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# *The telomerisation and polymerisation of fluoro-olefins*

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THE DURHAM COLLEGES IN THE  
UNIVERSITY OF DURHAM

A THESIS

entitled

THE TELOMERISATION AND POLYMERISATION OF  
FLUORO-OLEFINS

submitted by

PETER N. PLIMMER, B.Sc.

(St. Cuthbert's Society)

A candidate for the degree of Doctor of Philosophy

1962



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Summary of the work contained in this thesis.

Several co-polymer systems have been irradiated by gamma rays from  $\text{Co}^{60}$  in the presence of various telogens (chain transfer agents) to produce short chain co-telomers. Each system investigated contained one olefin, A, which did not homopolymerise under the conditions of the reaction; and one olefin, B, which readily homopolymerised under the conditions of the reaction. As a result of the initial investigation, two telogens were shown to be efficient, in that they successfully shortened the co-polymer chains, producing viscous liquids or semi-solids. These two telogens were  $\text{CH}_3\text{OH}$  and  $\text{CF}_3\text{COOH}$ .

The co-polymer systems investigated were, on the whole, ones which had not been investigated before; but two established systems, TEFLON 100-X, and VITON were also investigated. The systems are tabulated below, together with an indication of how good a yield of co-telomer was formed.

S Y S T E M	OLEFINS		TELOGEN	APPROXIMATE PRODUCT YIELD BASED ON (% CONVERSION OF OLEFINS B)
	A	B		
1	$\text{C}_3\text{F}_6$	$\text{C}_2\text{F}_4$	Nil	100% co-polymer
			$\text{CH}_3\text{OH}$	100% conversion to $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$ and co-polymer
			$\text{CF}_3\text{COOH}$	100% co-telomer

/cont.



SYSTEM	OLEFINS		TELOGEN	APPROXIMATE PRODUCT YIELD BASED ON (% CONVERSION OF OLEFINS B)
	A	B		
2	$C_3F_6$	$CF_2=CH_2$	Nil	100% co-polymer
			$CH_3OH$	100% co-telomer plus $H(C_3F_6)CH_2OH$
			$CF_3COOH$	80% co-telomer
3	$C_4F_6$ 	$CF_2=CH_2$	Nil	20% co-polymer
			$CH_3OH$	40% co-telomer plus $H(C_4F_6)CH_2OH$
4	$C_6F_{10}$ 	$CF_2=CH_2$	Nil	100% polyvinylidene fluoride
			$CH_3OH$	100% conversion to $CH_2OH(C_6F_{10})H + 50\% P.V.F.$
5	1,4- $C_6F_8$ 	$CF_2=CH_2$	Nil	100% co-polymer
			$CH_3OH$	100% co-telomer plus $H(C_6F_8)CH_2OH$
			$CF_3COOH$	50% co-telomer
6	1,3- $C_6F_8$ 	$CF_2=CH_2$	Nil	low yield of simple adduct
			$CH_3OH$ $CF_3COOH$	20% co-telomer poor yield co-telomer
7	1,3- $C_6F_8$ 	$(CH_2=CH)_2$	Nil	100% co-polymer
			$CH_3OH$ $CF_3COOH$	} mixed products

In each case the co-polymers themselves were prepared for reference. The co-polymers of 1,4- $C_6F_8$ ;  $CF_2=CH_2$  and  $C_4F_6$ ;  $CF_2=CH_2$  are new. In order to elucidate the products from a co-telomerisation reaction, it was necessary to prepare, separately, the possible by-products from such a reaction, i.e. adducts of methanol, say with  $C_6F_{10}$  or  $C_4F_6$ . The first part of this thesis describes, therefore, the reactions of various telogens with individual olefins. Several new alcohols were prepared during the course of this work i.e.  $H(C_6F_{10})CH_2OH$ ;  $H(C_6F_8)CH_2OH$  (1,4-diene);  $H(C_3F_6)CH_2OH$ , all in high yield, and  $H(C_4F_6)CH_2OH$  in moderate yield.

Some of the co-telomers tended to lose HF readily on standing in moist air, especially the 1,4- $C_6F_8$ ;  $CF_2=CH_2$ ;  $CH_3OH$  co-telomers. Attempts were made to stabilise this particular co-telomer (a) by catalytic hydrogenation, and (b) treatment with amine, to encourage cross-linking. Neither attempt led to the formation of stable co-telomers. The  $C_3F_6$ ;  $CF_2=CH_2$ ;  $CH_3OH$  co-telomer alcohols were investigated chemically by treatment with (a) amine, (b) anion exchange resin, and (c) esterification with a dibasic carboxylic acid using trifluoroacetic anhydride as promoter. The first (a) led to a certain amount of degradation while (b) led to an increase in molecular weight together with the formation of a high degree of unsaturation by HF removal. The last (c) led to a mixture of thermally stable esters being formed, part of which it was possible to distil. Esters of the adduct  $H(C_3F_6)CH_2OH$  were also prepared, and found to be colourless, high boiling, thermally stable liquids.

A certain amount of radiochemistry has been done, mainly concerned with

radio-iodine exchange with  $i\text{-C}_3\text{F}_7\text{I}$ , and source dosimetry, using the Ferrous/Ferric oxidation method.

### Conclusion.

Some general principles have emerged as a result of this work, the main ones being as follows:

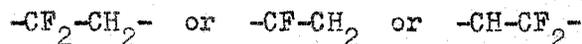
(a) If it is possible to prepare a co-polymer from a non-homopolymerisable olefin, and a homopolymerisable olefin, it should be possible to co-telomerise this mixture of olefins using a suitable telogen (chain transfer agent).

(b) Using a large excess of the non-homopolymerisable olefin, the resulting co-telomer should contain a one-to-one molar ratio of olefins.

(c) By diminishing the excess referred to in (b) a co-telomer could contain any required molar ratio of olefins, thus having various consistencies ranging from solid, through waxes to viscous liquids.

(d) The use of this co-telomerisation technique results in the final co-telomer mixtures having a functional end-group, which could be modified by either fluorination, or (in the case of  $-\text{CH}_2\text{OH}$  end groups) by ester formation, or formation of the iodide and subsequent coupling. Certain conditions must be taken into account for producing useful co-telomers however.

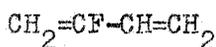
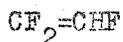
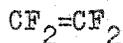
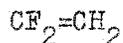
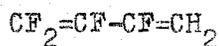
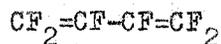
(e) It is necessary to have a certain amount of hydrogen present in the co-telomer backbone, since if it is required to cross-link the co-telomer chains it is useful to be able to eliminate HF to produce sites for cross-linking. This means that the backbone of the chain must contain units such as:



It is recommended therefore, that when selecting olefins for co-telomerisation experiments this is kept in mind. [Olefins which are possibly suitable for this are listed below.]

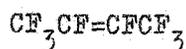
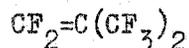
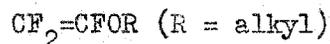
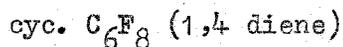
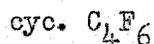
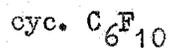
This hydrogen can be introduced via either olefin; for example  $\text{CH}_2=\text{CF}_2$  with a fully fluorinated non-homopolymerisable olefin, or  $(\text{CF}_3)_2\text{C}=\text{CH}_2$  plus a homopolymerisable fully fluorinated olefin.

HOMOPOLYMERISABLE



NON-HOMOPOLYMERISABLE

(By gamma irradiation)



Any combination of these two lists, bearing in mind the condition (e), should co-telomerise. Of course there are many other possible combinations. Only olefins containing C, H, F (with the exception of  $\text{CF}_2=\text{CFOR}$ ) have been considered, but chlorine containing olefins such as  $\text{CF}_2=\text{CFCl}$ ,  $\text{CF}_2=\text{CCl}_2$  or  $\text{CFCl}=\text{CFCl}$  would probably be well worth investigating.

Uses of co-telomers.

These viscous liquids could possibly be used as plasticisers,

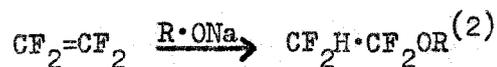
lubricants, or heat exchangers. The crystalline co-polymer (1,4- $C_6F_8$ ;  $CF_2=CH_2$ ) could be used as a coating since it is soluble in acetone and could be applied in solution, and on evaporation of solvent, leave a film.

The elastomers (1,3- $C_6F_8$ ;  $CH_2=CH-CH=CH_2$  and  $c$   $C_4F_6$ ;  $CF_2=CH_2$ ) fall in the same category as VITON A (the co-polymer of  $C_3F_6$  with  $CF_2=CH_2$ ).

CHAPTER 1: Introduction

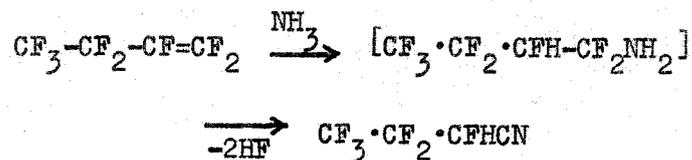
## Fluoro-olefins<sup>1</sup>

Fluoro-olefins undergo the same types of reactions as undergone by hydrocarbon olefins, i.e. electrophilic, nucleophilic, and free radical addition reactions. They differ from hydrocarbon olefins in their reluctance to undergo electrophilic addition, and their increased tendency to undergo nucleophilic additions, olefins containing a terminal =CF<sub>2</sub> group showing this tendency most pronouncedly. The reason for this tendency is due to the decreased electron density at the double bond, making the approach of an electrophile less favourable than the approach of a nucleophile. Thus, ether formation occurs readily<sup>2</sup>:-

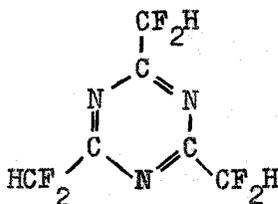
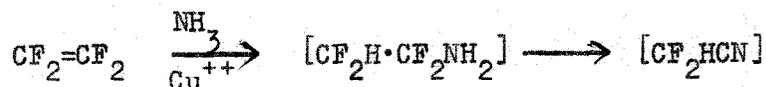


Base-catalysed or nucleophilic reactions, which are accompanied by loss of hydrogen fluoride, are interesting in their application to polymer chemistry for the creation of sources of unsaturation for the purpose of cross-linking.

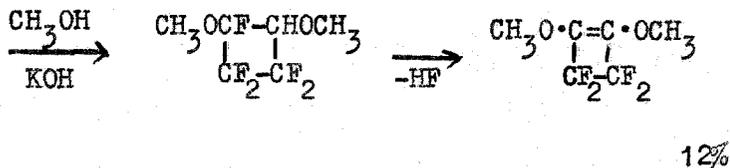
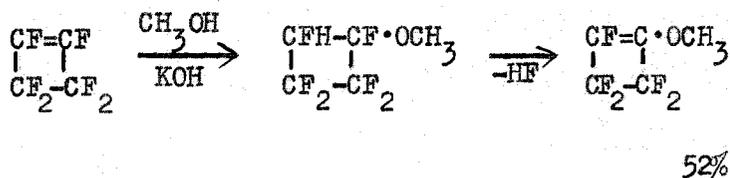
One such reaction involves simultaneous loss of hydrogen fluoride where ammonia, or a primary or secondary amine, is employed as the nucleophile<sup>3</sup>:-



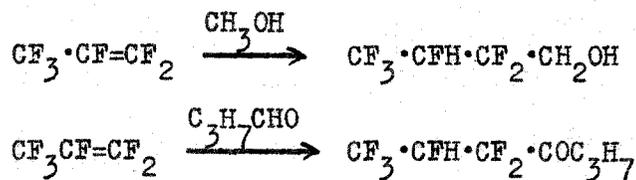
and in the case of tetrafluoroethylene an explosive reaction occurs with the formation of a triazine:



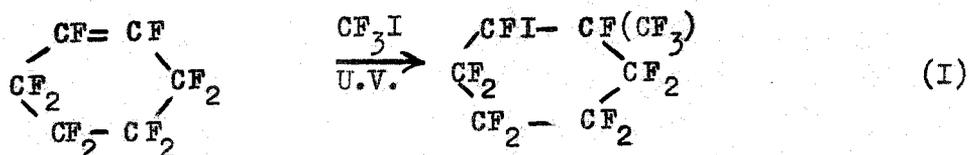
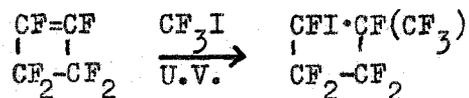
Base-catalysed addition of methanol to hexafluorocyclobutene results in dehydrofluorination of the product<sup>4</sup>:-



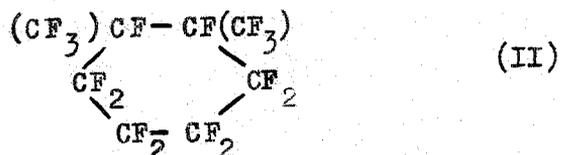
Alcohols or aldehydes can also be added to fluoro-olefins, by a free-radical mechanism, to form alcohols and ketones respectively<sup>5</sup>:-



This type of reaction is likewise applicable to cyclic fluoro-olefins<sup>6</sup> which are also susceptible to free-radical attack, although only slowly, with ultra-violet initiation:-



+

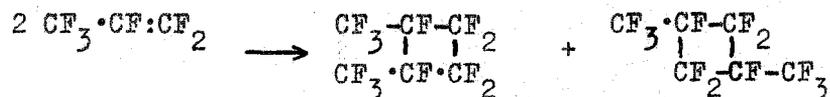


The formation of (II) is claimed to be the first example of ortho di-addition of such a group.

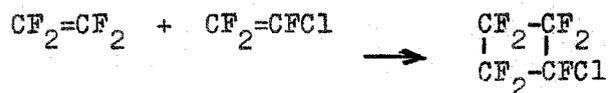
The more unusual type of free radical reaction undergone by fluoro-olefins, which is peculiar to fluoro-olefins, is their formation of cyclic dimers,<sup>7,8</sup> whereas non-fluorinated olefins form linear dimers on heating:-



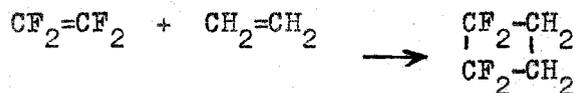
Some unsymmetrical fluoro-olefins,<sup>9,10</sup> such as perfluoropropylene, undergo mixed head-to-head, tail-to-tail dimerisation with the formation of three of the possible four stereo-isomers<sup>9</sup>:-



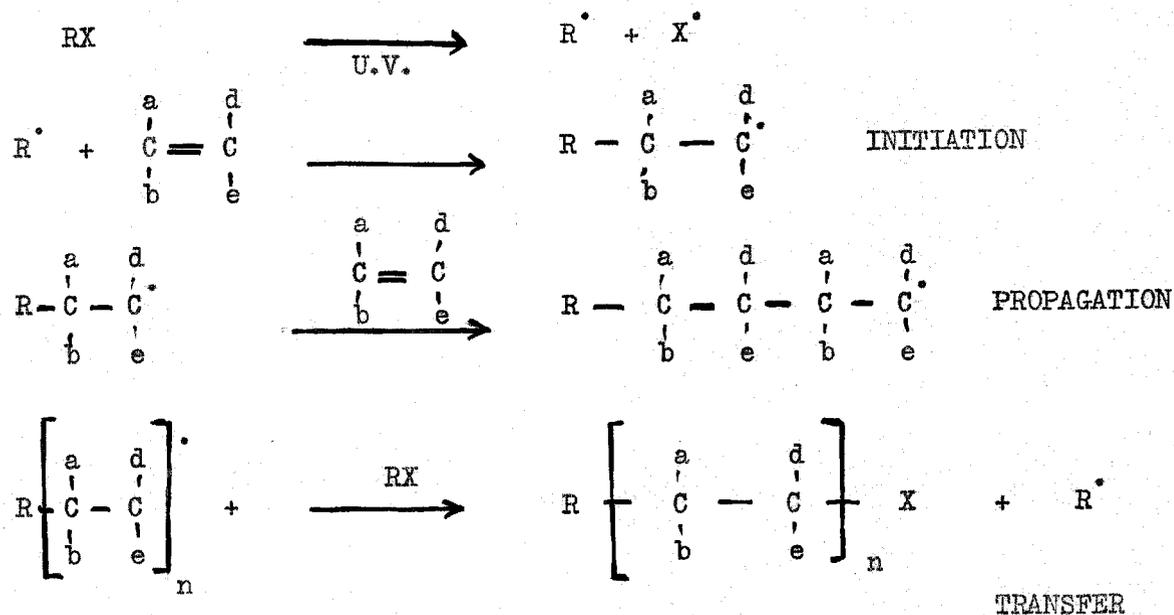
Cyclic dimers of mixed fluoro-olefins have also been prepared<sup>13</sup>:-



as well as dimers from fluoro-olefins with non-fluorinated olefins:<sup>11, 12</sup>



During the free radical additions to fluoro-olefins, there is a strong tendency for telomers to form. Telomerisation also occurs with hydrocarbon olefins, but the ease with which fluoro-olefins undergo this type of reaction provides a method for the preparation of fluorocarbon derivatives not involving fluorination of the corresponding hydrocarbon, the mechanism being as follows:-



The factors influencing telomerisation of fluoro-olefins will be discussed later, but it is a general observation that the proportion of

olefin units in a telomer depends a great deal on the relative molar proportions of olefin to chain transfer agent (RX) used, as has been shown by Haszeldine:<sup>14,15</sup>

MOLAR RATIOS		% OF MONOMER UNITS (n) IN THE TELOMER			
CHAIN TRANSFER AGENT $\text{CF}_3\text{I}$	OLEFIN $\text{C}_2\text{F}_4$	n = 1	2	3	720
		10	1	94	
1	1	16	10	65	
1	10				94

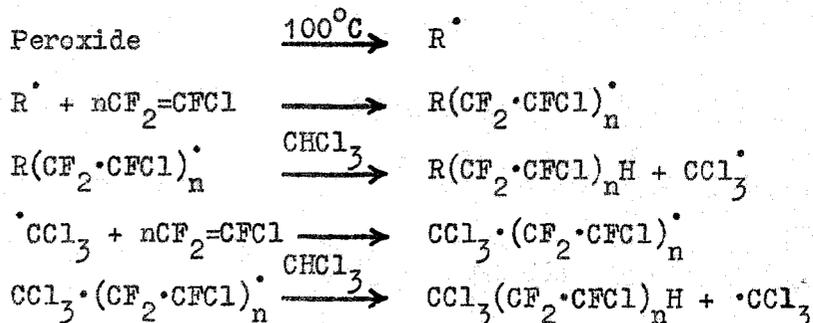
The chain length, n, is diminished by the use of a large excess of chain transfer agent. This type of process will now be discussed at length.

