}{I(CF_2{-}CFCl)nI} \qquad (3)$$

Unlike the addition of other halogens or mixed halogens to CTFE (Table 1), iodine did not add in the absence of light or γ-rays. As irradiation proceeded, **1** was produced (Table 2), followed as the dose increased by **2** with increasing average values of n (Table 3). By using a moderate dose of irradiation, it was possible to produce **1** in 84% yield, the balance being telomer. Telogen **1** was isolated by vacuum-transfer at room temperature and identified by elemental analysis, ^{19}F NMR and ^{13}C NMR spectroscopy, and by exact mass spectrometry. The ^{19}F NMR spectrum was first order and fluorines F_a and F_b in $IF_aF_bCCF_xClI$ were rendered non-equivalent due to the adjacent chiral centre.

The telogen, a colourless liquid, was stable for at least six months provided it was stored in a closed container in the dark under an aqueous sodium metabisulphite solution to remove trace elemental iodine. Unconfined **1** reverted to a mixture of iodine and gaseous CTFE upon exposure to light or temperatures above 50 °C. Thus formation of **1** is reversible, with an equilibrium constant estimated as not less than 0.22 at room temperature, but less than 0.01 at 100 °C. At −27 °C (the boiling point of CTFE), the equilibrium constant is also low, i.e. less than 0.04, probably due to the markedly lower solubility of iodine in liquid CTFE at this temperature. Thus attempts to devise a low-temperature atmospheric-pressure process for the synthesis of **1** were only marginally successful.

The instability of **1** made it impossible to record a UV adsorption spectrum free from iodine, but the related compound CF_3CFClI was observed to have an adsorption maximum at 272 nm in hexane that extended to 320 nm, while the telomer $CF_3(CF_2CFCl)_3I$ has been reported to exhibit an adsorption maximum at 292 nm [27]. Thus the ability of sunlight, which contains radiative energy only as low as 300 nm, to efficiently catalyse both the forward and reverse reaction suggests that elemental iodine may be the important energy-absorbing species. Elemental iodine absorbs visible light from 400 to 650 nm with a maximum at 540 nm [28] and, below 499 nm, dissociation to the atomic states $I(^2P_{1/2})$ and $I(^2P_{3/2})$ occurs. Even at longer wavelengths, iodine can photodissociate to ground-state atoms $I(^2P_{1/2})$ via an intersystem crossing mechanism. The photolytically-produced iodine atoms would produce **1** via Eqs. (4)–(6), while the destruction of **1** may involve direct photon-induced cleavage at wavelengths below 300 nm or attack by radicals.

$$I_2 \overset{h\nu}{\rightleftharpoons} I\cdot+I\cdot \qquad (4)$$

$$I\cdot+CF_2{=}CFCl \rightleftharpoons ICF_2CFCl\cdot \qquad (5)$$

$$ICF_2CFCl\cdot+I_2 \rightleftharpoons \mathbf{1}+I\cdot \qquad (6)$$

$$ICF_2CFCl\cdot+CF_2{=}CFCl \longrightarrow I(CF_2CFCl)_2\cdot \qquad (7)$$

The radical $ICF_2CFCl\cdot$ is the common intermediate both in the formation and destruction of telogen **1** and in the formation of telomer **2** ($n=2$) [Eq. (7)]. Telomers **2**, once formed, are much more stable than **1** towards irradiation and could be subjected to temperatures up to 160 °C for several hours in a sealed tube without decomposition. Thus, formation of such telomers during extended periods of irradiation irreversibly removed components from the equilibrating system [Eq. (2)].

