603. *The Reactions of Fluorocarbon Radicals. Part I. The Reaction of Iodotrifluoromethane with Ethylene and Tetrafluoroethylene.*

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The polymerisation reaction between iodotrifluoromethane and ethylene yields new compounds of the type $CF_3{\cdot}[CH_2{\cdot}CH_2]_n{\cdot}I$ (n = 1, 2, and 3). These fluoroiodides have been used to synthesise the mercurial 3 : 3 : 3-*trifluoropropylmercury iodide*, $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}HgI$, and 1 : 1 : 1-trifluoro-hydrocarbons of the general formula $CF_3{\cdot}[CH_2]_n{\cdot}CH_3$ (n = 1 and 3). New short-chain tetrafluoroethylene polymers of the general formula $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ (n = 1—10) have been obtained by the reaction of iodotrifluoromethane with tetrafluoroethylene, and some members of the series have been isolated.

There is already some evidence for the existence of the free trifluoromethyl radical (Haszeldine and Emeléus, *Research*, 1948, **1**, 715). The experiments now described show that this radical, produced photochemically or thermally from iodotrifluoromethane, is able to bring about the polymerisation of ethylene or tetrafluoroethylene. The reactions were of an unusual type and yielded addition polymers of the general formulæ $CF_3{\cdot}[CH_2{\cdot}CH_2]_n{\cdot}I$ and $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$, respectively. Iodotrifluoromethane and ethylene underwent no reaction in the dark at room temperature. When irradiated in quartz or Pyrex-glass vessels, however, there was a slow but quantitative reaction, the main product being 3-*iodo*-1 : 1 : 1-*trifluoropropane*, though in addition 5-*iodo*-1 : 1 : 1-*trifluoropentane* was isolated. A crystalline solid formed in traces during the reaction was possibly 7-iodo-1 : 1 : 1-trifluoroheptane. With optimum conditions no by-products were formed during this reaction.

Mercury catalysed the photochemical reaction between iodotrifluoromethane and ethylene, but, since the catalytic effect was observed when Pyrex-glass as well as silica reaction vessels were used, it is unlikely to be due to photosensitisation involving mercury-resonance radiation. Traces of mercury iodides were formed and it appears that the catalytic effect is related to the prevention of primary recombination of the CF_3 radical and the iodine atom by the reaction of mercury with iodine.

The purely thermal reaction between iodotrifluoromethane and ethylene occurred rapidly and without side-reactions above 200°, the product being similar to that from the reaction initiated by light. Mercury again acted as a catalyst and lowered the minimum temperature for complete reaction by 20—30°.

The reaction mechanism suggested is as follows :

(1) $CF_3I + h\nu = CF_3\cdot + \cdot I$
(2) $CF_3\cdot + CH_2{:}CH_2 = CF_3\cdot CH_2\cdot CH_2\cdot$ (chain initiation)
(3) $CF_3\cdot CH_2\cdot CH_2\cdot + CH_2{:}CH_2 = CF_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot$, etc. (chain propagation)
(4) $CF_3\cdot CH_2\cdot CH_2\cdot + CF_3I = CF_3\cdot CH_2\cdot CH_2I + CF_3\cdot$
or $CF_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot + CF_3I = CF_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2I + CF_3\cdot$ (chain termination)

An unusual chain termination reaction is postulated to explain why the polymer molecules all contain terminal iodine atoms and why molecular iodine is liberated only in traces during the reaction. Chain termination by the combination of a radical with an iodine atom

$$CF_3\cdot CH_2\cdot CH_2\cdot + \cdot I = CF_3\cdot CH_2\cdot CH_2I, \text{ etc.}$$

cannot be of major importance since the quantum yield in the irradiation of iodotrifluoromethane is very small (unpublished observation by Miss J. Banus), so that at any instant the concentration of iodine atoms and trifluoromethyl radicals is low, and the probability of a growing radical chain encountering and combining with an iodine atom to the complete exclusion of a trifluoromethyl or other radical is small. Compounds of the type $CF_3\cdot[CH_2\cdot CH_2]_n\cdot CF_3$ have not been detected in the reaction product. Furthermore, chain termination by the disproportionation of two trifluoropropyl radicals

$$CF_3\cdot CH_2\cdot CH_2\cdot + CF_3\cdot CH_2\cdot CH_2\cdot = CF_3\cdot CH_2\cdot CH_3 + CF_3\cdot CH{:}CH_2$$

or by hydrogen abstraction does not occur under the optimum conditions.