TELOMERISATION - historical, and empirical rules.

Telomerisation has been defined in general terms by Hanford and Joyce as: "The process of reacting together under polymerisation conditions, a molecule YZ, which is called a TELOGEN (chain transfer agent) and more than one unit of a polymerisable compound, A, having ethylenic unsaturation called a TAXOGEN, to form products called TELOMERS, having the formula  $\text{Y}(\text{A})_n\text{Z}$ , where n is an integer greater than one, and Y and Z are fragments of the telogen attached to the terminal taxogens."

One of the first examples of telomerisation of a fluorinated olefin monomer was discovered by Miller<sup>153</sup>, whilst attempting to polymerise

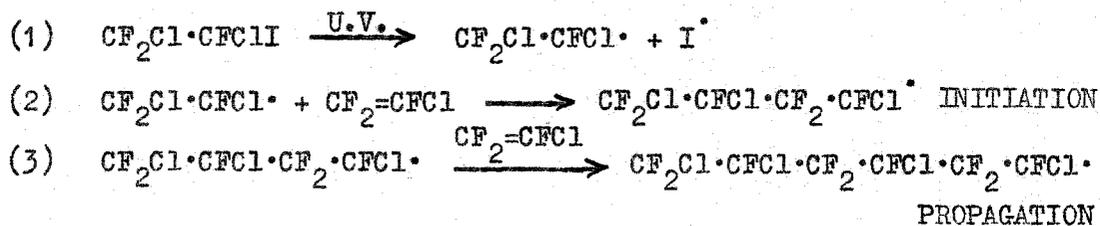
chlorotrifluoroethylene with peroxide initiation in a medium of chloroform and water. He obtained low molecular weight polymeric oils, containing more chlorine than expected for a homopolymer of chlorotrifluoroethylene. He concluded that the chloroform had taken part in the process by a chain-transfer mechanism which he postulated as:-

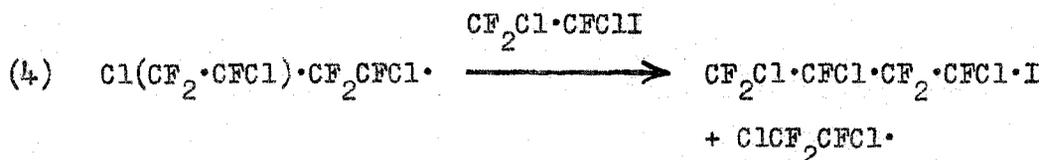


Hanford and co-workers<sup>18, 179</sup> also carried out a telomerisation reaction with ethylene using carbon tetrachloride as telogen.

In more recent years, an exhaustive study of the telomerisation of chlorotrifluoroethylene with a telogen prepared by the addition of iodine monochloride to chlorotrifluoroethylene ( $\text{CF}_2\text{Cl}-\text{CFClI}$ <sup>19</sup>) has been carried out by Haszeldine.<sup>20</sup> The olefin has been shown to homopolymerise and to be attacked by radicals at the  $\text{CF}_2$  end of the molecule.<sup>21, 22, 23, 24</sup>

By irradiating this mixture with ultra-violet light, an interesting series of compounds can be obtained in good yield with a very smooth reaction, the mechanism of which he proposes to be:





TRANSFER

Haszeldine has shown previously<sup>15</sup> that the chain length could be controlled by varying the ratio of telogen to telogen, i.e. by using a large excess of telogen and, if necessary, irradiating the liquid phase only, where telogen concentration is maximum, to ensure low telomer formation.

Using this excess, step (4) can compete with step (3) with the formation of telomers having low n values.

In the above reaction scheme, the following molar ratios were used:

TELOGEN	OLEFIN	n = 1	n = 2	n = 3	n = 4
13	1	75%			
1	1		18%	14%	56%
1	5				90%

giving the values of n as shown. As a result of this investigation, Haszeldine drew several conclusions about factors which influence the telomerisation of fluoro-olefins with polyhalogenoalkyl radicals.

#### FACTORS INFLUENCING TELOMERISATION.

The studies were carried out using telogens of the form R·CFXY.

- (1) INITIATION STEP. Initiation was achieved via the radical RCFX· (e.g. CF<sub>3</sub>·, C<sub>2</sub>F<sub>5</sub>·, CF<sub>2</sub>ClCFCl·) formed from RCFXY. The rate of generation of the initiating radical RCFX· (e.g. R = polyhalogenoalkyl, or F; X = halogen or hydrogen; Y = a halogen of higher molecular weight than X)

depends upon the following factors:-

(a) The strength of the C-Y bond, i.e. the weaker C-Y, the greater the ease of generation of RCFX (and the greater the stability of this radical). The nature of both Y and X determines the C-Y bond strength which decreases in the series:  $Y = F > Cl > Br > I$  for a given X, and which has been predicted to decrease in the series  $R \cdot CF_2 - Y (Y = F) > RCF_2 - Y (Y = Cl) > RCHF - Y (Y = Cl) > RCFCl - Y (Y = Cl) > RCF_2 - Y (Y = Br) > RCHF - Y (Y = Br) > RCFCl - Y (Y = Br) > RCFBr - Y (Y = Br) > RCF_2 - Y (Y = I) > RCHF - Y (Y = I) > RCFCl - Y (Y = I) > RCFBr - Y (Y = I) > RCFI - Y (Y = I)$  (e.g.  $CF_3CCl_2I$  and  $CF_2Cl \cdot CCl_2I$  are very efficient telogens<sup>19</sup>).

The effect of X on the C-Y bond energy has been investigated<sup>25</sup> and the reason for the effect has been attributed to the stability of the RCFX· radical produced and the increase in steric strain which occurs as X becomes larger.

(b) The means of supplying the energy for homolytic fission of the C-Y bond e.g. dose rate, intensity of ultra-violet light, temperature, concentration of peroxide, etc., depending on the initiation used.

After generation of RCFX·, attack on the olefin depends mainly on the reactivity of the olefin towards radical attack, and to a lesser extent on the reactivity of the attacking radical RCFX·.

In general, halogen, bonded to the doubly bonded carbon atoms, or to carbon atoms adjacent to these, in an olefin containing more than three carbon atoms, decreases the ease of radical attack, relative to the unsubstituted olefin.<sup>26, 27, 21, 122, 28, 29</sup>

Halogenoethylenes are special cases since the polyfluoro- and chloropolyfluoroethylenes polymerise readily. In general, the greater the atomic weight of the halogen in a halogenoethylene, and the more symmetrically it is distributed (i.e.  $\text{CFCl}=\text{CFCl}$  or  $\text{CF}_2=\text{CCl}_2$ ), the less readily does the olefin polymerise and the less readily is it attacked by a free radical.

The reactivity of  $\text{RCFX}\cdot$  is seldom of sufficient importance to be decisive in telomerisation reactions, since the more reactive olefins readily combine with even the least reactive radicals. It is only with olefins heavily, or symmetrically, substituted by halogen, such as chlorine or bromine, or in which inhibition of radical attack occurs, that the less reactive radicals fail to add, and more reactive radicals must be used.

## (2) PROPAGATION.

The efficiency of this step, which is always competing with the chain-transfer step:



depends upon:-

- (a) the ease of polymerisation of the olefin.
- (b) the reactivity of the intermediate free radical  $\text{RCFX}(\text{olefin})\cdot$  towards the olefin, and towards  $\text{RCFX}\cdot\text{Y}$ .
- (c) the stability of the product  $\text{RCFX}(\text{olefin})\text{Y}$ .
- (d) the relative ease of the chain transfer step.

Taking these points in turn and enlarging on them,

(a) An olefin which reacts readily with fragments of a decomposing peroxide to give a polymer of high molecular weight will, in general, tend to give a longer chain polymer with  $R\cdot CFXY$  than one which does not. This is illustrated by comparison of  $C_2F_4$ ,  $CF_2=CFCl$  or  $CF_2=CFH$ ; with say,  $CHCl=CCl_2$  or  $CF_3CF=CF_2$ . The ease of polymerisation is related to the ease of radical attack, and other factors, since in some cases the order of ease of radical attack is the reverse of the ease of homopolymerisation of the olefins (see page 15.).

(b) Why a radical such as  $R\cdot CFX\cdot CH_2\cdot CH_2\cdot$  should attack  $R\cdot CFXY$  rather than another molecule of ethylene, whereas another radical such as  $R\cdot CFX\cdot CF_2\cdot CF_2\cdot$  should attack another molecule of  $CF_2=CF_2$  rather than  $R\cdot CFXY$ , is related to the differences between the C-Y and the C-C bond energies in  $R\cdot CFX\cdot CH_2\cdot CH_2\cdot Y$  and  $R\cdot CFX\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot$  or in  $R\cdot CFX\cdot CF_2\cdot CF_2\cdot Y$  and  $R\cdot CFX\cdot CF_2\cdot CF_2\cdot CF_2\cdot CF_2\cdot$ . This is an aspect which has not yet been elucidated.

The choice of telogen in some cases is governed by the olefin to be telomerised. If  $CF_3I$  is used in the telomerisation of  $CF_2=CFCl$ , then the initiating radical  $\dot{C}F_3$  is more reactive than the intermediate free radical  $CF_3\cdot CF_2\cdot CFCl\cdot$  and the chain transfer process is efficient, short chains being produced when equimolecular proportions of reactants are used. Such cases do not often occur.

### (3) CHAIN TRANSFER.

(a) the C-Y bond in both telomer and telogen is important since if

that bond is weak in the telogen compared with the bond in the telomer, then chain transfer occurs easily and the products are mainly  $n = 1$  and  $n = 2$  compounds.

However, if the C-Y bond is stronger in the telogen, then the propagation step is favoured, giving long chains; coupling of growing chains can even occur.

It does not follow that short chain telomers are achieved by using a large excess of telogen.

(b) Cases arise where the C-Y bond strengths in the telogen  $RCFX_Y$  and the telomer  $R \cdot CFX_n$  (olefin) are similar and thus have an equal chance of fission, i.e. the  $n = 1$  or  $n = 2$  telomer reacting as telogens with monomer olefin units.

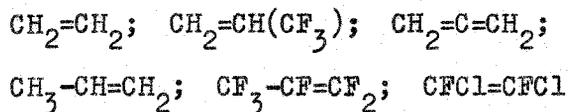
Thus a large excess of telogen has to be used to produce short chains of low  $n$  values.

(c) When an easily homopolymerisable olefin is used with an efficient telogen the chain transfer process is favoured but, to ensure short chain formation, a large excess of telogen is advisable.

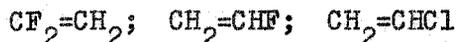
(d) When a telogen which is efficient, is used with an olefin which does not homopolymerise readily, the product tends to be  $RCFX_n$  (olefin) where  $n$  is chiefly unity, and it is difficult to encourage the increase in  $n$  values by increasing the proportion of olefin.

Of course, some olefins just do not homopolymerise and, whether the telogen is efficient or not, no values higher than  $n = 1$  can be obtained by a true telomerisation procedure.

Some difficultly homopolymerisable or non-homopolymerisable olefins are:



Olefins of intermediate homopolymerisability are:



Attempts have been made to cause olefins like  $\text{C}_2\text{H}_4$  or  $\text{C}_3\text{F}_6$  to give telomers with  $n$  greater than unity, by reducing the proportion of telogen. This resulted in the intermediate radical undergoing reactions other than addition to another molecule of olefin, i.e. disproportionation, dimerisation, or expulsion of halogen to give an olefin.

It must be kept in mind that an olefin referred to as non-homopolymerisable in this text, may homopolymerise under the correct conditions of high pressure, catalyst, or special process which are being developed at this time.

Telomer formation by peroxide, ultra-violet, and thermal initiation.

The factors influencing telomerisation can be applied as empirical rules to any telomerisation process. We now consider the three main methods for the initiation of telomerisation processes, beginning with the more usual peroxide or ultra-violet initiated processes. The initiation by purely thermal means is discussed next, with special reference to the process described by Hauptschein<sup>16</sup> to prepare telomer-like products from olefins which do not normally undergo telomerisation reactions (i.e. are non-homopolymerisable under the reaction conditions used).

A final section deals with isomer formation by radical attack on unsymmetrical olefins when forming one-to-one adducts and  $n = 1$  telomers. This has a direct bearing on the structures of long chain telomers, polymers and co-polymers.

TABLE 1.<sup>\*</sup> Summarises the addition of free radicals to olefins, to form either telomers, or simple one-to-one adducts. For the purpose of this thesis, such adducts are considered as  $n = 1$  telomers. It must be borne in mind however that true telomers can only be prepared from olefins which homopolymerise under the conditions of reaction. Thus, when discussing the thermal step-wise addition of fluorocarbon iodides to  $C_3F_6$  performed by Hauptschein,<sup>16</sup> the process will be termed "telomerisation" since the products are the same as if a true telomerisation process had taken place although the mechanism is rather unusual.

<sup>\*</sup> TABLE 1 is found in the wallet in the front of this volume.

Photochemical and peroxide initiated addition and telomerisation of fluoro-olefins - radical formation and attack on fluoro-olefins.

Where perfluoroalkyl iodides are employed as chain transfer agents, the attack is by  $Rf\cdot$  ( $Rf = CF_3, C_2F_5$  etc.) from  $RfI$ . The value of  $n$  can usually be controlled by varying the proportion of iodide to olefin<sup>15</sup> and the direction of attack of the radical on the fluoro-olefin is in general in the same direction as that of the bromine atom from  $HBr$ <sup>30</sup>. However, exceptions have been found where the bromine atom from  $HBr$  attacks the end of the carbon-carbon double bond in the opposite sense to the perfluoroalkyl radical.<sup>26</sup>

In these reactions, the free radicals are formed by homolytic fission of the carbon-halogen bond by ultra-violet light, or peroxides at  $100^\circ C$ . The radicals,  $Rf\cdot$ , formed are extremely reactive<sup>31</sup> and attack a fluorinated olefin at the double bond in such a way as to form the more stable of the two alternative intermediate free radicals.<sup>32</sup>

The direction of radical attack on fluoro-olefins is determined to a lesser extent by the steric accessibility of the carbon atom attacked.<sup>30, 33</sup>

Telomer formation only occurs readily when the olefin attacked by  $Rf\cdot$  is easily homopolymerised under the conditions used.

The ease of radical attack,  $Rf\cdot$ , on fluoro-olefins has been shown to be<sup>6</sup>

$$CF_2=CH_2 > CF_2=CF_2 > CF_2=CHCl > CF_2=CFC1 > CF_3-CF=CF_2^* > CF_3CF=CFCF_3^*$$

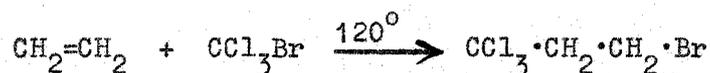
$$> CF=CF^* > \begin{array}{c} CF_2 \\ | \\ CF_2 \\ / \quad \backslash \\ CF_2 \quad CF^* \\ \quad \quad | \\ \quad \quad CF^* \end{array}$$

Not all these form telomers since they do not all homopolymerise.\* under the reaction

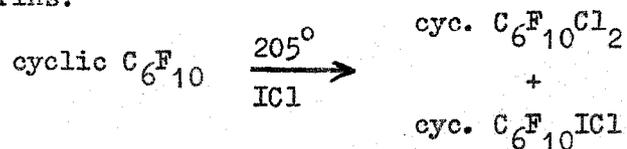
conditions; they all form  $n = 1$  adduct however, and in the case of  $C_3F_6$ , reactions have been carried out to give similar products to those obtained by true telomerisation processes. This type of reaction is dealt with in the next section. It is noted also, that for  $CF_2=CH_2$  and  $CF_2=CF_2$  the order of ease of homopolymerisation  $CF_2=CF_2 > CF_2=CH_2$  is opposite to the order of ease of radical attack which is  $CF_2=CH_2 > CF_2=CF_2$ <sup>6</sup>. This arises later in the discussion, Chapter 2, p. 73.