Table 2
Conditions favouring ICF_2CFClI formation

	Charge (recov.) (g)		Mole ratio	Conditions [a]	Time (h)	Product (g) [b]	Conversion [c]		n [d] (av.)	GLC $n=1:2:3$	K [e]
	$CF_2=CFCl$	Iodine					M.B.	I_2 (%)			
1	3.3	3.0	2.4	Dark	168	0	0	0			
2	65.5(53.9)	52.8(26.5)	2.7	1 in from 100 W	72	37.5	99	50	1.0	30:1	0.211
3	59.0(43.2)	26.1(5.9)	4.9	Rayonet, 300 nm	288	34.6	88	89	1.8	2:1:0.6	0.132
4	99.6	5.4(3.4)	40	100 W, −27 °C [f]	31	2.1		37		3:1:0.2	
5	39.2	10.2(0)	8.4	Rayonet, 254 mm, Qtz	200	16.6		100	1.4	4:1:0.7:trace [h]	0.122
6	58.9(39.6)	21.2(0)	6.1	1000 W, Qtz [j]	160	39.5	98	100	2.0	5:1:trace [h]	0.240
7	63.7(51.6)	21.1(3.7)	6.6	Sunlight (UK)	7 d	28.9	98	82	1.5		0.174
8	124(103)	72.7	3.8	γ-Ray [j]	120	45.7				1:0:0	0.138

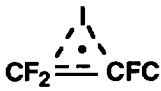
[a] Hanovia medium-pressure mercury lamp, 78 cm^3 borosilicate glass Carius tube, 25–35 °C unless otherwise indicated.
[b] Weight after evaporating CTFE.
[c] M.B. = wt. product × 100/wt. reactants consumed. I_2 is iodine conversion.
[d] n in $I(CF_2CFCl)_nI$, from mass balance ($n = 2.19C/I$, C = CTFE consumed, $I = I_2$ consumed) or from ^{19}F NMR.
[e] K = mol 2/mol CTFE remaining.
[f] Liquid-phase atmospheric pressure immersion reactor.
[g] ICF_2CFClI rather than I_2 reacted.
[h] Additional products formed.
[j] Rotated end-over-end 30 cm from source.

Table 3
Conditions favouring $I(CF_2CFCl)_nI$ formation

	Charge (recov.) (g)		Mole ratio	Conditions	Product (g) [b]	n (av.) NMR [c]	GLC $n=1:2:3$
	$CF_2=CFCl$	Iodine					
1	58.2	14.8(0)	8.57	7 d [6 sunny (US)]	28.7	3.6	1.3:1:0.66
2	56.5(47.1)	11.1(0)	11.1	5 d [5 sunny (US)]	19.4	3.7	1.6:1:0.82
3	172(101)	45(0)	8.33	8 d [5.5 sunny (US)]	96.3	4.0	1.2:1:0.84
4	58.7(20.4)	14.9(0)	8.6	25 cm from UV [d], 168 h	56.2	6.0 [e]	
5	61.5(9.0)	14.8(0)	9.0	14 d [11 sunny (US)]	66.1	8.7	

[a] 78 cm^3 borosilicate glass Carius tubes in a horizontal position. Sun at 45° lat., June.
[b] Weight after evaporating CTFE.
[c] See Table 4.
[d] 1000 W Hanovia medium-pressure mercury lamp.
[e] Analysis: Found: Cl, 21.9; F, 36.75%. $C_{12}Cl_6I_2F_{18}$ requires: Cl, 22.4; F, 36.03%.

The rate of formation of **1** from iodine and CTFE depends on the rate of dissolution of iodine and the intensity of light. Bleaching of the iodine colour in the CTFE solution was observed with intense light and poor mixing, indicating rate-limiting dissolution in this case. Although relatively low-energy light quanta were sufficient to achieve the syntheses of **1** and **2** [Eqs. (2) and (3)], the total radiation dose required was much larger than would be expected if the light served simply as an initiator for a free-radical halogen addition, followed by the classic chain telomerization reaction with each initiating free radical responsible for many alternating olefin addition and chain-transfer steps [25,26]. In the case of telogen formation, the reason for the large dose required is doubtless the reversibility of the steps illustrated in Eqs. (4) and (6). The unusual instability of $ICF_2CFCl\cdot$ suggests its chemistry and geometry is highly influenced by the β-iodine atom. Iodine also adds to hydrocarbon olefins to form unstable vicinal diiodides which, like **1**, are stable when stored in the dark if all excess elemental iodine is removed. Investigations of the stereochemistry and kinetics of addition of iodine to alkenes have concluded that a bridged species equivalent to **3** may be involved, being formed via a transition state which includes an additional iodine molecule [29,30]; the formation of an intermediate **3** is therefore a possibility in these systems.