The peroxide-initiated addition of carbon tetrachloride to ethylene to yield products containing 1—4 ethylene units per molecule (Joyce, Hanford, and Harmon, *J. Amer. Chem. Soc.*, 1948, **70**, 2529) and also a number of reactions studied by Kharasch and his co-workers, such as the peroxide-initiated addition of carbon tetrachloride to octene (Kharasch, Jensen, and Urry, *ibid.*, 1947, **69**, 1100), appear to proceed by similar mechanisms, although the conditions and method of initiation are different.

Although an ionic mechanism involving a trifluoromethyl anion would readily explain the nature of the products obtained by the polymerisation of iodotrifluoromethane and ethylene :

$$CF_3I = CF_3^- + I^+$$
$$CF_3^- + CH_2{:}CH_2 = CF_3\cdot CH_2\cdot CH_2^-, \text{ etc.}$$
$$CF_3\cdot CH_2\cdot CH_2^- + CF_3I = CF_3\cdot CH_2\cdot CH_2I + CF_3^-, \text{ etc.}$$

it is considered unlikely that a heterolytic bond fission occurs in these vapour-phase reactions.

Under the conditions used for the reaction between iodotrifluoromethane and ethylene, the main products, 3-iodo-1 : 1 : 1-trifluoropropane and 5-iodo-1 : 1 : 1-trifluoropentane, did not undergo a further reaction with ethylene to yield higher members of the polymer series. When irradiation was continued for several days or when the temperature was raised above 240°, particularly in the presence of mercury, the C–I bond in the iodofluoro-propane and -pentane was broken and molecular iodine (or mercuric iodide) was formed. The fluoro-hydrocarbon radicals underwent reaction as follows :

$$CF_3\cdot CH_2\cdot CH_2I = CF_3\cdot CH_2\cdot CH_2\cdot + \cdot I$$
$$I\cdot + \cdot I = I_2$$
$$CF_3\cdot CH_2\cdot CH_2\cdot + RH = CF_3\cdot CH_2\cdot CH_3 + R\cdot, \text{ etc.}$$

RH was a compound containing hydrogen, probably ethylene, since no fluoropropene or fluoropentene was detected. In this manner 1 : 1 : 1-trifluoropropane and 1 : 1 : 1-*trifluoropentane* were isolated. The combination of two trifluoropropyl radicals to yield hexafluorohexane did not occur. Since the proportion of the fluoropentane in the final product was greater than that of the corresponding iodofluoride in the initial polymer, it was evident that the chain-propagation reaction of the trifluoropropyl radical with ethylene took place to an appreciable extent, leading to a slow conversion of the polymer from iodotrifluoromethane and ethylene into fluoro-hydrocarbons of the general formula $CF_3\cdot[CH_2]_n\cdot CH_3$ where *n* is odd :

$$CF_3\cdot CH_2\cdot CH_2\cdot + CH_2{:}CH_2 \longrightarrow CF_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot \longrightarrow CF_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3, \text{ etc.}$$

There was some evidence for the presence of the compound where $n = 5$, and doubtless a further study of the reaction will lead to the synthesis of higher members of both series.

When the polymer formed initially from iodotrifluoromethane and ethylene was caused to react with excess of ethylene in the presence of mercury, the white crystalline compound 3 : 3 : 3-*trifluoropropylmercury iodide*, $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}HgI$, was produced in small yield. This provides further supporting evidence for a radical-reaction mechanism.