Thermally initiated addition to and telomerisation of fluoro-olefins

Initiation in this case being by free radicals formed from the thermal decomposition of chain transfer agent. Examples of thermal decomposition of bromo- and iodo- compounds leading to free radical addition to olefins have arisen in the literature both with hydrocarbon olefins:<sup>127</sup>



and fluoro-olefins:<sup>6</sup>



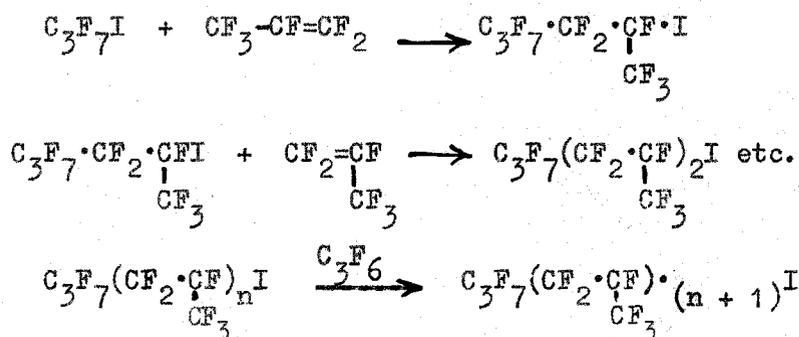
This type of initiation has been extended to cover four fluoro-olefins and is suitable for producing "telomers" from olefins, such as  $C_3F_6$ , which do not homopolymerise under the reaction conditions used, by a stepwise addition mechanism. These olefins are taken in turn.

(a) hexafluoropropylene.<sup>16</sup>

"Telomers" of molecular weights up to 2,500 have been formed, and

the process can be controlled to give  $n$  values from 1 to 15. It may also be adapted to produce "telomers" from other non-polymerisable or poorly polymerisable olefins.

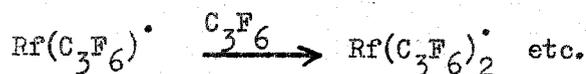
Hauptschein proposes a stepwise addition process, with little contribution from a chain mechanism (hence, by definition, this is not a true telomerisation process), each simple addition product acting as the next telogen, adding across the double bond of the olefin:-



He postulates that no chain transfer occurs, but  $\cdot\text{C}_3\text{F}_7$  and  $\text{I}\cdot$  from the same molecule, add simultaneously across the olefinic double bond without dissociation of the  $\text{C}_3\text{F}_7\text{I}$  molecule. It is more simply explained by saying that in such a system:



the intermediate free radical cannot propagate its own species, i.e.



on energy grounds, and the alternative step proceeds very efficiently, i.e. CHAIN TRANSFER



Increasing the temperature leads to scission of this new C-I bond, followed by addition of olefin, followed by chain transfer to give an

iodide  $\text{Rf}(\text{C}_3\text{F}_6)_2\text{I}$  and the reaction proceeds by this stepwise process - with chain transfer occurring at every discrete step. This excludes the idea of a four-centre reaction process.

He employed other telogens with this olefin, including  $\text{CF}_3\text{I}$ ,  $\text{C}_3\text{F}_7\text{I}$ ,  $\text{C}_4\text{F}_9\text{CFI}$ ;  $\text{C}_4\text{F}_9 \cdot \underset{\text{CF}_3}{\underset{|}{\text{CF}}} \cdot \underset{\text{CF}_3}{\underset{|}{\text{CF}_2}} \cdot \text{CFI}$  and  $\text{CF}_2\text{Cl} \cdot \text{CFClI}$ ; the last of these,  $\text{CF}_2\text{Cl} \cdot \text{CFClI}$ , failed to add to  $\text{C}_3\text{F}_6$  using peroxide initiation at  $100^\circ\text{C}$ ,<sup>34</sup> but this purely thermal method produces "telomers" from  $n = 1$  to bigger than 10, with this pair of reagents.

In thermal "telomerisations" of this sort, the "telomer" series is ascended using the previous "telomer" as the next telogen. The telogen in this context must contain the group  $-\text{CF}_2\text{I}$  or  $-\underset{\text{Rf}}{\underset{|}{\text{CF}}}\text{I}$  (where Rf is polyhalogenoalkyl) in order that this process will occur, otherwise the temperature required to break the  $-\text{C}-\text{I}$  bond is often excessive and leads to decomposition.

Hauptschein has heated excess  $\text{C}_3\text{F}_6$  with iodine monochloride,<sup>19</sup> so forming the telogen  $\text{CF}_2\text{Cl} \cdot \text{CF}(\text{CF}_3)\text{I}$ , which sets up the stepwise addition to  $\text{C}_3\text{F}_6$  forming  $\text{CF}_3-\underset{\text{CF}_2\text{Cl}}{\underset{|}{\text{CF}}}-\underset{\text{CF}_3}{\underset{|}{\text{CF}}}_n\text{I}$ . A similar reaction using iodine with excess  $\text{C}_3\text{F}_6$  is reported in this reference with no details of the products obtained.

At higher temperatures,  $\text{CF}_2\text{Br}_2$  and other bromides have acted as telogens to form "telomer" bromides of  $\text{C}_3\text{F}_6$ <sup>17</sup> with values  $n = 1$  to 6, and it was found unnecessary to control the proportions of olefin or telogen in the reaction mixture. The lower telomers ( $n = 1$  or 2) however were

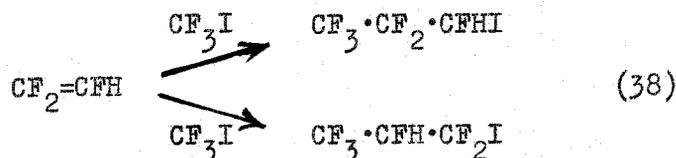


by purely thermal means using  $\text{CF}_2\text{Cl}\cdot\text{CFClI}$  as telogen at quite medium temperatures.<sup>19</sup>

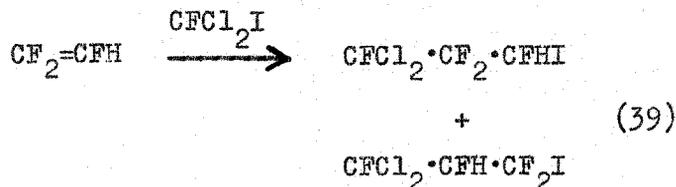
Isomer formation by free radical attack on unsymmetrical  
fluoro-olefins.

The olefins which are considered in this section, are all capable of telomer formation, but the investigations were carried out using very efficient chain transfer agents, and the correct condition for the formation of simple one-to-one adducts. The structure of these adducts could then be determined chemically.

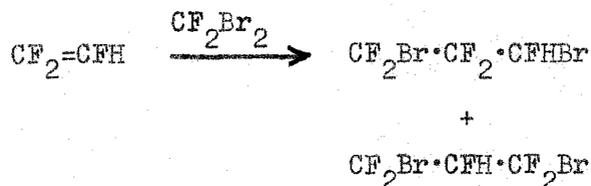
Only three fluoro-olefins to date, have been shown to form isomers on attack by a free radical. Until quite recently it was thought that free radicals added to unsymmetrical fluoro-olefins to yield single products. However, Haszeldine<sup>38</sup> demonstrated that addition of either  $\cdot\text{CF}_3$  or  $\text{Br}\cdot$  (from  $\text{HBr}$ ) to trifluoroethylene gave isomeric products



Two years later, Miller<sup>39</sup> showed isomer formation using  $\text{CFCl}_2\text{I}$  with the same olefin.



Coscia<sup>40</sup> repeated work done by Tarrant<sup>41</sup> using  $\text{CF}_2\text{Br}_2$  as a source of free radicals with trifluoroethylene, under more drastic conditions than used by Tarrant, and found that isomer formation occurred.

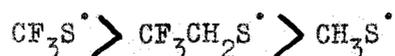


Harris et al<sup>42</sup> used an unusual set of telogens,  $\text{CF}_3\text{SH}$ ;  $\text{CF}_3\text{CH}_2\text{SH}$ , and  $\text{CH}_3\text{SH}$  and obtained isomers using  $\text{CF}_3\text{SH}$  and  $\text{CH}_3\text{SH}$ , the isomers being thioethers,  $\text{CF}_3\text{S}\cdot\text{CF}_2\cdot\text{CFH}_2$  and  $\text{CF}_3\text{S}\cdot\text{CFH}\cdot\text{CF}_2\text{H}$

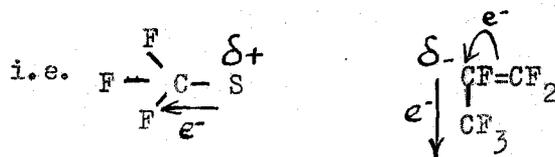
Worker	Initiator	Radical R	$\text{RCHF}\cdot\text{CF}_2\text{Y}$	$\text{RCF}_2\cdot\text{CHF}_2\text{Y}$
Haszeldine	U.V.	$\cdot\text{CF}_3$	80	20
		$\text{Br}\cdot$	60	40
Miller	Peroxide	$\cdot\text{CFCl}_2$	Mainly	
Coscia	Peroxide	$\cdot\text{CF}_2\text{Br}$	80	20
Harris	U.V.	$\text{CF}_3\text{S}\cdot$	98	2
	X-ray	$\text{CH}_3\text{S}\cdot$	75	25

Free-Radical Additions to  $\text{CF}_2=\text{CFH}$  Showing Proportions of Isomers Formed.

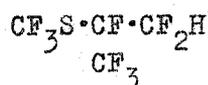
The second olefin found to form isomers on free radical attack is hexafluoropropylene. Harris<sup>42</sup> found both possible isomers of the one-to-one adduct formed, with  $\text{CF}_3\text{SH}$ ;  $\text{CF}_3\text{CH}_2\text{SH}$ ; and  $\text{CH}_3\text{SH}$  in varying proportions which could be correlated with the relative electrophilicities of the attacking thiyl radical which decrease in the order



The olefin is assumed to polarise as in an ionic process, and attack occurs at the negative centre.

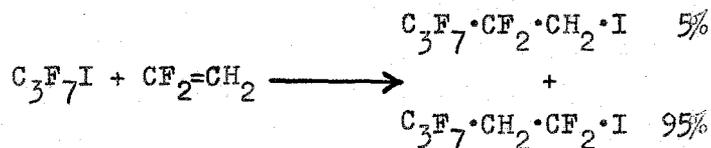


forming the unexpected isomer:



Worker	Initiation	Radical	$\text{R}\cdot\text{CF}_2\cdot\text{CF}(\text{CF}_3)\text{Y}$	$\text{R}\cdot\text{CF}\cdot\text{CF}_2\text{Y}$ $\text{CF}_3$
Harris	U.V. or X-ray	$\text{CF}_3\text{S}\cdot$	45	55
"	U.V.	$\text{CF}_3\text{CH}_2\text{S}\cdot$	70	30
"	X-ray	$\text{CH}_3\text{S}\cdot$	91	9
Hauptschein	Heat	$\cdot\text{CF}_3$	92	8
"	Heat	$\cdot\text{C}_3\text{F}_7$	97	3

Hauptschein<sup>19</sup> reports that small amounts of the unexpected isomer is detected, by gas chromatography, from the addition of  $\text{CF}_3\text{I}$  or  $\text{C}_3\text{F}_7\text{I}$  to  $\text{C}_3\text{F}_6$ . He also claims to have detected the isomers of the addition product of  $\text{C}_3\text{F}_7\text{I}$  with vinylidene fluoride<sup>19</sup>



But Harris,<sup>42</sup> who also used Nuclear Magnetic Resonance study with his products, reports no isomer formation in the additions to vinylidene fluoride. An electrophilic nature of free radicals could explain the formation of the isomers described, and this view is expressed by Waters<sup>180</sup> who suggests that radicals are electrophilic by nature and accordingly should add to the carbon atom of the double bond with the highest electron density i.e. the =CF- of  $\text{CF}_3\text{-CF=CF}_2$  assuming that the polarisation of the double bond is the same in radical additions as in IONIC addition

#### Polymers of fluorine containing olefins.

Polymers containing the elements carbon, fluorine and very little hydrogen or other halogen are extremely inert, being more resistant to chemical attack and to high temperature than hydrocarbon polymers.

This stability to chemical and thermal attack, is due to the high carbon-fluorine bond dissociation energy, and to the shielding effect of the highly electronegative fluorine atoms on the carbon skeleton.

Fluorine is a slightly bigger atom than hydrogen, and in a molecule,  $\text{C}_n\text{F}_{2n+2}$ , the fluorine atoms form a compact shield around the carbon chain, protecting it from chemical attack. These polymers can be classified as follows.

- (I) HOMOPOLYMERS, prepared by successive addition of one monomer olefin unit to itself "n" times, where n is a large integer.
- (II) COPOLYMERS, which can be a uniform or a completely random mixture of two different monomer olefin units prepared by polymerising these two units in the same environment.

In the case of homopolymers, their characteristics (consistency, etc.) are completely unalterable, i.e. for a large 'n' value the homopolymer will always possess the same physical properties, be they thermoplastic, elastomeric or infusible materials.

The consistency of co-polymers, on the other hand can be guided by altering the ratio of the two olefins in the reaction mixture, to give materials having certain desired physical properties, ranging from elastomers to thermoplastics, with complete control. The outstanding point in the preparation of co-polymers is that it is NOT necessary for both olefins to be homopolymerisable. A non-homopolymerisable olefin will sometimes readily co-polymerise with a homopolymerisable olefin in such a way that the resulting co-polymer can often contain up to 50% of the non-homopolymerisable monomer. Some examples follow.

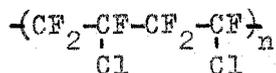
Homopolymers (a) POLYTETRAFLUOROETHYLENE  
(TEFLON)

This polymer was discovered by Plunket<sup>157</sup> in 1941, and is a highly crystalline white solid, with extremely high resistance to chemicals, and thermal attack. In fact, it is the most stable organic synthetic polymer known to date, but has the serious disadvantage that it has no melt stage (i.e. is not a thermoplastic) and needs tedious fabrication by special techniques. It is prepared industrially by peroxide initiation either in an inert fluorocarbon or aqueous medium.<sup>43</sup> Its structure has been studied by infra-red<sup>44</sup> and electron microscope examination.<sup>45</sup> It is an un-cross-linked polymer consisting of co-linear difluoromethylene chains. The patent literature is full of preparative techniques.<sup>46, 160; 47</sup>

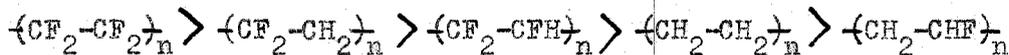
(b) POLYCHLOROTRIFLUOROETHYLENE  
(KEL-F)

This homopolymer is a true thermoplastic, and can be extruded and moulded. It has been prepared by numerous methods<sup>48-54</sup> and is very inert to chemical attack. At higher temperatures and in basic solvents (amines especially) chlorine splits off easily however.

It differs from the TEFLON structure only in the fact that the rigidity of the backbone of highly crystalline Teflon has been diminished by the inclusion of a "pendant" chlorine, a bulky atom. The structure of KEL-F has been shown to be:<sup>24</sup>



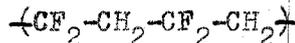
Some other fluoro-olefins which have been homopolymerised to useful polymeric material (transparent films etc.) are those which contain varying amounts of hydrogen in the fluoro-carbon backbone. These tend to be less thermally stable than TEFLON and KEL-F, splitting out hydrogen fluoride at high temperatures. Madorski<sup>57</sup> et al has shown a series of decreasing thermal stability to be:



We now discuss these further.

(c) POLYVINYLIDENE FLUORIDE

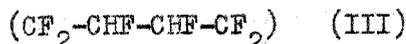
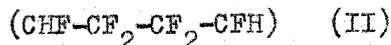
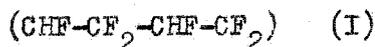
This polymer is a structure made up entirely of alternate methylene and difluoromethylene groups.<sup>118</sup>



The methylene groups diminish the rigidity of the carbon skeleton and establish a site for cross-linking, but give the polymer poor stability thermally. It has been prepared by usual techniques<sup>55, 56</sup> and by gamma-irradiation.<sup>54</sup> Its crystallinity even at low n values is thought to be due to orientation of chains through a type of hydrogen bonding between chains. Madorsky and Strauss have compared the thermal stability of polyvinylidene fluoride and TEFLON,<sup>58</sup> and found the former to lose HF to become very stable above 520°C at 70% weight loss.

(d) POLYTRIFLUOROETHYLENE

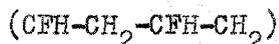
The monomer is seen to undergo radical attack at either end of the double bond,<sup>38, 42, 40, 39</sup> hence the polymer must contain sequences such as



and it is to structure (III) that Haszeldine<sup>38</sup> attributes the poor thermal stability of this polymer and places it below polyvinylidene fluoride in the thermal stability sequence quoted (p.25). He postulates that hydrogen fluoride is eliminated from this element of structure. This polymer has been prepared by  $\gamma$ -irradiation<sup>54</sup> and peroxide techniques.<sup>59</sup> The third polymer of this latter type is

(e) POLYVINYLFLUORIDE<sup>27, 60, 61</sup>

This polymer consists entirely of the repeating fundamental structure



which, by Haszeldine's theory on thermal instability, is an intrinsically unstable structure which loses HF on heating. Madorsky,<sup>57</sup> in fact, places polyvinyl fluoride below polyethylene in the stability sequence.

These five homopolymers have exemplified how the physical properties of a rigid structure, like Teflon, can be changed by the introduction of either flexible methylene groups in the backbone, or by introducing a "pendant" group, or in fact, both. This technique has been adapted for co-polymerising systems to produce thermally stable elastomers and thermoplastics as will be described later.

Some olefins have not yet been homopolymerised, although new techniques and conditions are being developed all the time. At the time of writing non-homopolymerising fluorine-containing olefins include  $\text{CH}_2=\text{CH}(\text{CF}_3)$ ;  $\text{CFCl}=\text{CFCl}$  cyc.  $\text{C}_6\text{F}_{10}$ , cyc.  $\text{C}_4\text{F}_6$ , and hydrocarbon olefin  $\text{CH}_2=\text{C}=\text{CH}_2$ .