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Iodine and liquid CTFE formed **1** in high conversion when exposed to an intense γ-ray source for 5d at room temperature with agitation and only very small amounts of telomers formed. Almost no reaction occurred when the reaction was repeated at 100 °C.

2.2. Synthesis of telomers

Telomers were formed upon extended UV or visible-light irradiation of either iodine and CTFE or **1** and CTFE. Iodine was completely consumed. Telomers became the dominant product after, for example, 7-d exposure to sunshine in a borosilicate Carius tube, and were virtually the exclusive product after 14-d exposure (Table 3). The reason for the large irradiation dose required may be the presence of excess elemental iodine. In many catalytic free-radical chain reactions, iodine acts as a free-radical poison by intercepting the propagating carbon radical to produce relatively unreactive iodine atoms which recombine [31,32]. In the present telomerization of CTFE, competition between the reaction indicated in Eq. (6) over telomer formation [Eq. (7)] results in a quantum efficiency of less than unity for the addition of a CTFE unit.

We attempted chain telomerization using catalytic amounts of peroxide to generate free radicals. A mixture of iodine-free **1** and CTFE was heated for 4–16 h at temperatures from 50–85 °C with various commercial peroxy ester free-radical initiators in proportions up to 2.0%. Formation of iodine colour occurred but no telomer was observed, even though CTFE formed high polymer in the absence of telogen under these conditions. In the absence of telogen, the presence of aqueous sodium metabisulphite with either peroxide at 50 °C or with a redox couple of ammonium persulphate and perfluorooctanoic acid emulsifier at room temperature did not inhibit the polymerisation of CTFE [33,34]. In the presence of telogen, although the formation of iodine colour was suppressed by bisulphite reduction, telomer was still not formed. In the absence of elemental iodine, carbon-centred radicals were probably still lost at a significant rate by abstraction of iodine atoms directly from **1**, followed by decomposition according to Eqs. (5) and (1), thus interrupting the chain telomerisation process via iodine-atom recombination.

During telomerisation, iodine was completely consumed leaving excess CTFE. As previously noted, **2** was formed irreversibly. Thus with additional exposure to light, most of the remaining CTFE was consumed and the degree of telomerisation (n of **2**) increased, being limited eventually by the ratio of CTFE to iodine charged. Almost no telogen, CTFE or iodine remained. The telomers were oils and low-melting greases. The average value of n could be determined from the ^{19}F NMR spectrum and agreed with that expected from material balance. The end functional units, ICF_2CFCl- and $-CF_2CFClI$, exhibited unique peak positions that were distinguishable from the $-CF_2CFCl-$ repeat units (Table 4). GLC showed a series of telomers, $n=1$–3, but at higher elution temperatures only decomposition products derived from the higher telomers. Telomer fractions were concentrated by distillation but could not be isolated in high purity.

To identify individual components, telomers **2** ($n=2.3$ av.) from an 8-d sunlight exposure of a 0.24 mole ratio of iodine/CTFE were heated with excess liquid bromine [35] in Carius tubes to produce the corresponding more thermally stable and volatile bromine functional telomers, $Br(CF_2CFCl)_nBr$ (**5**). Whereas **2** exhibited a series of telomer peaks in GLC at 11.8, 17.3 and 21.7 min after 4-h exposure of the mixture to bromine at 90 °C, a new series of peaks at 8.5, 15.0, 19.8 and 23.6 min dominated. The ^{19}F NMR spectrum of the mixture was consistent with these being $I(CF_2CFCl)_nBr$ (**4**) and there was also some $BrCF_2CFClBr$ present, probably formed by decomposition of **1** followed by addition of bromine to CTFE. Continued heating for a total of 112 h at 112 °C resulted in yet another series of peaks at 4.7, 12.5, 17.7, 22.0, 25.4 and 28.5 min, due to **5** becoming dominant (Fig. 1). The ^{19}F NMR spectrum of the mixture indicated that 87.5% of ICF_2 telomer ends were brominated (at δ −56 to −60 ppm) and that the average n value was 2.04 (89% yield of **5**, based on iodine initially charged). The product was successfully fractionated into pure component telomers, $n=2$, 3 and 4. Structures were confirmed by exact mass MS, IR and ^{19}F NMR (Fig. 2). Telomers **5** ($n=2$) contained 8.5% $BrCF_2CFClCFClCF_2Br$, as evidenced by signals at δ −54.8, −56.4 and −116.9 ppm [13]. Indeed, in the GLC trace, a series of peaks or shoulders at slightly shorter retention times comprising about 3%–4% of the product might be due to the series of related telomers $Br(CF_2CFCl)_nCFClCF_2Br$, although the NMR spectra of isolated telomers higher than $n=2$ were too complex to demonstrate this. The residue from distillation was a liquid with an average $n=5.6$ value. This affirms that the entire telomer distribution is relatively narrow and is desirably entirely in the liquid range.