The reaction of iodotrifluoromethane with tetrafluoroethylene was of interest because, although the latter polymerises readily to inert polymers of high molecular weight, no method has so far been found for producing short-chain polymers. The reaction was found to give short-chain polymers containing a terminal iodine atom, which, by reaction with chlorine or a fluorinating agent, could be converted into inert oils and greases. As in the case of ethylene, the reaction was initiated either by irradiation at room temperature or by heat. Mercury had little effect on the reaction. The main product was a white solid, but small amounts of a liquid product were formed which, when treated with excess of tetrafluoroethylene, yielded the solid polymer. From the liquid product the compounds 1-*iodoheptafluoropropane* and 1-*iodoundecafluoropentane* were isolated. The mechanism postulated is

$$CF_3I + h\nu = CF_3{\cdot} + {\cdot}I$$
$$CF_3{\cdot} + CF_2{:}CF_2 = CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}, \text{ etc.}$$
$$CF_3{\cdot}CF_2{\cdot}CF_2{\cdot} + CF_3I = CF_3{\cdot}CF_2{\cdot}CF_2I + CF_3{\cdot}$$

The liquid iodofluorides formed from tetrafluoroethylene, unlike those formed from ethylene, show properties very similar to those of iodotrifluoromethane itself, and readily undergo further reaction with the olefin to yield solid products.

The white solid reaction product from iodotrifluoromethane and tetrafluoroethylene could consist either of straight-chain fluorocarbons of the type $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}CF_3$ formed by the combination of two fluorocarbon radicals, or of iodo-compounds of the type $CF_3{\cdot}[CF_2{\cdot}CF_2]_m{\cdot}I$. The lower members of the fluorocarbon series where $n = 2$, 3, and 4 are liquids with boiling points of 52°, 104°, and 144°, respectively (Haszeldine, unpublished results). These liquids were not present in the reaction product and it is therefore likely that the solid product (which contained iodine), like the liquid, consists of iodofluorides of the type $CF_3{\cdot}[CF_2{\cdot}CF_2]_m{\cdot}I$. With this assumption, the chain length m may be determined by analysis, since chain branching necessitating a C–F bond fission is unlikely. From the solid product ether extraction gave on this basis products represented by formulæ between $CF_3{\cdot}[CF_2{\cdot}CF_2]_6{\cdot}I$ and $CF_3{\cdot}[CF_2{\cdot}CF_2]_{10}{\cdot}I$. The insoluble material, which also contained iodine, was of longer chain length.

Further experiments, to be described later, indicate that the control of reaction conditions will lead to satisfactory yields of the lower iodofluorides. It has also been found that iodopentafluoroethane (Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188) reacts similarly with ethylene and tetrafluoroethylene, and that trifluoromethyl or pentafluoroethyl radicals derived from bistrifluoromethylmercury and bispentafluoroethylmercury (Emeléus and Haszeldine, forthcoming communication) will initiate the polymerisation of olefins. In the case of iodopentafluoroethane the polymers contain an even number of carbon atoms, so that the iodotrifluoromethane and iodopentafluoroethane in their reactions with tetrafluoroethylene appear to offer a means of synthesising straight-chain aliphatic fluorocarbon iodides of any desired molecular weight and with a reactive terminal iodine atom.

EXPERIMENTAL.

Iodotrifluoromethane was prepared in 95% yield by the action of iodine pentafluoride on carbon tetraiodide as described by Banks, Emeléus, Haszeldine, and Kerrigan (*loc. cit.*). Efficient mixing of the reactants by vigorous shaking is essential for good yields. Iodine pentafluoride was prepared in 80% yield (based on fluorine consumption) by passing fluorine over iodine in a 25-cm. silica tube (3 cm. internal diam.) which was slowly rocked and cooled in water. Loss of iodine pentafluoride by conversion into the volatile heptafluoride was avoided by this continuous mixing of unreacted iodine with iodine pentafluoride. The completion of the reaction was indicated when the liquid was decolorised.

The vessels for the polymerisation reactions were Pyrex-glass or silica tubes of approximately 50-ml. capacity, into which the reactants were condensed from a vacuum system. The source of ultra-violet radiation was a Hanovia fluorescent lamp (Code name YEKUL, with an S250 U-type self-starting arc tube) used without the Woods filter; the amount of radiation of wave-length less than 3000 A. penetrating the Pyrex vessels was small.

Reaction between Iodotrifluoromethane and Ethylene under the Influence of Ultra-violet Light.—Typical experiments carried out at room temperature are shown in Table I. The extent of reaction was proportional to the time of exposure to the light source, and the rate of reaction was increased when silica vessels were used.

TABLE I.