Hexafluoropropene, an olefin used extensively in this thesis, was thought to be non-homopolymerisable, all attempts up to 1952 having failed<sup>62</sup> to form a homopolymer. Such attempts up to 1960 had resulted in the formation of dimers,<sup>28, 9, 10</sup> trimers<sup>28</sup> and tetramers.<sup>28</sup>

Manowitz<sup>63</sup> claimed to produce a homopolymer by gamma irradiation getting 14% conversion per megarep, and a patent described a technique for polymerising several monomers including  $\text{C}_3\text{F}_6$ .<sup>48</sup>

However, in 1960, Eleuterio,<sup>64</sup> using drastic conditions of temperature and pressure (300°C at 10,000 atmospheres) with a hydrogen-free initiating radical,  $\text{CF}_3\text{-S-Hg-S-CF}_3$ , homopolymerised  $\text{C}_3\text{F}_6$  forming a highly stable thermoplastic.

Thermal stability of fluorecarbon co-polymers and  
homopolymers<sup>178</sup>

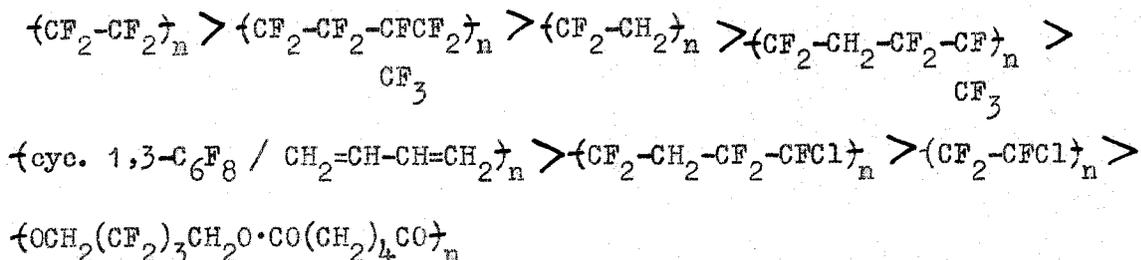
Thermal degradation of fluorine containing polymers has been investigated in some detail by Madorski et al<sup>57, 58</sup> who found that polytetrafluoroethylene could be pyrolysed to almost 100% monomer; polychlorotrifluoroethylene gives approximately 28% monomer, and 72% saturated chlorofluorocarbons. Thermal degradation of hydrofluorocarbon polymers is complicated by the loss of hydrogen fluoride, with the consequent introduction of double bonds into the polymer chain. Polytrifluoroethylene and polyvinyl fluoride degrade with complete volatilisation, but polyvinylidene fluoride becomes stabilised at about 70% weight loss.<sup>57</sup>

Some of the working ranges of homo- and co-polymers mentioned in this thesis are listed in table 2.

POLYMER	WORKING	RANGE	LIMIT
$\text{-(CF}_2\text{-CF}_2\text{)}_n$	-80	250	300
$\text{-(CF}_2\text{-CFCl)}_n$			200
$\text{-(CF}_2\text{-CF}_2\text{-CF}_2\text{-CF(CF}_3\text{))}_n$	-85	200	225
$\text{-(CF}_2\text{-CH}_2\text{)}_n$	-70	150	260
$\text{-(CF}_2\text{-CF(CF}_3\text{)CH}_2\text{-CF}_2\text{)}_n$	-44	315	-44
$\text{-(CF}_2\text{CF(Cl)CF}_2\text{-CH}_2\text{)}_n$	-43	205	-43
$\text{-(OCH}_2\text{(CF}_2\text{)}_3\text{·CH}_2\text{·O·CO(CH}_2\text{)}_4\text{·CO)}_n$	-72	150	-72

TABLE 2

Wright<sup>178</sup> has also measured weight loss in various fluorocarbon polymers after heating in vacuum for 2 hours at different temperatures; he obtained a series of decreasing stability on this basis:



He also found polyvinylidene fluoride became stabilised at about 70% weight loss.

#### CO-POLYMERS

The properties of co-polymers can vary over a wide range, since they are determined, not only by their qualitative, but also quantitative composition. They differ from homopolymers in their crystallinity, being composed of monomers which are chosen to produce thermoplastic or elastomeric properties in the resultant co-polymer, rather than highly crystalline materials.

The resinous state of polytetrafluoroethylene can be diminished in three ways:

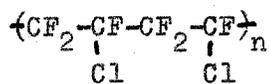
- (a) The tightly coiled polymer backbone can be converted to a more mobile structure by the inclusion of methylene groups in the backbone.
- (b) Heterogeneity can be introduced into the polymer in the form of a bulky atom or group, by using a co-monomer of the type  $\text{CF}_2=\text{CFX}$

(where X is the atom or group providing the heterogeneity.

- (c) Providing sites for cross-linking by introducing methylene groups at points where, by elimination of hydrogen halide, unsaturation can occur; thus converting the linear structure into a "space" polymer.

A co-polymer which was adapted from tetrafluoroethylene by route (b) has been described where  $X = CF_3$ . It is a true thermoplastic, TEFLON 100-X<sup>65-68</sup>

$\left( CF_2 - CF_2 - \underset{\substack{| \\ CF_3}}{CF} - CF_2 \right)_n$  incorporating the olefin hexafluoro-propylene into the tetrafluoroethylene chain. It is not cross-linked, but is a less-rigid structure than TEFLON itself. Basically, its resemblance to polychlorotrifluoroethylene can be seen



as far as the use of a pendant group to reduce the heterogeneity of the polymer goes. In TEFLON 100-X the pendant trifluoromethyl group only occurs (at a maximum) on alternate  $C_5$  atoms in the backbone, since hexafluoropropylene does not homopolymerise under the conditions of preparation and thus can only take up 50% of the polymer molecule at a maximum.

Unlike polytrichloroethylene, it has high thermal stability since the pendant  $-CF_3$  group is not as labile as the pendant  $-Cl$  atom. The latter can be removed in order to cross-link polychlorotrifluoroethylene by inter molecular splitting off of chlorine by organic bases<sup>69</sup> and metal oxides.<sup>69</sup>

Another adaptation of the TEFLON structure has been to co-polymerise

tetrafluoroethylene with an olefin as in (b) where X = Cl, again to produce thermoplastics<sup>70, 71, 72, 150</sup> of varying properties according to the proportions of monomers  $\left\langle \text{CF}_2-\text{CF}_2-\text{CF}_2-\underset{\text{Cl}}{\text{CF}}-\text{CF}_2-\text{CF}_2 \right\rangle$  used, since both monomers homopolymerise (with varying degrees of speed) under the conditions of the copolymerisation.

An example of the modification of the TEFLON structure by both routes a and c, is to copolymerise  $\text{CF}_2=\text{CF}_2$  with  $\text{CF}_2=\text{CH}_2$ <sup>79, 135, 156</sup> where again both monomers homopolymerise under the conditions of the copolymerisation. The resulting copolymer has  $\left\langle \text{CF}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2 \right\rangle$  intermediate properties between polytetrafluoroethylene and polyvinylidene fluoride with the possibility of cross-linking through the methylene groups.

#### Co-polymers derived from polyvinylidene fluoride

The homopolymer  $\left\langle \text{CF}_2-\text{CH}_2 \right\rangle_n$  is a resinous material, with a low softening point, but is highly crystalline. It can be modified using the techniques stated in (b) and is a suitable monomer to use as a basis for copolymers since it contains the methylene units necessary for cross-linking sites.

A copolymer where X = Cl (in  $\text{CF}_2 = \text{CFX}$ ) is described in the literature as an elastomer<sup>73, 74, 75, 76, 77</sup> which has fairly high thermal stability. The proportion of olefins can be adjusted to determine the nature of the resulting copolymer, i.e. to produce thermoplastic solids or elastomers. The usual method of copolymerisation with peroxide initiation<sup>78</sup> is used, but there is at least one example of the copolymer being prepared by

$\gamma$ -irradiation.<sup>79</sup> These co-polymers still contain the intrinsic instability conferred by the presence of so much chlorine.

The co-polymer of vinylidene fluoride with  $\text{CF}_2 = \text{CFX}$  where  $\text{X} = \text{CF}_3$ , VITON, is a distinct improvement on the previous one described, not only is it more thermally stable, but its composition can be more accurately controlled by simply altering the amount of  $\text{C}_3\text{F}_6$  in the reacting system, since this monomer does not homopolymerise under the reaction conditions. The maximum amount of  $\text{C}_3\text{F}_6$  which can be included in the structure is 50 mole %.

$$\left( \text{CF}_2 - \underset{\text{CF}_3}{\text{CF}} - \text{CH}_2 - \text{CF}_2 \right)_n$$

VITON is the one co-polymer whose structure has been investigated by nuclear magnetic resonance,<sup>80</sup> which shows the structure quoted, as being the dominant one, with some slight contribution from short polyvinylidene fluoride chains, but containing no adjacent  $\text{C}_3\text{F}_6$  units. VITON was first prepared in 1957<sup>81, 82, 141</sup> and later in 1959 by another industrial concern.<sup>83, 84</sup> Large scale production began in 1958.<sup>85</sup>

The physical properties of VITON have been studied extensively,<sup>86</sup> but its chemistry has not been studied at any length<sup>87</sup> apart from the chemistry of curing<sup>88, 89</sup> and vulcanisation<sup>90, 91, 92, 93, 94</sup> (see discussion, Chapter 2). It has been compared with the KEL-F elastomers<sup>74, 75</sup> ( $\text{CF}_2 = \text{CH}_2$  with  $\text{CF}_2 = \text{CFCl}$ ) as regards physical properties and stability.

Some excellent reviews of fluorocarbon polymers have appeared in the literature<sup>95-97, 178</sup> dealing with all the systems mentioned, as well as some interesting silicon containing elastomers with fluorine containing groups in their side chains.

Fluoro-olefin co-monomer	$CF_2=CF_2$	$CF_2=CF \cdot CF_3$	$CF_2=CFCl$	$CF_2=CH_2$	$CF=CF$   $CF_2=CF_2$	$CF=CF$   $CF_2=CF$   $CH_2=CF$
$CH_2=CHCN$	12 <sup>***</sup> 184 <sup>***</sup>		70B 148		148	
$CH_2=CHOR$ <sup>*</sup>		62	133			143
$CH_2=CCl_2$	184 <sup>***</sup>		137			
$CH_2=CFCl$			136			
$CH_2=CH_2$ 0		55	55	55		143
$CH_2=CH-Si(CH_3)_2$   Cl			140			
$CF_2=CF-CF=CH_2$		143				
$CH_2=CHCl$	12 <sup>***</sup> 184 <sup>***</sup> 149	62 67	137 148 149		148	
$CH_2=CF-CH=CH_2$	130		130			
$C_6H_5CH=CH_2$	183 <sup>***</sup> 184 <sup>***</sup>		148			

/CONT.

TABLE 3

CO-POLYMERS OF FLUORINE-CONTAINING OLEFINS

\* Alkyl groups

\*\*\* Inhibited reaction

NUMBERS REFER TO  
BIBLIOGRAPHY P.185

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Fluoro-olefin co-monomer	$CF_2=CF_2$	$CF_2=CF \cdot CF_3$	$CF_2=CFCl$	$CF_2=CH_2$	$CF=CF$ $CF_2=CF_2$	$CF_2=CF$ $CH_2=CF$
$CH_2=CH_2$	184 <sup>SEE</sup> 131 132	62 67		135	100 150	
$CH_2=C \begin{matrix} CH_3 \\ \diagup \\ CH_3 \end{matrix}$	12 <sup>SEE</sup> 132					
$CF_2=CFOR^{\#}$	134					
$CH_2=CHF$	149		70 149	135		
$CF_2=CHF$			70A			
$CHF=CHCl$			70A			
$CF_2=CCl_2$			70A 138			
$CFCl=CFCl$			70			
$CF_2=CFBr$			70			
$CF=CF$ $CF_2=CF_2$	100		70			

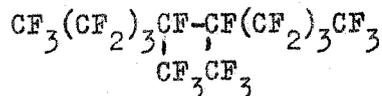
CO-TELOMERISATION

Not much work seems to have been done on co-telomer formation, since the only reported instance of such a reaction in the literature arises in a patent, where the system vinylidene fluoride - chlorotrifluoroethylene<sup>77</sup> has been co-polymerised in the presence of various hydrocarbon telogens.

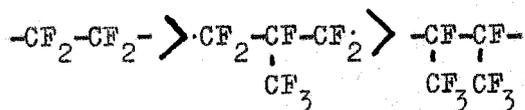
Hauptschein has produced some structures which resemble co-telomers (the terminal iodine could be replaced by fluorine) during his thermal telomerisation reactions with vinylidene fluoride,<sup>35</sup> and with hexafluoropropylene.<sup>16</sup> But in all his examples, the products are very simple forms of the co-polymer structure, although he did achieve the formation of light oils. A summary of his results follows on the next page.

TELOGEN	FORMED FROM	OLEFIN	PRODUCT	THEORETICAL CO-POLYMER
$\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{I}$	$\text{CF}_3\text{I} / \text{C}_2\text{F}_4$	$\text{CF}_2 = \text{CH}_2$	$\text{CF}_3 [\text{CF}_2 \text{CH}_2 \text{CF}_2]_n \text{I}$	$\text{CF}_2 = \text{CF}_2 / \text{CF}_2 = \text{CH}_2$
$\text{CF}_3 \cdot \text{CFI}$ $\text{CF}_2 \text{Cl}$	$\text{ICl} / \text{C}_3\text{F}_6$	$\text{CF}_2 = \text{CH}_2$	$\text{CF}_3 [\text{CF} \cdot \text{CH}_2 \text{CF}_2 \text{CH}_2 \text{CF}_2]_n \text{I}$ $\text{CF}_2 \text{Cl}$	$\text{CH}_2 = \text{CF} \cdot \text{CF}_2 \text{Cl} / \text{CF}_2 = \text{CH}_2$
$\text{CF}_3 \text{CF}_2 \text{CFI}$ $\text{CF}_3$	$\text{CF}_3\text{I} / \text{C}_3\text{F}_6$	$\text{CF}_2 = \text{CH}_2$	$\text{CF}_3 [\text{CF}_2 \cdot \text{CF} \cdot \text{CH}_2 \cdot \text{CF}_2]_n \text{I}$ $\text{CF}_3$	$\text{C}_3\text{F}_6 / \text{CF}_2 = \text{CH}_2$ VITON
$\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CF}_2$ $\text{CFI}$ $\text{CF}_3$	$\text{C}_4\text{F}_9\text{I} / \text{C}_3\text{F}_6$	$\text{CF}_2 = \text{CH}_2$	$\text{CF}_3 [\text{CF}_2 \cdot \text{CF}_2 \text{CF} \text{CF} \text{CH}_2 \text{CF}_2]_n \text{I}$ $\text{CF}_3$	$\text{C}_2\text{F}_4 / \text{C}_3\text{F}_6 / \text{CF}_2 = \text{CH}_2$ TERPOLYMER
$\text{CF}_3 \text{CF}_2 \text{CF}_2 \text{I}$	$\text{CF}_3\text{I} / \text{C}_2\text{F}_4$	$\text{C}_3\text{F}_6$	$\text{CF}_3 [\text{CF}_2 \text{CF}_2 \text{CF}_2 \text{CF}(\text{CF}_3)]_n \text{I}$	$\text{C}_2\text{F}_4 / \text{C}_3\text{F}_6$

He arrived at a useful conclusion when investigating the relative instability incurred in a molecule when pendant groups are too close to each other<sup>98</sup>, in coupled iodides such as  $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CFI}$ , which give:

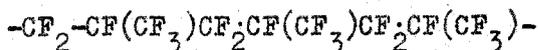


He states that replacing a  $\text{>CF}_2$  by a  $\text{>CF}(\text{CF}_3)$  in a fluorocarbon chain creates an increased strain, thus diminishing the  $\text{-C-C-}$  bond dissociation energy and leading to thermal instability. He quotes a series of decreasing thermal stability:



Thus:

Polyhexafluoropropylene, prepared by Eleuterio<sup>64</sup> would have a structure

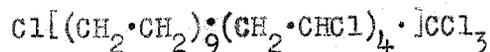


i.e. falling into the middle group in this stability sequence.

Paciorek<sup>99</sup> has synthesised compounds close to the fundamental structure of VITON to investigate the cross-linking mechanism of the elastomer using amines (see discussion).

Workers in this laboratory<sup>36</sup> have also synthesised fundamental structures of VITON by coupling reactions of fluorocarbon iodides.

In the field of hydrocarbon co-polymers, Hanford<sup>179</sup> reports the co-telomerisation of ethylene with vinyl chloride using carbon tetrachloride as telogen, giving a co-telomer



Polymerisation and co-polymerisation of cyclic mono-enes  
and di-enes

Little information has been published about the polymerisation and free radical reactions of perfluorocyclic olefins. It has been reported that hexafluorocyclobutene co-polymerises with ethylene and tetrafluoroethylene,<sup>100</sup> and its reactivity towards trifluoro methyl radicals has been compared with that of decafluorocyclohexene<sup>6</sup> - the latter being fairly unreactive. Linear dienes and vinyl cyclobutenes have been prepared from  $\underline{\text{C}}_4\text{F}_6$  by radical attack from  $\text{CF}_2\text{ClCFCl}$ .<sup>101</sup>

Octafluorocyclohexa-1,3-diene becomes cloudy on storage,<sup>102</sup> forming acidic products by absorption of oxygen from the air. This formation of cloudiness indicates that the diene is fairly reactive towards free radicals.