Irradiation of **1** below 300 nm, in quartz using a mercury lamp, resulted in a product that may be accounted for by initial telomerisation [Eqs. (2) and (3)], elimination of iodine chloride [Eq. (8)] and subsequent re-addition [Eq. (9)], followed by telomerisation [Eq. (10)].

$$I(CF_2CFCl)nI \longrightarrow CF_2{=}CF(CF_2CFCl)_{n-1}I + ICl \quad (8)$$

$$CTFE + ICl \longrightarrow ClCF_2CFClI \quad (9)$$

$$ClCF_2CFClI + CTFE \longrightarrow Cl(CF_2CFCl)_mI \quad (10)$$

Compound **2** reacted with elemental fluorine at 10 °C to give quantitative conversion to **6**. When n was

Table 4
^{19}F NMR spectra of $I(CF_2CFCl)_nI$ telomers, integral areas

Structure:	ICF_2-	$-CFCl-$	$-(CF_2-CFCl)_{n-2}-$		$-CF_2-$	$-CFClI$	n
δ (ppm)	49–54	115–122	105–111	123–130	96–104	65–71	
1	2	1.1	3.5	1.3	1.8	0.4	3.6
2	2	1.3	3.6	1.5	1.6	0.4	3.7
3	2	1.3	4.1	1.9	2.0	0.8	4.0
3a	2	0.9	0.6	0.2	1.8	0.8	2.3
3b	2	0.8	2.5	1.0	1.8	0.8	3.2
4	2	0.9	8.1	3.9	1.6	0.9	6.0
5	2	1.0	14.9	5.3	1.8	0.6	8.7

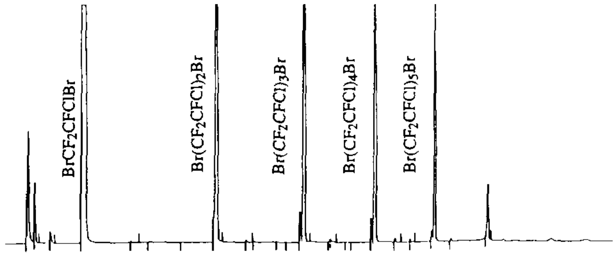

Fig. 1. Gas–liquid chromatogram of telomers $Br(CF_2CFCl)_nBr$.

below 10 oils were formed, but when n was above 10 the product was a grease.

$$I(CF_2CFCl)_nI + F_2 \longrightarrow \underset{(6)}{F(CF_2CFCl)_nF} \qquad (11)$$

Whereas heating a seven-fold excess of hexafluoropropene with **2** for 28 h at 200 °C gave an adduct in less than 40% yield, heating a four-fold excess of tetrafluoroethylene with **2** for 16 h at 165 °C gave $I(CF_2CFCl)_nCF_2CF_2I$. In one experiment, ethylene added to both ends of **2** in low yield.