Expt. no.	CF_3I (g.).	C_2H_4 (g.).	Time of reaction (hrs.).	CF_3I recovered (%).	C_2H_4 recovered (%).	Polymer (g.).	1 : 1-Adduct in polymer (%).
1	3·0	0·7 [a]	2·2	92	93	0·15	82
2	3·0	0·7	108	54	74	3·10	
3	3·0	0·7	108				
4	3·0	0·7	12	0	61	6·66	82
		0·7	72				
5	3·0	0·7	12				
		0·7	72				

[a] 3·0 G. of iodotrifluoromethane would theoretically react with 0·42 g. of ethylene to give a 1 : 1 adduct.

Expts. 1—3 in Pyrex-glass vessels illustrate the comparatively slow reaction in the absence of mercury. In Expts. 4 and 5, which were carried out in silica vessels, the iodotrifluoromethane and ethylene were irradiated for 12 hours, then an additional 0·7 g. of ethylene was added and the irradiation continued for a further 72 hours. The composition of the polymer was unchanged, and the adducts formed initially had not undergone reaction with excess of ethylene to yield higher members of the polymer series. The prolonged irradiation in Expts. 4 and 5 yielded some 1 : 1 : 1-trifluoropropane (0·24 g.; see later).

The polymeric material from reactions of the type described above was found to contain 3-*iodo*-1 : 1 : 1-*trifluoropropane*, b. p. 90°, n_D^{17} 1·423 (Found : C, 16·0; H, 1·9; I, 57·1; F, 24·3%; *M*, 224. $C_3H_4IF_3$ requires C, 16·2; H, 1·8; I, 56·7; F, 25·4%; *M*, 224), and 5-*iodo*-1 : 1 : 1-*trifluoropentane*, b. p. 153°, n_D^{17} 1·439 (Found : C, 23·6, 23·9; H, 3·0, 3·1; I, 50·0; F, 23·0%; *M*, 250. $C_5H_8IF_3$ requires C, 23·8; H, 3·2; I, 50·4; F, 22·6%; *M*, 252).

The results in Table II illustrate the catalytic effect of a globule of mercury (0·1 g.) on the reaction at room temperature.

TABLE II.

Expt. no.	CF_3I (g.).	C_2H_4 (g.).	Time (hrs.).	CF_3I recovered (%).	C_2H_4 recovered (%).	Polymer (g.).	1 : 1-Adduct in polymer (%).
6	3·0	0·7	2·2	0	40	3·45	78
7	3·0	0·7	120	0	0	4·25	57
8	3·0	0·7	120				

If Expt. 6 in Table II is compared with Expt. 1 in Table I, it is clear that the rate of reaction has been considerably increased, whilst the composition of the polymer is essentially the same. In Expts. 7 and 8, irradiation for a long period brought about some decomposition and 1 : 1 : 1-trifluoropropane (0·45 g.) was isolated (Found : C, 38·7%; *M*, 98. Calc. for $C_3H_5F_3$: C, 36·7%; *M*, 98), b. p. −11°; Henne and Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157) report b. p. −13°. The constitution of the trifluoropropane was confirmed by chlorination to a mixture of 1 : 1 : 1-trifluoro-3 : 3-dichloro- and -3 : 3 : 3-trichloropropane (cf. Henne and Whaley, *loc. cit.*).

Reaction between Iodotrifluoromethane and Ethylene under the Influence of Heat and in the Absence of Light.—The reaction tubes were heated in a rocking-tube furnace in the dark. Specimen experiments are recorded in Table III. In these no mercury was used.

TABLE III.

Expt. No.	CF_3I (g.).	C_2H_4 (g.).	Temp.	Time (hrs.).	CF_3I recovered (%).	C_2H_4 recovered (%).	Polymer (g.).	1 : 1-Adduct in polymer (%).
9	3·0	0·7	180°	40	93	90	0·42	—
10	3·0	0·7	180	40				
11	3·0	0·7	250	48	0	37	6·80	75
12	3·0	0·7	250	48				
13	3·0	0·7	250	20	0	75	6·66	74
		0·7	250	24				
14	3·0	0·7	250	20				
		0·7	250	24				

At 180° (Expts. 9 and 10) the reaction was incomplete, but at temperatures between 200° and 250° (*e.g.*, Expts. 11 and 12), the reaction was complete and no side-reactions could be detected. In experiments such as 13 and 14, attempts were made to convert the polymer formed after 20 hours' reaction into higher members of the polymer series by treatment with a further 0·7 g. of ethylene. These failed and the amount and composition of the product were unaltered.