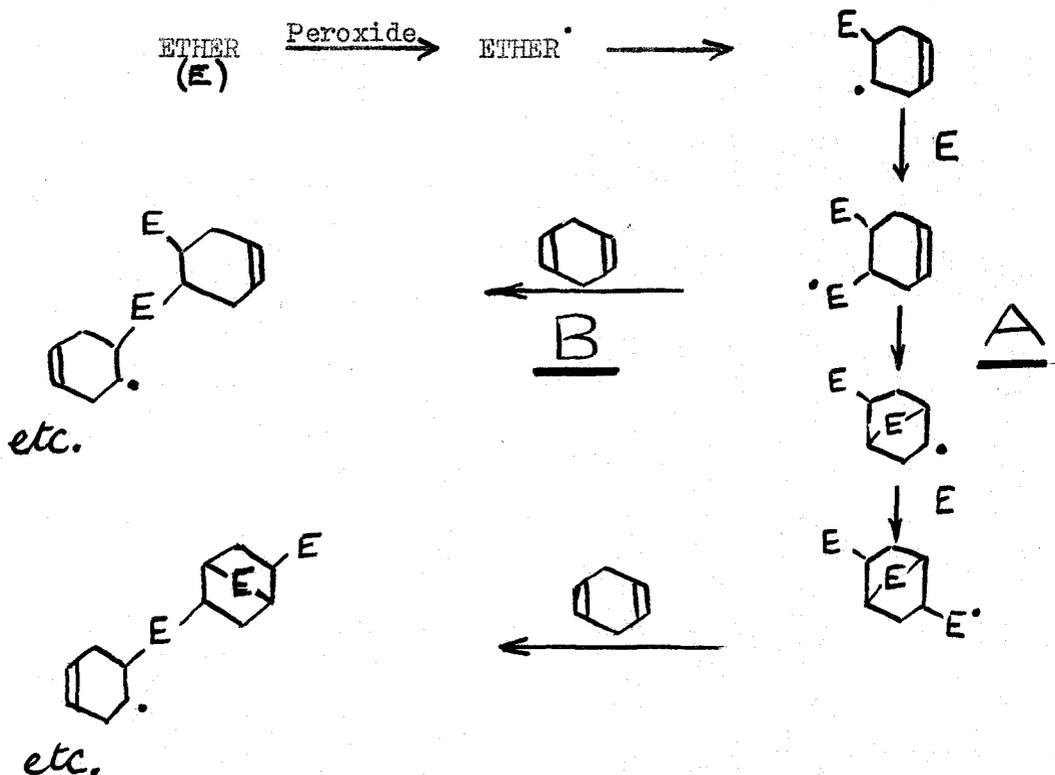
Decafluorocyclohexene and octafluorocyclohexa-1,4-diene are stable in air, suggesting that they are less readily attacked by free radicals. It has been found that using gamma initiation from  $\text{Co}^{60}$ , no polymeric material is obtained from either diene or cyclohexene,<sup>103</sup> on the other hand Hopkin<sup>104</sup> has found hydrocarbon monomers co-polymerise with the 1,3-diene very readily. Butadiene, for instance, and other conjugated monomers co-polymerised to form elastomeric materials. However 1,1,2-trifluorobutadiene was reluctant to undergo co-polymerisation, and 1,1,4,4-tetrafluorobutadiene as well as hexafluorobutadiene failed to co-polymerise

at all.

Unconjugated hydrocarbon olefins tended to form solid co-polymers with the 1,3-diene, but tetrafluoroethylene and trifluoroethylene failed even to homopolymerise in the presence of diene.

The 1,4-diene failed to co-polymerise with hydrocarbon olefins completely. In fact only vinyl-n-butyl ether formed a high molecular weight co-polymer, although this co-polymerisation proceeded smoothly.

Hopkin, postulates on examination of infra-red data that only ONE of the double bonds of the 1,3-diene participates in co-polymerisation reactions, with a mixture of 1,2 and 1,4 addition occurring. In the case of the 1,4-diene, both double bonds are thought to participate in the reaction with vinyl-n-butyl ether. The mechanism for this reaction he suggests as:



Although step B is thought to occur, it is step A which predominates.

The fundamental weakness in all these diene-olefin co-polymers is that at the point of attachment to the fluorinated ring there arises a structure where a methylene group is adjacent to a tertiary fluorine atom. This can lead to hydrogen fluoride elimination at fairly low temperatures.

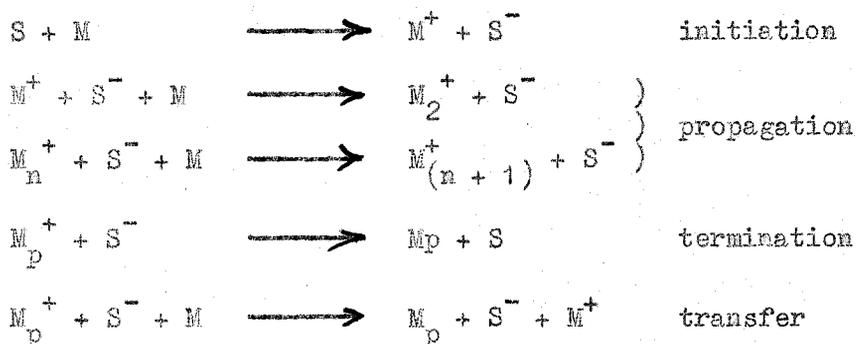
Gamma radiation from  $\text{Co}^{60}$  as an initiator.

Radiation induced polymerisation proceeds through the agency of free radicals, an irradiated molecule A giving rise to the cation  $\text{A}^+$  and an electron. The electron can then excite other molecules, giving up its energy in the process, and will probably be captured eventually by the ion  $\text{A}^+$  to give an excited molecule  $\text{A}^*$ . These excited molecules split up into free radicals, one of these radicals being in an excited state.<sup>147</sup> The situation in a polymerising system, containing a chain transfer agent, is fundamentally the same as that existing in any polymerising system which is reacting by a free radical mechanism, except that the initiating free radicals will generally have a higher energy.

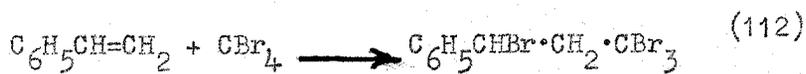
The use of gamma irradiation, from  $\text{Co}^{60}$ , to produce polymers having a narrower molecular weight range than those produced by conventional methods, was employed by Ballantine in the preparation of poly-n-vinyl pyrrolidene.<sup>105</sup>

Hydrocarbon olefins which have been homopolymerised by gamma rays include ethylene,<sup>106</sup> methyl methacrylate,<sup>107</sup> vinyl chloride,<sup>108</sup> vinyl cyanide<sup>108</sup> and styrene.<sup>109</sup> In the last case, an IONIC mechanism is postulated, since the rate of polymerisation was seen to be linear with

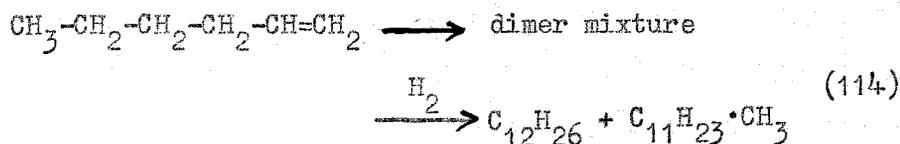
dose rate, whereas a radical process requires a square root dependence on dose rate. Another instance where an IONIC mechanism is thought to occur is in the gamma initiated polymerisation of styrene in methylene dichloride.<sup>110</sup> The mechanism is postulated as:



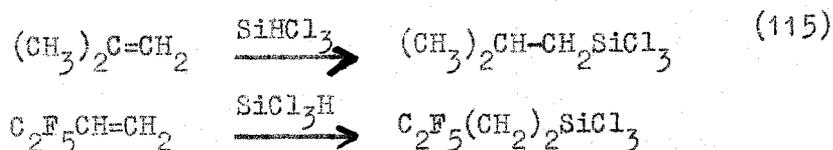
Simple adducts of hydrocarbon olefins have been formed under the influence of gamma irradiation<sup>106, 111, 113</sup> being identical to those formed by ultra-violet irradiation, but, in general, at a faster rate and in better yield.



Terminal hydrocarbon olefins have been shown to dimerise to products which are olefinic or branch chained<sup>114</sup>



Adducts of both fluorinated and non-fluorinated olefins are also formed with silicon hydrides under gamma-irradiation<sup>115</sup> in good yield



Several fluoro-olefins, such as  $\text{CF}_2=\text{CFCl}$ <sup>54</sup>,<sup>117</sup>  $\text{CF}_2=\text{CFH}$ <sup>54</sup>;  $\text{CF}_2=\text{CHCl}$ <sup>54</sup> and  $\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$ <sup>116</sup> have been homopolymerised by gamma-irradiation, also the co-polymerisation of  $\text{CF}_2=\text{CFCl}$  with  $\text{CF}_2=\text{CH}_2$  by gamma irradiation is reported<sup>79</sup>, all proceeding by a free radical mechanism, since to date, there has been insufficient evidence of any gamma-initiated process proceeding by an ionic mechanism. The effects of gamma radiation on fluorocarbon polymers has been investigated by Florin and Wall<sup>173</sup> using a source of  $10^{22}$  ev./gm. and this, of course, is very relevant to this work, since co-polymers and co-telomers formed under the influence of gamma irradiation, are exposed to further irradiation as the reaction proceeds. They found that products from scission of C-F <sup>and</sup> or C-C bonds are less than those from C-H or C-C bonds in hydrocarbon polymers. Cross-linking and degradation occurred in polymers containing F and H, and in the TEFLON 100X co-polymer ( $\text{C}_3\text{F}_8/\text{C}_2\text{F}_4$ ). Chain scission only occurs in KEL-F (polychlorotrifluoroethylene). Scission in TEFLON and TEFLON 100-X is accelerated in air or  $\text{O}_2$ . Free radicals are always present after irradiation, as was found by Melville<sup>175</sup> in his work.

Florin and Wall found<sup>173</sup> that perfluoro-aromatic polymers have high radiation resistance.

Baxendale and Mellows<sup>174</sup> irradiated pure methanol with a  $2 \times 10^{15}$  ev/cc/min. gamma source and found that the main products were hydrogen formaldehyde and glycol.

CHAPTER 2.

Discussion

## INTRODUCTION

The telomerisation reactions of fluoro-olefins have been studied extensively over the last few years - as indicated in Chapter 1. However, little work appears to have been performed on the telomerisation of co-polymer systems, i.e., co-telomerisation, where two dissimilar fluoro-olefins are polymerised together in the presence of a chain-transfer agent (telogen). Work in this department has led to the discovery that certain co-polymer systems can be co-telomerised, using various hydrocarbon and fluorocarbon telogens, to give viscous liquids, oils or greases, containing functional groups.

The reactions were carried out initially in carius tubes in the absence of air, or other inhibitors of free radicals. The more successful reactions were repeated on a larger scale, in a stainless-steel autoclave, into which a well was fitted to receive the gamma source-guide-tube. Initiation in all cases was by gamma irradiation from either a low intensity source ( $6.83 \times 10^4$  rads per hour) or a high intensity source ( $7.17 \times 10^5$  rads per hour) both of which were calibrated using a ferrous-ferric oxidation dosimetry system. (see Chapter 3).

The olefin systems investigated contained, in each case, an olefin which homopolymerised readily under the

reaction conditions, and one which did not homopolymerise under the reaction conditions.

The systems which have been investigated are listed below, where A is the non-homopolymerisable olefin, and B the homopolymerisable olefin under the conditions of the reaction.

A (nonhomopolymerisable)	B (homopolymerisable)
hexafluoropropene $\text{CF}_2=\text{CF}(\text{CF}_3)$	tetrafluoroethylene $\text{CF}_2=\text{CF}_2$
hexafluoropropene	vinylidene fluoride $\text{CF}_2=\text{CH}_2$
perfluorocyclobutane $\text{C}_4\text{F}_6$	vinylidene fluoride
perfluorocyclohexene $\text{C}_6\text{F}_{10}$	vinylidene fluoride
octafluorocyclohexa-1,4-diene $\text{C}_6\text{F}_8$	vinylidene fluoride
octafluorocyclohexa-1,3-diene	vinylidene fluoride
octafluorocyclohexa-1,3-diene	butadiene

PHYSICAL MEASUREMENTS ON CO-TELOMERS

Apart from the one-to-one adducts described, no simple compounds have been prepared in the course of this work. The co-telomerisation reactions have led to the formation of a complex mixture of co-telomer products, of various chain lengths, and it is impossible to separate such a mixture into its components for characterisation. Investigation of these products has thus been limited to average molecular weight determination, infra-red spectrum investigation, and fluorine analysis. Of these three, the least useful is the fluorine analysis; but molecular weight determination and infra-red spectrum combined, have been used as far as possible to interpret the nature of the mixed products. Since there is a large amount of infra-red data quoted in this thesis, it was thought necessary to draw up a correlation of infra-red data for the region  $5\mu - 7\mu$  (unsaturation region) in order to interpret the infra-red spectra available.

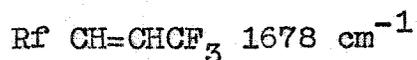
Types of unsaturation are listed, together with the state in which the infra-red spectrum of the compound concerned was measured whenever possible.

The correlation number is in the column at the extreme left of the table and is referred to when wave-numbers are quoted in the text.

Infra-red correlation<sup>189</sup>

In general, the replacement of an ethylenic hydrogen by fluorine only causes a slight shift in the  $\text{C}=\text{C}$ -absorption peak, from  $1626\text{ cm}^{-1}$  (in ethylene) to  $1648\text{ cm}^{-1}$  (in vinyl fluoride). Replacement of two hydrogens by fluorine (as in vinylidene fluoride) causes a large shift to  $1730\text{ cm}^{-1}$  however. A fully fluorinated propene,  $\text{C}_3\text{F}_6$ , shows  $\text{C}=\text{C}$  stretching absorption at  $1798\text{ cm}^{-1}$ , as does perfluorobutene-1; perfluorobutene-2 however, has this absorption at  $1733\text{ cm}^{-1}$ .

A  $\text{C}=\text{C}$  double bond to which perfluoroalkyl groups are attached i.e.  $\text{Rf CH}=\text{CH}_2$  or  $\text{Rf CH}=\text{CHCF}_3$  has an absorption peak very little different from a double bond carrying no perfluoroalkyl groups i.e.



Thus as the peaks move from  $1798\text{ cm}^{-1}$  towards  $1640\text{ cm}^{-1}$  it is an indication that either:

- (a) the double bond carries hydrogen or
- (b) the double bond does not have fluorine attached directly to it.

It is with this in mind, that deductions from infra-red examination of co-telomer mixtures have been made.

PEAKS IN THE REGION  $5\mu$  -  $7\mu$  OF INFRA-RED SPECTRA OF FLUORO-CARBON OLEFINS

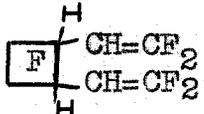
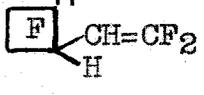
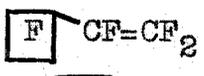
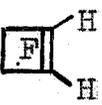
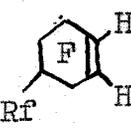
LINEAR OLEFINS

No.	$\text{cm}^{-1}$	TYPE	COMPOUND	STATE	REFERENCE
1	1652	-CF=CH <sub>2</sub>	CF <sub>2</sub> =CF-CF=CH <sub>2</sub>	gas	143
1A	1678	CH=CH	Rf CH=CHCF <sub>3</sub>	-	199 200
1B	1669	CH=CH <sub>2</sub>	Rf CH=CH <sub>2</sub>	-	199
2	1681	CF=CH <sub>2</sub>	CF <sub>2</sub> Cl · CFC1 · CF=CH <sub>2</sub>	-	143
3	1698	CF=CH <sub>2</sub>	CF <sub>3</sub> CF=CH <sub>2</sub>	gas	143
4	1709	CH=CF <sub>2</sub>	CF <sub>2</sub> =CH-CH=CF <sub>2</sub>	gas	143
5	1720	-CH=CF <sub>2</sub>	CF <sub>2</sub> =CH-CH=CF <sub>2</sub>	gas	187
6	1661	-CH=CFH	CF <sub>2</sub> =CF-CH=CFH	gas	143
7	1779	-CF=CF <sub>2</sub>	CF <sub>2</sub> =CF-CH=CFH	gas	143
8	1764	-CF=CF <sub>2</sub>	CF <sub>2</sub> =CF-CF=CH <sub>2</sub>	gas	143
9	1760	-CF=CF <sub>2</sub>	CF <sub>2</sub> =CF-C(CF <sub>3</sub> )=CH <sub>2</sub>	gas	186
10	1767	-CF=CF <sub>2</sub>	CF <sub>2</sub> =CF-CF=CF <sub>2</sub>	gas	143
11	1770	-CF=CF <sub>2</sub>	CF <sub>2</sub> =CF-CF=CF <sub>2</sub>	gas	188 200
12	1798	-CF=CF <sub>2</sub>	CF <sub>3</sub> CF=CF <sub>2</sub>	gas	21 36 189
13	1792	-CF=CF <sub>2</sub>	C <sub>2</sub> F <sub>5</sub> CF=CF <sub>2</sub>	gas	189 198 199
14	1724	-CF=CF-	(CF <sub>2</sub> -CF=CF-CH <sub>2</sub> ) <sub>n</sub>	solid	143
15	1733	-CF=CF-	CF <sub>3</sub> CF=CFCF <sub>3</sub>	gas	36 188 189 198
15A	1730	-CF=CF-	Rf CF=CFR	-	199 200
16	1713	-CF=CF-	C <sub>2</sub> F <sub>5</sub> CF=CFC <sub>2</sub> F <sub>5</sub>	-	21 188
17	1648		CH <sub>2</sub> =CFH	gas	189
18	1730		CH <sub>2</sub> =CF <sub>2</sub>	gas	189