3. Experimental details

3.1. Materials and procedures

Products were identified by capillary GLC using 25 m×0.2 mm glass HP-1 dimethylsilicone column and an FID detector. The oven temperature was programmed at 40 °C for 5 min followed by heating at 10 °C min^{-1} to 270 °C. Peaks were identified by GLC–mass spectrometry. Major products were isolated by distillation or preparative GLC and identities confirmed by GLC–MS, and ^{19}F ($CFCl_3$ reference) and ^{1}H NMR spectroscopy. Iodine beads were obtained from the Aldrich Chemical Company. Chlorotrifluoroethylene (CTFE) was obtained from the PCR company and Fluorochem Ltd.

3.2. 1,2-Diiodochlorotrifluoroethylene (1)

CTFE (63.69 g, 0.55 mol) and iodine crystals (21.11 g, 0.083 mol) were sealed into a heavy-walled borosilicate glass Carius tube and the tube was irradiated outdoors in sunlight (55° lat., June) with the tube held in a horizontal position. Liquid CTFE occupying about three-quarters of the tube, coloured pink with some dissolved iodine. Most of the iodine was as a solid on the bottom of the tube. Reaction was qualitatively followed by the depth of free iodine crystals remaining when the tube was temporarily held in a vertical position. Iodine consumed (days of irradiation) was 6.4 g (1), 9.3 g (2), 13.2 g (3.6) and 17.4 g (7). Cooling and opening of the tube followed by evaporation of gaseous material yielded recovered CTFE (51.6 g, 0.44 mol), wetted iodine (3.71 g, 14.6 mmol) and a purple liquid (28.9 g). A portion of the liquid was vacuum-transferred at room temperature (0.3 Torr) and this fraction contained 97% (by ^{19}F NMR) of 1,2-diiodochlorotrifluoroethylene (**1**). (Analysis: Found: C, 6.3; Cl+F, 25.8%. C_2ClF_3I requires: C, 6.47; Cl+F, 24.94%.) ^{19}F NMR (235 MHz, $DCCl_3$) δ: −43.40 (1F, dd, J=187 and 12.4 Hz, 1-F_aFC); −52.20 (1F, dd, J=192 and 28.8 Hz, 1-FF_bC); −65.91 (1F, dd, J=15.8 and 27.86 Hz, 2-CFClI) ppm. ^{13}C NMR (62 MHz) δ: 77.5 (dt, J=318.1, 36.4 Hz, 2-CFClI); 99.8 (td, J=321.5, 37.6 Hz, 1-CF_2) ppm. MS m/z: 370, 372 (M^+, 20%, 6.5%); 335 (M^+ −Cl, 3%); 243, 245 (M^+ −I, 100%, 32%). Exact mass: M^+, 369.7734. $C_2F_3ClI_2$ requires: 369.7730.

3.3. α,ω-Diiodopoly(chlorotrifluoroethylene) telomers from liquid CTFE under pressure

Iodine (45.1 g, 0.35 mol) was divided between three 75 cm^3, 25 mm o.d. heavy-wall borosilicate Carius tubes fitted with Teflon™ plug-type high-vacuum stopcocks. These were attached to a vacuum line, evacuated, cooled to −78 °C and filled with CTFE (172 g, 1.48 mol total). Iodine is slightly soluble in liquid CTFE. The tubes were exposed to the open sky in a horizontal position for 8 d with 5.5 d of 100% June sunshine (45° lat.)