Table IV shows typical experiments carried out in the presence of mercury (0·1 g.).

Expts. 15 and 16 should be compared with Expts. 9 and 10 (Table III); the effect of mercury as a catalyst is clearly seen. The reaction products from catalysed reactions contained rather more of the longer-chain material than those from non-catalysed reactions. In Expts. 17 and 18, 1 : 1 : 1-trifluoropropane was formed in small amount (0·3 g.). Experiments of this type also yielded high-boiling material which appeared to contain 7-iodo-1 : 1 : 1-trifluoroheptane and 9-iodo-1 : 1 : 1-trifluorononane, although these compounds have not yet been isolated in a pure state.

TABLE IV.

Expt. no.	CF_3I (g.).	C_2H_4 (g.).	Temp.	Time (hrs.).	CF_3I recovered (%).	C_2H_4 recovered (%).	Polymer (g.).	1 : 1-Adduct in polymer (%).
15	3·0	0·7	180°	40	10	50	5·70	70
16	3·0	0·7	180	40				
17	3·0	0·7	220	18	0	31	6·05	62
18	3·0	0·7	220	18				

Mercury enters into the reaction to a slight extent at higher temperatures and some mercuric iodide is formed. Extraction of the mercuric iodide with ether, evaporation of the ethereal solution, and sublimation of the residual crystalline solid, yielded 3 : 3 : 3-*trifluoropropylmercury iodide*, which sublimes at 60° in the form of glistening needles (Found : C, 9·0; H, 1·0; Hg, 47·0. $C_3H_4IF_3Hg$ requires C, 8·5; H, 0·9; Hg, 47·2%).

Synthesis of 1 : 1 : 1-*Trifluoro-hydrocarbons*.—Iodotrifluoromethane (6·0 g.) was heated at 250° with ethylene (1·4 g.) for 3 hours in the presence of mercury (2 ml.) and in the absence of light. A trace of mercuric iodide could be observed, and the iodofluoride had been completely converted into 3-iodo-1 : 1 : 1-trifluoropropane and 5-iodo-1 : 1 : 1-trifluoropentane. A further quantity of ethylene (1·4 g.) was added to the reaction vessel, which was then reheated for a further 30 hours. Only a small amount of material with a b. p. >50° then remained (1·7 g.), and the amount of mercuric iodide present had increased considerably. In addition to unchanged ethylene (0·39 g.; 14%), there were two compounds present in the product with b. p. <50°. These were (*a*) 1 : 1 : 1-trifluoropropane, b. p. −12° (Found: *M*, 98. Calc. for $C_3H_5F_3$: *M*, 98), isolated in 33% yield and identified as described previously; (*b*) 1 : 1 : 1-*trifluoropentane*, b. p. 47°, isolated in 26% yield (Found : C, 46·8; *M*, 126. $C_5H_9F_3$ requires C, 47·6%; *M*, 126).

Fractionation of the material, b. p. >50°, from experiments of this type showed it to contain unchanged starting material and small amounts of what appeared to be 1 : 1 : 1-trifluoroheptane. This compound has not been fully characterised.

Reaction between Iodotrifluoromethane and Tetrafluoroethylene under the Influence of Ultra-violet Radiation.—When tetrafluoroethylene (1·56 g.) was irradiated alone in a Pyrex tube for 14 hours, polymerisation occurred and a white solid was deposited on the walls of the vessel. Fractionation of the volatile products showed that 60% of the tetrafluoroethylene had polymerised. The long-chain polytetrafluoroethylene was completely insoluble in boiling organic solvents even after extraction for several days, and no sublimation could be detected when the solid was heated at $200°/10^{-5}$ mm. Tetrafluoroethylene (1·25 g.) and iodotrifluoromethane (3·0 g.) were mixed in a silica reaction tube and irradiated. After only a few minutes' exposure, the liquid in the tube set to a translucent jelly which on vigorous shaking was converted into a white solid. Polymer granules were deposited on the sides of the tube and could be seen moving about inside the tube. The reaction was stopped after 45 minutes by immersion in liquid air. The volatile compounds were fractionated *in vacuo* and a liquid (*A*) (0·03 g.) which had a b. p. above room temperature was stored for later examination; 90% of the iodofluoride and 30% of the olefin were recovered unchanged. The solid polymer scraped from the reaction tube (0·3 g.) was extracted with ether in a micro-Soxhlet apparatus for 5 hours. Evaporation of the ethereal extract yielded a solid amounting to 25% of the crude polymer.