LINEAR OLEFINS (continued)

No.	cm <sup>-1</sup>	TYPE	COMPOUND	STATE	REFERENCE
19	1751	C=CF <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> C=CF <sub>2</sub>	gas	36 198
20	1780		CF <sub>2</sub> =CFH	gas	189
21	1736 1715		CFH=CFH	gas	188
21A	1742	-CF=CFH	CF <sub>3</sub> CF=CFH	gas	21
21B	1695	-CH=CH	CF <sub>3</sub> CH=CHCH <sub>3</sub>	gas	27
21C	1695	-CH=CHF	CF <sub>3</sub> CH=CHF	gas	24

CYCLIC OLEFINS

22	1755	-CH=CF <sub>2</sub>		-	185
23	1755	-CH=CF <sub>2</sub>		-	185
24	1785	-CF=CF <sub>2</sub>		-	185
25	1795	-CF=CF-		gas	8
26	1799	-CF=CF-		gas	8 200
27	1685	-CF=CH		gas	8 200
28	1565	-CH=CH-		gas	8 200
29	1640	-CH=CH-		-	185
30	1802	-CF=CF-		gas	188 36

CYCLIC OLEFINS (continued)

No.	cm <sup>-1</sup>	TYPE	COMPOUND	STATE	REFERENCE
31	1754	-CF=CF		gas	36 188
	1739			CCl <sub>4</sub>	192 199
32	1739	CF=CF		liq	36
	1739			gas	36 200
	1753			CCl <sub>4</sub>	188 191 192
33	1754	CF=CF		gas	36
	1721			CCl <sub>4</sub>	188 191 192 200
	1754				
	1712				

Substituted aromatic, skeletal vibrations

No.	cm <sup>-1</sup>	COMPOUND	STATE	REFERENCES
38	1525	C <sub>6</sub> F <sub>6</sub>	gas	190
	1550		gas	36
	1536		"	188
	1531		"	188
39	1535	C <sub>6</sub> F <sub>5</sub> H	-	195
	1512			
40	1530	C <sub>6</sub> F <sub>5</sub> H	-	36 196
	1506			
41	1522	C <sub>6</sub> F <sub>5</sub> CH <sub>3</sub>	liq	197
	1502			
42	1529	C <sub>6</sub> F <sub>5</sub> C <sub>4</sub> H <sub>9</sub>	liq	"
	1504			
43	1520	(C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub>	NUJOL	"
	1506			
44	1528	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> Cl	liq	"
	1515			
45	1522	C <sub>6</sub> F <sub>5</sub> CHCl <sub>2</sub>	liq	"
	1506			
46	1522	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> Br	liq	"
	1508			
47	1520	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> OH	liq	"
	1504			
48	1515	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	liq	"
	1499			
49	1522	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> COOH	NUJOL	"
	1508			
50	1524	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	liq	"
	1506			
51	1414	C <sub>6</sub> F <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	liq	188

Substituted aromatic, skeletal vibrations (continued)

No.	cm <sup>-1</sup>	COMPOUND	STATE	REFERENCE
52	1534 1515	C <sub>6</sub> F <sub>5</sub> OH	liq	188
53	1543 1522	C <sub>6</sub> F <sub>5</sub> OH	vap.	"
54	1497 1479	C <sub>6</sub> F <sub>5</sub> OK	NUJOL	"
55	1520	C <sub>6</sub> F <sub>5</sub> OCOC <sub>6</sub> H <sub>5</sub>	"	"
56	1524	C <sub>6</sub> F <sub>5</sub> OCOC <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub>	"	"

Substituted cyclohexadienes1,4 dienes

No.	cm <sup>-1</sup>	TYPE	COMPOUND	STATE	REFERENCE
57	1767	CF=CF	1H heptafluoro-	gas	36 200
58	1718	CH=CF	"	"	"
59	1744 1711	CH=CF	1H, 5H hexafluoro-	"	194 200
60	1737 1707	CH=CF	1H, 4H hexafluoro	"	"
61	1729	CH=CF	1H, 4H, 5H pentafluoro	"	190
62	1676	CH=CH	"	"	"
63	1770	CF=CF	1H, 2H hexafluoro	"	193 200
64	1688	CH=CH	"	"	"

1,3 dienes

65	1734	CF=CF	1H, 2H hexafluoro	"	193 200
66	1635	CH=CH	"	"	"
85	1740	-CF=CF-	1H heptafluoro	"	200
85A	1676	CF=CH	"	"	"
86	1740	CF=CF	2H heptafluoro	"	"
86A	1684	CF=CH	"	"	"

Substituted cyclohexenes

No.	cm <sup>-1</sup>	TYPE	COMPOUND	STATE	REFERENCE
67	1717	CF=CH	1H,5H octafluoro	gas	193
68	1750	CF=CF	4H,5H octafluoro (trans) (cis)	"	193 200
68A	1745	CF=CF			
69	1746	}	3H,4H octafluoro (cis) (trans)	"	193 200
69A	1755				
70	1713	CF=CH	1H,4H octafluoro	"	193 200
71	1715	CF=CH	1H,3H octafluoro	"	194
72	1710	CF=CH	2H,3H,3H,5H,6H pentafluoro	"	190
73	1710	CF=CH	2H,3H,3H,5H hexafluoro	"	190
74	1710	CF=CH	1H,3H,4H,6H hexafluoro	"	190
75	1711	CF=CH	1H,4H,6H,6H hexafluoro	"	190
76	1736	CF=CF	3-nbutylnonafluoro	liq	36
77	1752	CF=CF	3H nonafluoro	gas	200
78	1747	CF=CF	4H nonafluoro	"	200
79	1714	CH=CF	1H nonafluoro	"	200
80	1717	CH=CF	1H,5H octafluoro	"	200
81	1722	CH=CF	1H,4H,5H(trans)heptafluoro	"	200
82	1720	CH=CF	" (cis)	"	200
83	1695	CH=CH	1H,2H octafluoro	"	200
84	1682	CH=CH	1H,2H,4H heptafluoro	"	200

### Co-telomer systems

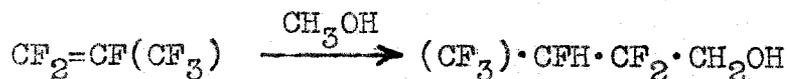
In a co-telomerising reaction there is a three component system, olefin A, olefin B, and telogen. Thus there is always the possibility of intercombination to form, - adducts with A; telomers of B; plus homopolymers of B, and a co-polymer, AB. It was imperative therefore, that preliminary experiments were performed to prepare these possible by-products, in order that they could be identified in the co-telomer reaction products, using analytical scale gas-liquid chromatography. All the co-polymers, AB, were prepared, and these are discussed in their respective sections. The adducts of A, and the homopolymers of B, were shown to be the usual impurities from a co-telomer reaction.

Of all the telogens used in the course of this work, methanol and trifluoroacetic acid were found to be the most successful. Thus these telogens were reacted with olefins of type A, and type B, to prepare the possible by-products mentioned above. Several other prospective telogens were also used with this in mind.

ADDITION OF TELOGENS TO NON-HOMOPOLYMERISABLE OLEFINS OF  
TYPE A

Hexafluoropropylene and methanol

A one-to-one adduct was formed in high yield no matter what molar ratio of reagents were employed. It could be deduced from the presence of a band in the infra-red spectrum at  $3436\text{ cm}^{-1}$ , that an hydroxyl group was present. There were no bands in the region  $5\mu-6.5\mu$ , indicating that the compound was fully saturated. The spectrum was identical with a sample prepared by the method of LaZerte and Koshar using peroxide initiation.<sup>5</sup>



attack by the radical being on the terminal =  $\text{CF}_2$  group.<sup>28</sup> There was no trace of ether formation, i.e.  $\text{CH}_3\text{O}\cdot\text{CF}_2\cdot\text{CFH}(\text{CF}_3)$  thus the process is a free radical and not an ionic one.

Hauptschein<sup>16</sup> found that a simple adduct prepared by the action of heat on a mixture of  $\text{C}_2\text{F}_5\text{I}$  and hexafluoropropene:



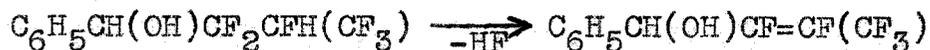
could be made to add to another hexafluoropropene molecule due to the ease of cleavage of its C-I bond. However the methanol; hexafluoropropene adduct failed to add across

the double bond of either hexafluoropropene itself, vinylidene fluoride, or chlorotrifluoroethylene.- In the first case, all the hexafluoropropylene, and adduct were recovered, but in the other two cases, homopolymer of the vinylidene fluoride and chlorotrifluoroethylene, respectively, were recovered together with the starting adduct. These results indicate that, if any reaction occurs at all, to form either  $\text{H(olefin)CF(CF}_3\text{)CF}_2\text{CH}_2\text{OH}$  or  $\begin{matrix} \text{H(olefin)} \\ \text{H(C}_3\text{F}_6\text{)} \end{matrix} > \text{CH(OH)}$ , it must be extremely slow, due to the stability of the C-H bonds concerned. It also proves that in the co-polymerisation of hexafluoropropene with vinylidene fluoride, in the presence of methanol, a true co-telomerisation reaction is occurring - not a succession of stepwise additions. This will be discussed later.

#### Hexafluoropropene with benzyl alcohol

It was thought that this alcohol would behave similarly to methanol in its reaction with hexafluoropropene. Although an adduct did form in poor yield, corresponding to a one-to-one combination, an inert solvent ( $\text{CF}_2\text{ClCFCl}_2$ ) had to be employed since the reagents were immiscible. The presence of a band at  $3436 \text{ cm}^{-1}$  in the infra-red spectrum of the yellow liquid adduct suggested it to be an alcohol. The spectrum contained a strong band at  $1733 \text{ cm}^{-1}$ , which when compared to structures 15 and 15A in the correlation

table could correspond to an unsaturated structure,  $C_6H_5CH(OH)CF=CF(CF_3)$  formed by HF loss during the distillation of the adduct at reduced pressure, to form



a substituted butene.

Molecular weight determination by ebullioscopy supported this structure. The yellow liquid gave a single peak on analytical gas-liquid chromatography (silicone elastomer at  $215^\circ C$ ). The solvent took no part in the reaction.

#### Hexafluoropropylene with chloroform

Again there was poor conversion of olefin to adduct, a colourless liquid was isolated, which gave two peaks on analytical gas-liquid chromatography (silicon elastomer at  $200^\circ C$ ) close together, which could possibly be the isomeric one-to-one adducts.

#### Hexafluoropropene with trifluoroacetic acid

Only a trace amount of product was isolated and this was not investigated further.

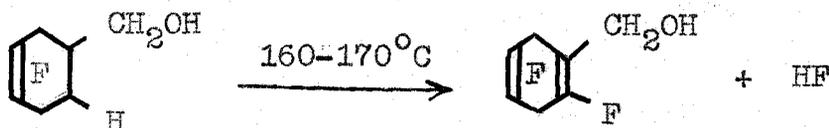
#### Octafluorocyclohexa-1,4-diene with methanol

A high yield of the simple one-to-one adduct formed, indicating the susceptibility of this diene to radical attack. A wide band at  $3436\text{ cm}^{-1}$  in the infra-red spectrum of this adduct indicated the colourless liquid to be an

alcohol. A further peak at  $1754\text{ cm}^{-1}$  indicates the diene to have used only one of the available double bonds for reaction (this peak is in the infra-red spectrum of the original diene) thus:



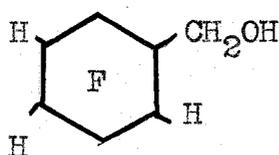
This structure was verified by molecular weight determination (ebullioscopy) and fluorine analysis. It was noticed that on distillation at atmospheric pressure, this adduct tended to evolve acid gases at its boiling point.



A polymeric tar was left in the distillation flask - an indication that HF elimination was occurring. It has, in fact, been suggested that tertiary fluorine atoms are fairly labile (Fluorine Chemistry, Ed. Simons. Vol. 2., Academic Press 1954, p. 215). A second tube of this mixture, containing a large excess of  $\text{CH}_3\text{OH}$  was irradiated for an extremely long time. On opening this tube by hot-spotting whilst cooling it in liquid air, there was found to be an excessive pressure inside the tube, possibly of hydrogen, since the gamma irradiation of methanol produces hydrogen<sup>174</sup>.

The product from this experiment was not the simple one-to-one adduct, but a high boiling ( $160^\circ/0.05\text{ mm}$ ) pale

yellow, viscous, clear liquid. Infra-red spectrum examination revealed that there was no unsaturation present in this compound (no peaks in the region  $5\mu-6.5\mu$ ) but a strong OH band ( $2.91\mu$ ) and C-H stretch ( $3.38\mu$  and  $3.5\mu$ ). Molecular weight determination by ebullioscopy gave a value corresponding to a structure B.



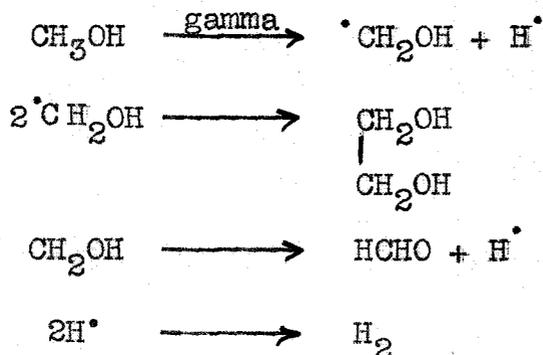
B

This evidence points to a mechanism involving formation of the one-to-one adduct, as described

previously:



Once all the diene has been converted to this adduct, the excess methanol becomes subjected to gamma irradiation, giving the following<sup>174</sup>



Thus the simple one-to-one adduct can be attacked by hydrogen atoms, to form the fully saturated compound.



The by product of this reaction could possibly be co-polymers of ethylene glycol and formaldehyde or homo-polymer of formaldehyde.

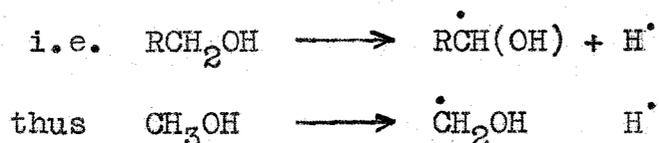
Octafluorocyclohexa-1,4-diene with benzyl alcohol

This reaction was carried out in an inert solvent ( $\text{CF}_2\text{Cl} \cdot \text{CFCl}_2$ ) which proved to be only partially efficient as a mutual solvent. A poor yield of material was obtained as a residue from a reduced pressure distillation, which tended to decompose on heating above  $110^\circ\text{C}$ . Molecular weight determination by ebullioscopy indicated a one-to-one addition compound from which HF had been lost. It could be deduced from a peak at  $3436 \text{ cm}^{-1}$  in the infra-red spectrum of this compound, that an hydroxyl group was present, and peaks in the region  $5\mu-6.5\mu$  indicated a highly unsaturated structure.

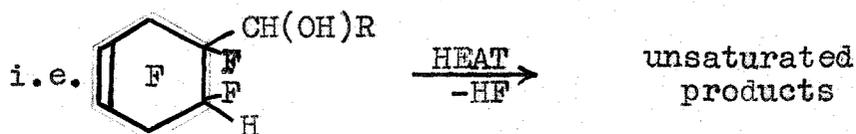
Octafluorocyclohexa-1,4-diene with 1,1-dihydro-2,2,2-trifluoroethanol

A poor yield of colourless unsaturated liquid was obtained, which decomposed on distillation at reduced pressure to give a brown viscous liquid which was highly unsaturated (peaks in the region  $5\mu-6.5\mu$  in the infra-red spectrum).

LaZerte and Koshar<sup>5</sup> state that in free-radical addition of alcohols to fluoro olefins, it is the alpha-carbon atom which becomes detached to form a radical pair:



Thus the alcohols discussed above, on irradiation, give similar  $R\dot{C}H(OH)$  radicals. i.e.  $C_6H_5CH_2OH$  and  $CF_3CH_2OH$  form the radicals  $C_6H_5\dot{C}H(OH)$  and  $CF_3\dot{C}H(OH)$  respectively. These radicals, on becoming attached to a cyclic diene form unstable structures in which tertiary fluorine atoms are adjacent to carbon atoms carrying a single hydrogen atom. This would probably explain why HF elimination occurs so readily on heating during distillation:



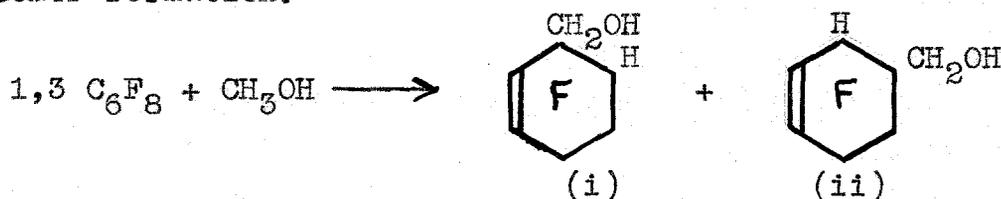
Octafluorocyclohexa-1,4-diene with trifluoroacetic acid

Trace amount of a red, viscous, liquid was isolated by reduced pressure distillation. The infra-red spectrum of this distillate contained peaks in the region  $5\mu-6.5\mu$ , from which it could be deduced that an unsaturated cyclic structure was present. This product was not investigated further.