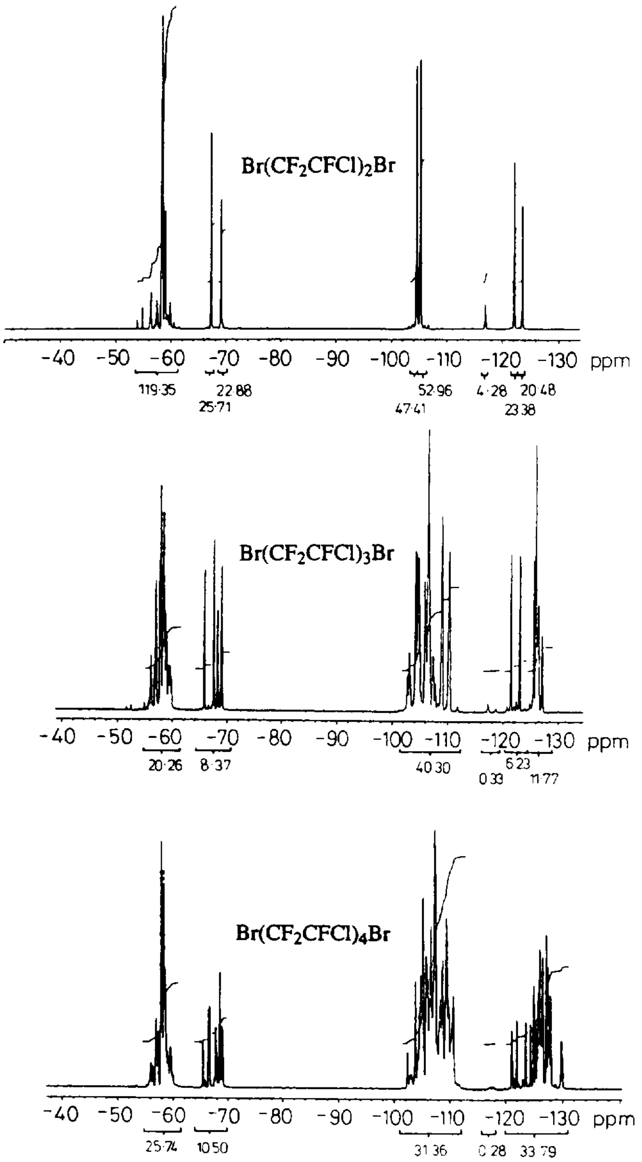

Fig. 2. ^{19}F NMR spectra of individual pure telomers $Br(CF_2CFCl)_nBr$, $n=2,3$ and 4.

at 18–30 °C. At the end of this period, no solid iodine remained. The tubes were cooled, opened and most of the excess CTFE evaporated (101 g, 0.87 mol) with warming to 25 °C. A liquid (96.3 g) and no iodine remained in the tubes. Material balance was consistent with the formula $I(CF_2CFCl)_{3.5}I$ (**2**, $n=3.5$). GLC showed **1**, 15.0%, **2** ($n=1$, 23.3%), **2** ($n=2$, 18.8%), **2** ($n=3$, 15.5%) as well as many other peaks broadened at higher retention time. ^{19}F NMR spectroscopy showed that 27 mol% of the product was **1** and that the remainder was **2**, average $n=4.0$.

The product was separated into four fractions by distillation through a Vigreux column under vacuum: 31 g (25–32 °C/0.09 mmHg), which was shown by GLC to contain **1** (80%); 11 g (52–75 °C/0.01 mmHg), shown by GLC to contain **1** (19%), **2** ($n=2$, 64%), **2** ($n=3$, 14%); 20 g (90–140 °C/0.007 mmHg), shown by GLC to contain **1** (7%), **2** ($n=2$, 51%), **2** ($n=3$, 30%) and broad peaks at higher retention time; 21 g liquid residue. NMR data are listed in Table 4. Repeating the experiment with exposure for 14 d with 11 d of 100% June sunshine (45° lat.) resulted in 9.0 g CTFE recovery (85% conversion) and 66.1 g of a transparent pink grease **2** ($n=8.3$) that melted at 42 °C, but no iodine crystals.

3.4. α,ω-Diiodopoly(chlorotrifluoroethylene) telomers from liquid CTFE at its boiling point