Iodotrifluoromethane (3·0 g.) and tetrafluoroethylene (1·56 g.), sealed in a Pyrex vessel and exposed to ultra-violet radiation, underwent a slower reaction than in silica, but the products were very similar and a small amount of (*A*) (0·04 g.) was again isolated. When the time of reaction was extended to 12 hours, more solid polymer was produced (0·45 g.) but no (*A*) could be isolated. Again, if the liquid (*A*) was isolated and irradiated in the presence of tetrafluoroethylene, it was converted into a solid polymer, part of which was soluble in ether.

Iodotrifluoromethane or liquid (*A*) and tetrafluoroethylene showed no reaction in the dark.

The yield of liquid (*A*) was increased (0·1 g.) when iodotrifluoromethane (3·0 g.) and tetrafluoroethylene (1·56 g.) were irradiated for 9 hours in a Pyrex tube packed with glass wool. The solid polymer was not examined in this case.

The combined liquid (*A*) fractions from several experiments with iodotrifluoromethane and tetrafluoroethylene were examined and found to contain 1-*iodoheptafluoropropane* (Found : I, 43·0; F, 44·5%; *M*, 293. C_3IF_7 requires I, 42·9; F, 44·9%; *M*, 296), and 1-*iodoundecafluoropentane* (Found : I, 32·0; F, 54·0%; *M*, 380. C_5IF_{11} requires I, 32·1; F, 52·8%; *M*, 396). The physical constants of these compounds have not yet been determined.

Reaction between Iodotrifluoromethane and Tetrafluoroethylene under the Influence of Heat.—When tetrafluoroethylene was heated alone under the conditions used for the polymerisation reaction with iodotrifluoromethane, no solid polymer was formed; 60% of the tetrafluoroethylene was unchanged, and the remainder had been converted into a saturated dimer of molecular weight 200, presumably cyclic. In addition, small amounts of a compound of molecular weight 150, possibly hexafluoro*cyclo*propane (Benning, Downing, and Park, U.S.P. 2,394,581) but more probably hexafluoropropene, $CF_3\cdot CF\colon CF_2$ (*J. Amer. Chem. Soc.*, 1948, **70**, 2814, 2816, 2817), were isolated.

When iodotrifluoromethane (2·4 g.) and tetrafluoroethylene (1·56 g.) were heated to 200° for 10 hours in the dark, a white solid polymer was formed and 31% of the olefin was recovered unchanged (it proved impossible to separate unchanged iodotrifluoromethane and the dimer of tetrafluoroethylene quantatively). Liquid (*A*) was again present (0·08 g.). The solid polymer (1·17 g.) was soluble to the extent of 35% in ether. Liquid (*A*) was examined as described earlier.

Part of the ether-soluble products from the light- or heat-initiated polymerisation of tetrafluoroethylene and iodotrifluoromethane sublimed at 100—150° at atmospheric pressure in the form of white plates. This *compound* had an average composition corresponding to 6 $-CF_2\cdot CF_2-$ units per molecule of iodotrifluoromethane, *viz.*, $CF_3\cdot[CF_2\cdot CF_2]_6\cdot I$ (Found : C, 19·5; I, 16·1. $C_{13}IF_{27}$ requires C, 19·6; I, 16·0%). Small amounts of shorter-chain polymer could be isolated. The remainder of the ether-soluble material sublimed *in vacuo* and gave products containing 7—10 $-CF_2{\cdot}CF_2-$ units per molecule; *e.g.*, for $CF_3{\cdot}[CF_2{\cdot}CF_2]_{10}{\cdot}I$—Found: C, 20·9; I, 10·8. $C_{21}IF_{43}$ requires C, 21·1; I, 10·6%.

Part of the ether-insoluble products from the polymerisation reactions could be purified by sublimation in high vacuum and contained 10—15 $-CF_2{\cdot}CF_2-$ units per molecule.

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