Octafluorocyclohexa-1,3-diene with methanol

Only after prolonged irradiation did any quantity of addition product form. This yellow viscous liquid could be distilled at reduced pressure, and up to 180°C. On attempting to isolate a sample of simple one-to-one adduct from this distillate by further distillation at reduced pressure, the initial distillate began to turn brown and evolve HF at 100°C. It was impossible therefore to isolate any one-to-one adduct. The initial distillate was investigated by molecular weight determination and infra-red spectrum study. Its molecular weight indicated a polymeric structure, and peaks in the  $5\mu-6.5\mu$  region of the infra-red spectrum indicated unsaturation. It would appear that intermolecular HF elimination is occurring, as well as intra-molecular elimination. The mechanism is postulated as follows.

Addition of methanol to this diene leads to possible isomer formation:



Once this adduct has formed, further irradiation, combined with the heating during the ensuing reduced pressure distillation, leads to the formation of a viscous polymeric

liquid by HF elimination.

If we consider the infra-red evidence available we can postulate a mechanism for the formation of the polymer.

### Infra-red evidence

The stable polymeric viscous liquid has strong peaks at the following wavenumbers.

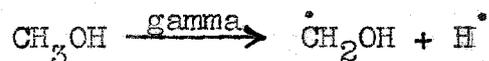
cm <sup>-1</sup>	unsaturation type		correlation
1650	C=C	cyclic	29 66 83
	CH=CF	cyclic 1,3 diene	
1724	CF=CF	cyclic 1,3 diene	65 85 86
	CF=CF	linear polymeric	14
	CF=CF	cyclic hexene	75
	CH=CF	cyclic 1,4 diene or hexene	58 61 67 81

A strong band at 2.91  $\mu$  also indicates an hydroxyl group to be present. Furthermore a doublet arises at 1520 cm<sup>-1</sup> and 1504 cm<sup>-1</sup> similar to that found in C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>OH (correlation 47) and in many aromatic pentafluorocyclic compounds (correlations 39-56) of the type C<sub>6</sub>F<sub>5</sub>R where R = H; OH, CH<sub>3</sub> etc.

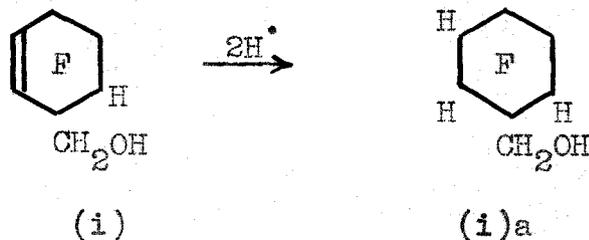
### Polymer formation

Assuming that the initial products from the reaction are compounds (i) and (ii) by analogy with the 1,4-diene; methanol reaction, it is possible that because of the

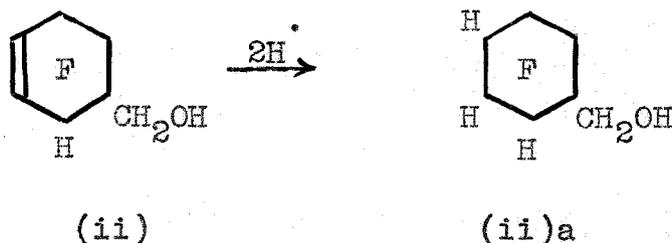
excessive amount of irradiation used, structures (i)a, and (ii)a could be formed, through attack by atomic hydrogen produced by the irradiation of the methanol since:



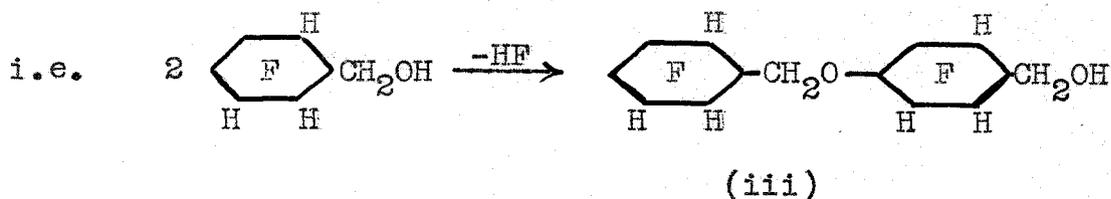
thus:



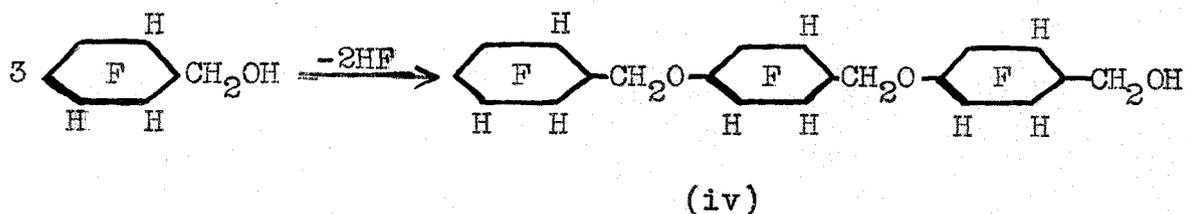
and



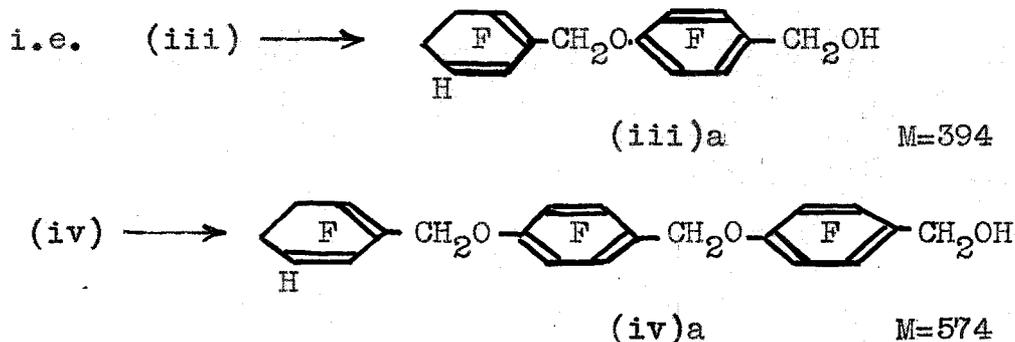
Compound (i)a, especially, could eliminate HF intermolecularly to produce a dimer, or trimer on heating



or

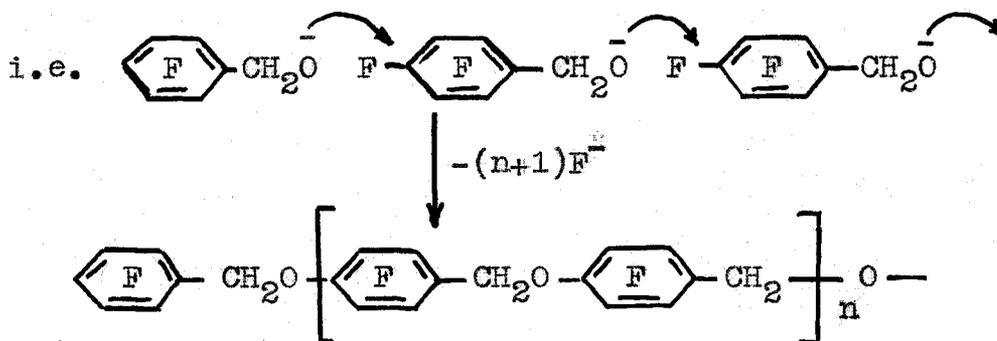


These structures could again lose HF, to produce both aromatic, and 1,3 diene structures:



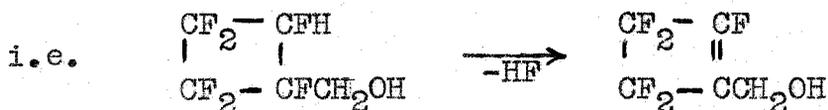
Looking back to the infra-red data on this mixture, it can be seen that structures (iii)a and (iv)a contain the type of unsaturation quoted, i.e. 1,3-diene type. The molecular weight value determined by ebullioscopy (477) indicates a mixture of (iii)a and (iv)a.

A polymeric structure of this type was prepared by Haszeldine<sup>197</sup> as a byproduct in the preparation of  $C_6F_5CH_2OH$  from  $C_6F_5CH_2Br$  by the action of aqueous KOH:



The ether linkage in a compound of this sort cannot easily be detected in its infra-red spectrum, since its frequency falls at a value lying in the region of intense C-F absorption frequency.

together. The infra-red spectrum of this distillate showed a peak in the unsaturation region at  $1639\text{ cm}^{-1}$ . This could be attributed to dehydrofluorination on distillation:



(correlation 27, 28, 29).

The two components were not isolated, molecular weight determination on the mixture showed it to consist of a 60%  $\text{C}_5\text{F}_6\text{H}_4\text{O}$  to 40%  $\text{C}_5\text{F}_5\text{H}_3\text{O}$  molar ratio. It could be deduced from a band at  $3436\text{ cm}^{-1}$  that the adduct contained an alcohol group.

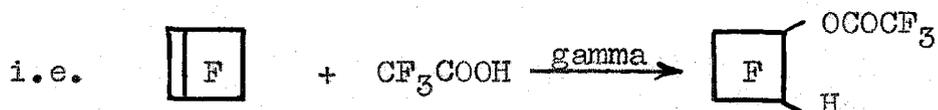
#### Hexafluorocyclobutene with trifluoroacetic acid

A series of reactions were carried out with this mixture forming in one case an elastomeric solid, and in the other cases viscous liquid, all of which liberated  $\text{CF}_3\text{COOH}$  on standing in moist air, or on hydrolysis with dilute acid.

The formation of these materials was rather surprising, since they appeared to be polymeric. It was shown, however, that (a) perfluorocyclobutene did not homopolymerise under the influence of  $\gamma$  irradiation and, (b) without irradiation the perfluorocyclobutene; trifluoroacetic acid mixture did not undergo any reaction.

The literature contains references to the ring opening of perfluorocyclobutene by the action of heat<sup>6</sup>, to give perfluoro-1,3-butadiene, and fluorocyclobutenes carrying a hydrogen on ethylenic carbons are reported as undergoing ring opening to give 1,3-dienes in good yields.<sup>162,176</sup>

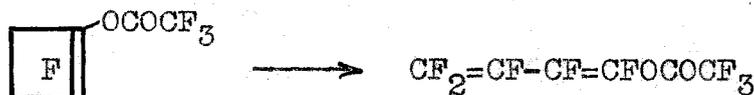
Thus it is possible that in our case adduct formation occurs:



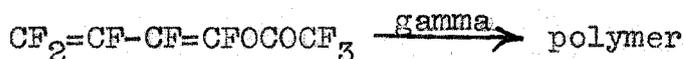
followed by HF elimination:



followed by ring opening:



and homopolymerisation of this olefin:

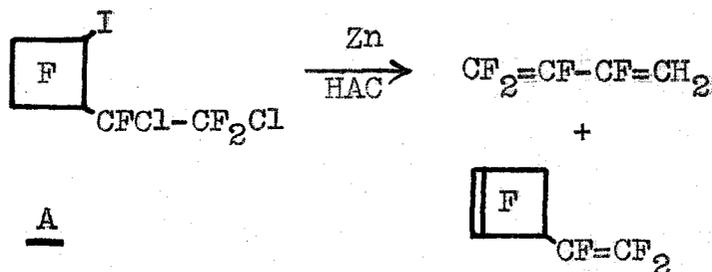


The infra-red spectrum of the viscous liquid shows no unsaturation, hence the unsaturation could have been removed by further addition of  $\text{CF}_3\text{COOH}$  across the double bonds. Hydrolysis, of course, regenerates the  $\text{CF}_3\text{COOH}$ , leaving a saturated structure.

There are cases quoted in the literature where perfluoro-

cyclobutane with a side chain have, on treatment with acid, formed linear compounds. For instance, Haszeldine<sup>158</sup> found that perfluorocyclobutene, on treatment with HI, formed  $\text{CF}_2\text{H}-\text{CFH}-\text{CFH}-\text{CF}_2\text{H}$  and explains this isomerisation in two ways.\*

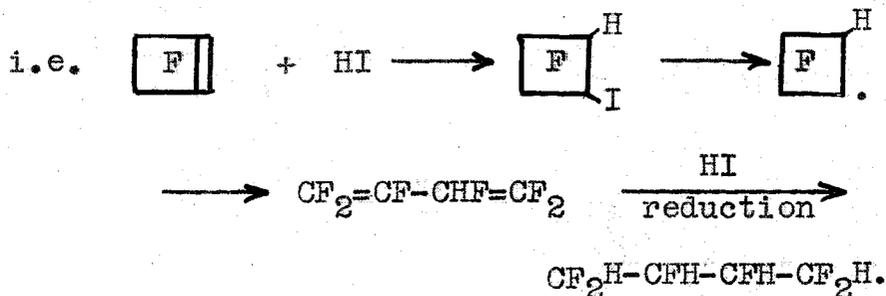
Hauptschein<sup>181</sup> found that dechlorination, using zinc in glacial acetic acid, of a compound A, produced a linear diene



This evidence shows that perfluorocyclobutene, and its addition compounds can undergo ring opening to form a homopolymerisable buta-1,3-diene.

\* (i) the reduction of  $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$  by HI, swinging the equilibrium<sup>6</sup> at high temperature to the right.

(ii) a scheme involving rearrangement of a free radical formed by C-I bond cleavage at high temperature



ADDITION OF TELOGENS TO HOMOPOLYMERISABLE OLEFINS OF TYPE B

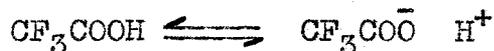
Since vinylidene fluoride was the most used olefin, B, it was important to investigate the reactions of this olefin with methanol and trifluoroacetic acid; these being the most successful telogens in the co-telomerisation reactions which will be discussed later.

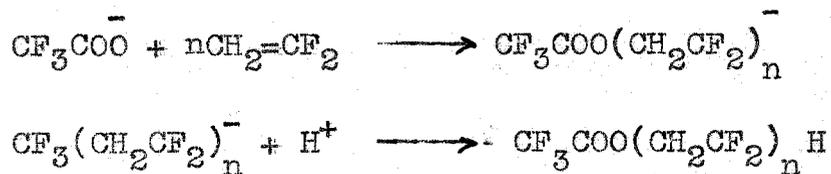
Vinylidene fluoride

With methanol, trifluoroacetic acid or 1,1,2-trichlorotrifluoroethane, vinylidene fluoride failed to form anything but its homopolymer, the other reagent being recovered in each case. This meant that in a system olefin A; vinylidene fluoride, and either methanol or trifluoroacetic acid, the molar proportion of A must be kept high in order to avoid the formation of homopolymer of vinylidene fluoride.

Attempts were also made to produce a homopolymer of vinylidene fluoride by placing the olefin together with excess trifluoroacetic acid in an autoclave. No irradiation was employed, and the olefin was recovered quantitatively. This indicates that under ionic conditions the homopolymerisation does not take place.

i.e. in the dark





does not occur.

### Theoretical approach to co-telomer formation - mechanism

In the co-telomerising systems, it can be visualised that the olefins B (those which will homopolymerise) would be the ones to be attacked by free radicals, since it has been shown that in the presence of methanol no telomer of vinylidene fluoride forms, but homopolymerisation occurs readily, i.e. efficient propagation but inefficient chain transfer occurs. If initial radical attack were on the olefin A (non-homopolymerisable) no propagation would occur until this intermediate radical reacted with a molecule of olefin B. By this time the rest of olefin B would have homopolymerised. However, olefins of the type A are extremely efficient at removing hydrogen atoms from the telogen,<sup>64</sup> i.e. undergo chain transfer efficiently. This mechanism is best expressed diagrammatically.

#### Olefin A (non-homopolymerisable) alone

Radical attack from telogen, RH, gives:

1.  $\text{R}^\cdot + \text{A} \longrightarrow \text{RA}^\cdot$  initiation step, this would normally be followed by a propagation step:



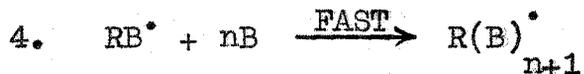
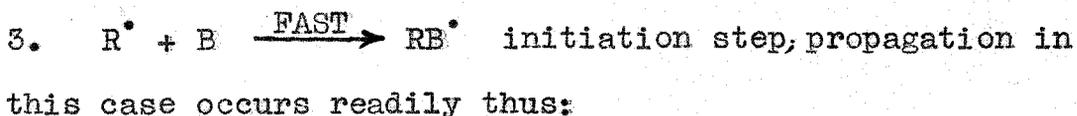
But, by definition this cannot occur since olefin A cannot form a homopolymer. The next step, hence, is chain transfer i.e. hydrogen abstraction from the telogen:



Thus the overall step is the production of a one-to-one adduct and regeneration of a radical  $\text{R}^\bullet$

Olefin B (homopolymerisable) alone

Radical attack from telogen, RH, gives:



Chain transfer in this system is inefficient (cf.  $\text{CF}_2=\text{CH}_2 + \text{CH}_3\text{OH}$  reaction) thus  $n$  becomes very large before either chain transfer, or disproportionation occurs, to terminate the chain. i.e.,



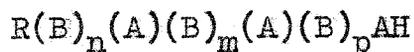
The mechanism shows how the copolymer propagation proceeds, to produce a long chain, consisting of short chains of B ( $n$  and  $m$  are less than say 5 depending on the ease of homopolymerisation of B) broken by single units of A (since A cannot propagate its own species, by definition).