A mixture containing liquid CTFE refluxing at −27 °C boiling point (99.7 g, 0.85 mol) and iodine (5.4 g, 21.3 mmol) was irradiated for 31 h by means of a Hanovia 100 W medium-pressure mercury lamp quartz immersion apparatus, modified with a special low volume reaction vessel, 5 cm in diameter by 16 cm in height, and a borosilicate glass filter sleeve. CTFE (71.68 g, 615 mmol), solid iodine (3.38 g wetted) and liquid **2** (2.12 g) ($n=1$, 39.6%; $n=2$, 12.5%; $n=3$, 3.0%) were recovered. The experiment was repeated with irradiation for 11.5 h, but without the borosilicate glass filter. A red/brown liquid (5.23 g) was recovered which showed two series of telomers by GLC, together with a paste of iodine and liquid (4.12 g). A portion of the liquid was fractionated into four mixtures, (a) 3.3 g (25 °C/1 Torr), (b) 0.35 g (50 °C/0.7 Torr), (c) 0.165 g (100 °C/0.1 Torr) and (d) 1.4 g residue. Fraction (a) contained 40% of a volatile product isolated by preparative-scale GC 97% purity and found to be 4-chloro-4-iodohexafluorobutene {^{19}F NMR, (235 MHz) δ: −88.7 (1F, t, $J=44$ Hz, 1-F_a); −103.7 (1F, m, 1-F_b); −183.8 (1F, m, 2-F); −105 to −111 (2F, m, 3-F); −76 (1F, s, 4-F) ppm. MS *m/z*: 324 (M^+)}. The following were identified by GLC–MS: $CF_2=CF(CF_2CFCl)_2I$, *m/z* 440 (M^+); $CF_2CF(CF_2CFCl)_3I$, *m/z* 521 (M^+-35); and the telomer series $Cl(CF_2CFCl)_nI$, $n=2$, *m/z* 359 (M^+-35); $n=3$, *m/z* 383 (M^+-I).

3.5. α,ω-Dibromopoly(chlorotrifluoroethylene) telomers

Tubes containing iodine (30.5 g, 0.24 mol) and CTFE (115.2 g, 0.993 mol) were exposed to the open sky for 8 d with 5 d of 100% sunshine at 18–30 °C. At the end of this period no solid iodine remained. The tubes were cooled, opened and most of the excess CTFE evaporated (83.7 g, 0.72 mol) on warming to 25 °C. Residues in the tubes were combined as a liquid (62.0 g). Material balance was consistent with the formula $I(CF_2CFCl)_{2.3}I$ (**2**, $n=2.3$). GLC peaks included **2** ($n=1$, 21.9%), **2** ($n=2$, 19.5%) and **2** ($n=3$, 5.9%).

The product (59.9 g) was heated with elemental bromine (56.3 g, 0.705 mol), divided between two Carius tubes in an aluminium block heater held at 112 °C for

112 h. The Teflon stopcocks protruded outside the block. The liquid product containing excess bromine (72.5 g) was poured from solid IBr (43.9 g, 0.212 mol) on to a mixture consisting of 200 g crushed ice and 13 g sodium metabisulphite in a separating funnel. The mixture was shaken as the ice melted, and phase separation gave a liquid lower layer (43.2 g). GLC showed the major product to be the telomer series **4**, with less than 1% telomer impurity (Fig. 1). Identification by GLC–MS was based on the observations of peaks at the corresponding M^+ and $M^+ - Br$ *m/z* values having isotope intensities at the correct ratios. Fractional vacuum distillation from a 50 ml flask through a vacuum-jacketed Vigreux distillation apparatus gave 1,2-dibromo-1-chlorotrifluoroethane (**4**, $n=1$) (17.5 g, 63.4 mmol) (b.p. 88 °C/750 mmHg; lit. value: 92 °C [4]), 1,4-dibromo-1,3-dichloroperfluorobutane (**4**, $n=2$) (5.5 g, 14.0 mmol) (b.p. 44 °C/6.5 mmHg) {^{19}F NMR (188 MHz, $CDCl_3$) δ: −58.2 to −59.0 (m, 2F, $BrCF_2-$); −67.2, −69.1 (2 s, 1F, CFClBr); −104.5, −105.2 (2 m, 2F, $-CF_2CFCl-$); −122.1, −123.6 (2 s, 1F, $-CF_2CFCl-$) ppm. MS *m/z*: 390 (M^+); 310.84682 (M^+-Br) (310.84646 calc. for $C_4F_6Cl_2Br$); 195 ($M^+-C_2F_3ClBr$). IR (capillary film, cm^{-1}): 1234; 1197; 1181; 1155; 1119; 1096; 1028; 960; 893; 864; 822; 696; 659; 622}, 1,6-dibromo-1,3,5-trichloroperfluorohexane (**4**, $n=3$) (4.28 g, 8.42 mmol) (b.p. 42.5 °C/0.07 mmHg) {^{19}F NMR (188 MHz, $CDCl_3$) δ: −56 to −60 (m, 2F, $BrCF_2-$); −65.9, −67.5, −68.2, −68.9 (4 s, 1F, −CFClBr); −102 to −111 (m, 4F, $-CF_2CFCl-$); −121 to −130 (m, 2F, $-CF_2CFCl-$) ppm. MS *m/z*: 506 (M^+); 471 (M^+-Cl); 426.81096 (M^+-Br) (426.81052 calc. for $C_6F_9Cl_3Br$). IR (capillary film, cm^{-1}): 1264; 1194; 1122; 1094; 1026; 997; 892; 861; 670; 600}, 1,8-dibromo-1,3,5,7-tetrachloroperfluorooctane (**4**, $n=4$) (2.97 g, 4.76 mmol) (b.p. 72 °C/0.06 mmHg) {^{19}F NMR (188 MHz, $CDCl_3$) δ: −56 to −60 (m, 2F, $BrCF_2-$); −65 to −69 (m, 1F, −CFClBr); −102 to −111 (m, 6F, $-CF_2CFCl-$); −121 to −130 (m, 3F, $-CF_2CFCl-$) ppm. MS *m/z*: 622 (M^+); 587 (M^+-Cl); 542.77422 (M^+-Br) (542.77459 calc. for $C_8F_{12}Cl_4Br$). IR (capillary film, cm^{-1}): 1273; 1197; 1124; 1028; 970; 878; 856; 796; 670; 597}, 2.75 g of transition fractions and a pot residue (4.8 g) which was liquid at room temperature.

3.6. α,ω-Difluoropoly(chlorotrifluoroethylene) telomers

Telomer **2** ($n=6$) (4.95 g, 5.21 mmol) was dissolved in $CF_2ClCFCl_2$ (6.8 g) and fluorinated by bubbling elemental fluorine, 50% in nitrogen, slowly through the solution over a period of 16 h at 10 °C. The product was mixed with ether, washed with water and dried over magnesium sulphate. ^{19}F NMR analysis indicated complete replacement of iodine with fluorine had occurred to give the average composition $F(CF_2CFCl)_{10}F$, the distribution of *n* (as determined by mass spectrometry–GLC) increasing from 1 in the order 0:0:2.5:1:0.93:0.45:0.17.

3.7. Addition of ethylene to 2

A mixture containing $I(CF_2CFCl)_{5.3\ av.}I$ (0.51 g), 0.02 g of 5% platinum on carbon, $CFCl_3$ (0.5 g) and ethylene (0.10 g) was contained in a 2.2 ml Carius tube and heated for 16 h at 70 °C. Upon evaporation of ethylene and solvent, a liquid (0.52 g) was recovered that had been partially converted to $ICH_2CH_2(CF_2CFCl)_{5.26\ av.}$-$CH_2CH_2I$ (**5**) as evidenced in the ^{19}F NMR spectrum by a 22% reduction of the CF_2I signals at δ 49–54 ppm and a 42% reduction of the CFClI signals at δ 65–71 ppm, and by the ^1H NMR spectrum which exhibited δ 2.7–2.9 (2H, m, CF_2CH_2); 3.23–3.31 (2H, m, CH_2I) ppm.

3.8. Addition of tetrafluoroethylene to 2

$I(CF_2CFCl)_6I$ (1.27 g, 1.33 mmol) was sealed in a 2.5 ml Carius tube with inhibitor-free tetrafluoroethylene (52 g, 5.2 mmol) and hexafluoropropylene (0.14 g, 0.9 mmol). The mixture was heated at 165 °C for 16 h. Unreacted gas, (0.44 g) and a light pink viscous liquid (1.46 g) was recovered. **Caution: TFE polymerisations and tube fracture occurred if a TFE-rich liquid phase separated.** Analysis by ^{19}F NMR spectroscopy showed an 80% reduction in the CFClI signals at δ 65–71 ppm and an equivalent increase in the CF_2I signals at δ 49–54 ppm consistent with 80% conversion to the structure $I(CF_2CFCl)_{5.6\ av.}CF_2CF_2I$.

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