### Termination

It is most likely that termination occurs via olefin A extracting hydrogen from the telogen RH:

i.e.  $R(B)_n(A)(B)_m(A)(B)_pA^\bullet$  - the growing polymer chain reacts with telogen (chain transfer occurs) to give the co-telomer:



### By-products

These always include homopolymer of olefin B formed by step 4, and the one-to-one adduct of A and telogen from step 1 (where the telogen is  $CH_3OH$ ). In system ONE (see later) these by-products are the only products when methanol is used as the telogen, due to the high affinity of  $C_3F_6$  for hydrogen atoms and the readiness with which  $C_2F_4$  homopolymerises.

### Proportions of olefin B in co-telomers

This depends largely on the ease of homopolymerisation of the olefin i.e. the efficiency of steps 4 and 5, competing with 3.

For example, where A is  $C_3F_6$  and B is  $C_2F_4$  the co-telomer or co-polymer (where the telogen is not  $CH_3OH$ ) prepared from equimolar amounts of olefins, contains 75 mole % of B. Where A is  $C_3F_6$  and B is  $CF_2=CH_2$ , co-polymerised

in an equimolar mixture, the co-polymer or co-telomer contains approximately 50 mole % B. This is because  $C_2F_4$  homopolymerises more readily than  $CF_2=CH_2$  allowing less  $C_3F_6$  to be incorporated into the co-polymer chain.

### Co-polymerisation and co-telomerisation

#### LARGE SCALE POLYMERISATION

Since the more successful experiments were to be repeated on a large scale in the 380 ml stainless-steel autoclave, it was first ascertained that co-polymerisation or homo-polymerisation would proceed in such a vessel. For this purpose, four samples of tetrafluoroethylene were irradiated in the autoclave. The first two samples were prepared in this laboratory by the pyrolysis of TEFLON.

Sample 1 was shown to contain a 20% impurity of hexafluoropropylene, and sample 2 a 3% impurity of hexafluoropropylene (by molecular weight determination, Regnault's method.) These two samples were polymerised by us, and were tested by I.C.I. Ltd., Plastics Division, and shown by infra-red measurement to contain only 6% and 0.9% of hexafluoropropylene respectively. They were slightly less crystalline than the commercial homopolymer of tetrafluoroethylene.

Samples 3 and 4 consisted of pure tetrafluoroethylene; and their homopolymers prepared by gamma irradiation were

of considerably lower molecular weight than the homopolymer prepared by emulsion polymerisation; this was shown by melt viscosities of  $3 \times 10^7$  poises and  $1 \times 10^7$  p, compared with a figure larger than  $10^{11}$  p for the emulsion polymer. In other respects there was little difference.

Sample 4 was irradiated twice as long as sample three, but this did not appear to alter the polymer (no breakdown apparently occurs).

One important point emerges from the results on samples 1 and 2. Initially the gas consisted of 80%  $C_2F_4$  and 20%  $C_3F_6$  in sample 1, and 97%  $C_2F_4$  with 3%  $C_3F_6$  in sample 2. However, the polymers from the gamma irradiation of these impure samples contained only 6% and 0.9%  $C_3F_6$  respectively. This indicates that  $C_3F_6$  is not readily included into a co-polymer with  $C_2F_4$ , and that to form such a co-polymer containing a high proportion of  $C_3F_6$  excess of this olefin must be employed.

#### CO-TELOMERISATION

With the first two co-polymer systems investigated, several telogens were employed, and it emerged that the two most efficient of these were trifluoroacetic acid (which diminished the chain length in both systems) and methanol (which was efficient when used with system 2) giving viscous liquids and semi-solids. The reactions which were repeated

on a large scale in an autoclave all involved these two telogens. The co-polymer systems are now discussed in the order in which they appear on page iii.

SYSTEM ONE tetrafluoroethylene and hexafluoropropylene.

The co-polymer was prepared in the absence of telogen, using an equimolar mixture of olefins. There was 100% conversion of tetrafluoroethylene, and the white solid co-polymer contained approximately 17% hexafluoropropene (by recovered gas analysis). It was analysed by I.C.I. Ltd., Plastics Division and found to contain 12% hexafluoropropene, whereas the commercial co-polymer contains 15% hexafluoropropene. The gamma-prepared sample had a melt viscosity of  $1.2 \times 10^4$  poises, compared with  $1 \times 10^5$  poises for the commercial co-polymer.

It was thought that if a co-telomer could be prepared from this co-polymer, the former would retain properties close to those of the parent co-polymer, and that any instability caused by the telogen fragments in the structure could be eliminated by further reaction. Using methanol as a telogen resulted in the formation of the one-to-one adduct  $(CF_3).CFH.CF_2.CH_2.OH$  with hexafluoropropene (identified by comparison of infra-red spectra with an authentic sample, and comparative analytical gas-liquid chromatography), plus a white solid, similar in appearance to the co-polymer of hexafluoropropene with

tetrafluoroethylene. Comparison with the infra-red spectrum of this co-polymer confirmed this.

With acetone a solid, white polymer was produced, which contained little hexafluoropropylene, and no acetone.

Acetaldehyde gave no solid product with this system, the colourless liquids were shown to be simple adducts of the olefins with the aldehyde (as found by LaZerte and Koshar<sup>5</sup> who found that ketones are formed by the free radical addition of aldehydes to hexafluoropropene) or a low 'n' value co-telomer. The separation of liquid products was confused by the decomposition of poly-acetaldehyde formed in the early stages of the reaction. With benzyl cyanide a solid formed which contained nitrogen, but closely resembled the telogen-free co-polymer.

Pentafluoroiodoethane has been shown on numerous occasions to be an efficient telogen with either of the olefins used in this system.<sup>15,103</sup> The soft solid which was produced melted at 170°C and, after cooling, re-melted at 170°C. This indicates a stable structure, and it is probably a co-telomer containing a little C<sub>3</sub>F<sub>6</sub>. The other products being possibly the simple adduct C<sub>2</sub>F<sub>5</sub>(C<sub>3</sub>F<sub>6</sub>)I. In such a system where all three components are volatile it is extremely difficult to estimate the proportions of unreacted material. It was intended to investigate

this reaction further, but this as yet has not been attempted.

Trifluoroacetic acid as a telogen yielded a white solid polymeric material, and all the acid was recovered. The solid was identical to the telogen-free co-polymer, by comparison of infra-red spectra.

It was concluded that since tetrafluoroethylene was so readily homopolymerised, excess hexafluoropropene would have to be employed if the co-telomer is to contain a high percentage of this olefin. On the other hand we have noted that hexafluoropropene seems to have an affinity for hydrogen atoms,<sup>64</sup> hence methanol, acetaldehyde, acetone or any hydrogen containing compound used as a telogen will encourage the formation of a simple, one-to-one adduct with hexafluoropropene rather than a co-telomer.

It was decided that trifluoroacetic acid as a telogen, with, say, sixfold excess of hexafluoropropene (compared with tetrafluoroethylene) would lead to co-telomer formation, since no simple adduct forms with trifluoroacetic acid and hexafluoropropene,

This was carried out in an autoclave, and yielded a semi-solid which melted at 215°C, and was shown by I.C.I plastic division to contain 24% C<sub>3</sub>F<sub>6</sub> (whereas the co-polymer formed by using a molar ratio of unity of olefins contained

only 12%  $C_3F_6$ ). The material contained 3.3 - COOH groups per 1000 carbon atoms, i.e. a possible chain length of 250 carbon atoms. The infra-red spectrum was poor, but indicated a structure similar to the parent co-polymer, being completely saturated, i.e. having no peaks in the region  $5\mu-6.5\mu$ .

The co-telomer did not develop an odour of trifluoroacetic acid on standing, nor did it liberate acid on hydrolysis which was surprising, for if a trifluoroacetate group had either initiated or terminated the chain this group would be very susceptible to aerial hydrolysis to give the free acid; trifluoroacetates being very hydrolytically unstable. An explanation of this observation is discussed later in this Chapter.

Following from this, it may be possible to produce a co-telomer containing a higher proportion of  $C_3F_6$ , and having a shorter chain length, by using a twentyfold excess of  $C_3F_6$  with trifluoroacetic acid; or, on the other hand using another telogen which does not contain available hydrogen, but is as efficient a telogen as trifluoroacetic acid. It was with this in mind that hexafluoropropene was irradiated with chloroform as stated in an early section.

SYSTEM TWO Hexafluoropropene and vinylidene fluoride.

This co-polymer is less crystalline than the one in system one, being elastomeric. Thus a shortened chain (a co-telomer) of this co-polymer was more likely to take the form of a viscous liquid, rather than a semi-solid, with the thermal properties of the co-polymer retained.

An equimolar gaseous mixture, on irradiation, produced a sticky pink elastomer, containing equimolar amounts of olefin monomers. It was soluble in acetone, and had an infra-red spectra which differed from the one given by Smith<sup>94</sup> for untreated VITON in that it was a fairly unsaturated structure, having peaks in the  $5\mu$ - $6.5\mu$  region. This could be explained by saying that a partial "cure" had been brought about by the gamma irradiation, after the co-polymer had formed. (unsaturated sites being set up, but no cross-links will occur until an oven cure is performed.<sup>94</sup>) This idea is substantiated by Smith<sup>94</sup> who subjected VITON to irradiation from a Van der Graaf generator, and showed the infra-red spectrum of the resulting material to contain unsaturation peaks at  $5.7\mu$  and  $5.8\mu$ ., similar to the ones observed in our sample.

This system lends itself readily to co-telomer formation, since the tendency for vinylidene fluoride to homopolymerise is not as strong as with tetrafluoroethylene, and the co-telomer mechanism can compete successfully with

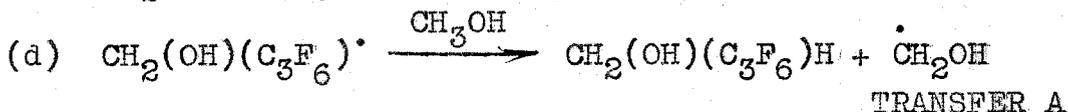
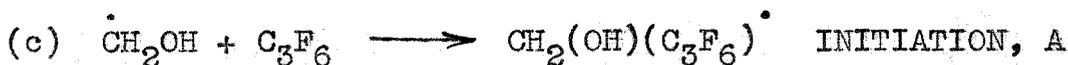
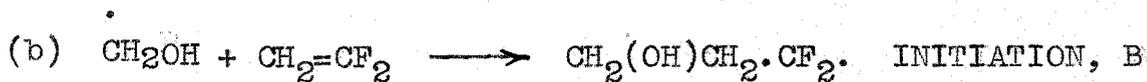
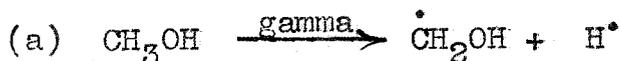
homopolymer formation.

With Methanol, chain shortening occurred with total conversion of olefins to form a mixture of viscous liquid products. It could be deduced from the infra-red spectrum of this mixture, by a wide band at  $3436\text{ cm}^{-1}$ , that hydroxyl groups were present.

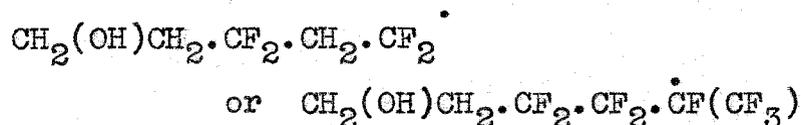
These co-telomer alcohols could be distilled into crude fractions up to  $160^{\circ}\text{C}$ , at reduced pressure. Above this temperature decomposition occurred, forming a viscous brown oil of high molecular weight. This reaction was repeated on a large scale, giving identical results to the small scale reaction. The viscous residue formed at  $160^{\circ}\text{C}$  may be assumed to be the result of hydrogen fluoride elimination, followed by a certain amount of polymer formation. This would account for the high molecular weight of the residue. All the crude fractions obtained by distillation at reduced pressure had peaks in the region  $5\mu$ - $6.5\mu$  in their infra-red spectra indicating unsaturated centres, plus the band at  $3436\text{ cm}^{-1}$  showing the presence of an hydroxyl group. Molecular weight determinations (by ebullioscopy in acetone solution) varied from 300 to 800 corresponding to a chain length of up to four units 1 unit =  $(\text{CF}_2 \cdot \text{CF}(\text{CF}_3)\text{CH}_2 \cdot \text{CF}_2)$ .

The byproduct was always the one-to-one adduct  $\text{CH}_2(\text{OH})\text{CF}_2 \cdot \text{CFH}(\text{CF}_3)$ . The mechanism of this co-telomerisa-

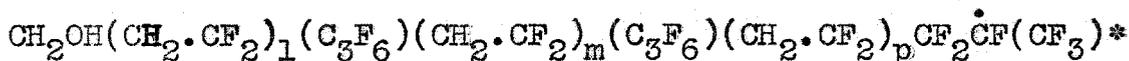
tion based on experimental evidence is postulated as:



Initiation, A, is not likely to lead to co-telomer formation since step (d) is very efficient.<sup>64</sup> The intermediate free radical from initiation, B, can attack either olefin present to give:



The former can attack either olefin present to continue the co-polymer chain, the latter can only attack  $\text{CH}_2=\text{CF}_2$ , or undergo chain transfer by abstracting a hydrogen atom, as in (d), forming the  $n = 1$  co-telomer. The final longest chain co-polymer which will form will be:



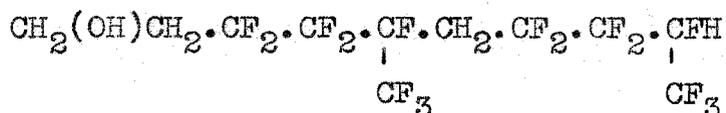
where  $l$ ,  $m$ , and  $p$  are either one or two. This co-polymer

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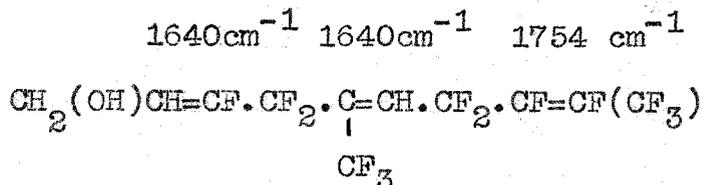
\* radical attack on  $\text{CH}_2=\text{CF}_2$  is exclusively on the  $\text{CH}_2$  and on  $\text{C}_3\text{F}_6$ , exclusively on the  $\text{CF}_2$  <sup>28</sup> 118

now undergoes chain transfer to form a co-telomer by hydrogen abstraction as in (d).

No homo-polymer of vinylidene fluoride was detected in the product. As stated before, the slight unsaturation in the crude fractions corresponds to HF elimination from structures such as:



giving as an extreme example:



The peaks which arise in the unsaturation region can be explained as follows:

cm <sup>-1</sup>	unsaturation	correlation
1640	-CF=CH <sub>2</sub> linear	1
	-CH=CFH linear	6 17
1754	-CF=CF- linear	15 15A 16
	-CF=CF <sub>2</sub> linear	8 9 10

The distillation at 160°/.03 mm led to the formation of as much as 50% by weight of the telomer mixture as brown viscous residue.

Using acetone or acetaldehyde with system two, led to the formation of low boiling, colourless liquids,

which tended to decompose to tars when attempting to distil them at atmospheric pressure. This decomposition was further confused in the latter case by decomposition of polyacetaldehyde formed early in the reaction.

With pentafluoroethyl iodide as telogen an unidentified iodide, which decomposed above 40°C, was detected on gas-liquid chromatography. Separation of gaseous and volatile product and starting material was extremely difficult, and not attempted.

Trifluoroacetic acid as telogen led to the formation of an off-white, semi solid, co-telomer mixture, with complete conversion of a one-to-one molar ratio of olefins. On standing, this co-telomer mixture liberated  $\text{CF}_3\text{COOH}$  fumes, indicating that the mixture contained trifluoroacetate end-groups. These end-groups would be very susceptible to hydrolysis in moist air. Hydrolysis with dilute acid (since bases cause decomposition) eliminated  $\text{CF}_3\text{COOH}$  and HF. These acids were separated by steam distillation and, by volumetric analysis, a chain length of approximately 30 units was arrived at; one unit being  $-\text{CF}_2\cdot\text{CH}_2-\text{CF}_2-\text{CF}(\text{CF}_3)-$ .

The hydrolysed co-telomer mixture no longer eliminated acid fumes, and was a brown very viscous semi-solid, having a much lower fluorine content than the original mixture.

A molecular weight determination, by ebullioscopy, gave a value for molecular weight of 1600 indicating that hydrolysis has led to chain scission to form small chains of up to 10 units. The infra-red spectrum of the hydrolysed co-telomer mixture showed large peaks at  $1709\text{ cm}^{-1}$  and at  $1739\text{ cm}^{-1}$  which could be unsaturation of the type:

$\text{Cm}^{-1}$	unsaturation	reference
1695	-CH=CH-	correlation 21B 21C
1698	-CF=CH <sub>2</sub>	" 3
1709	-CH=CF <sub>2</sub>	" 4
1733	-CF=CF-	" 15 15A
1739	-C=O	reference 168
1742	-CF=CFH	correlation 21A

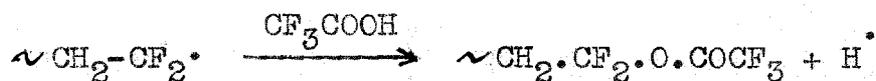
brought about by the hydrolysis of the trifluoroacetate end-group, which is discussed later.

This reaction was repeated on a large scale, in an autoclave. Using equimolar proportions of olefins, only the telogen-free co-polymer formed. Using a six-fold excess of  $\text{C}_3\text{F}_6$ , however, led to the formation of a semi-solid material, similar in appearance to the product from the small scale reaction. The infra-red spectrum of this product resembled the parent co-polymer in the region  $1890\text{cm}^{-1}$  to  $1740\text{ cm}^{-1}$ ; moreover it did not eliminate acid gases

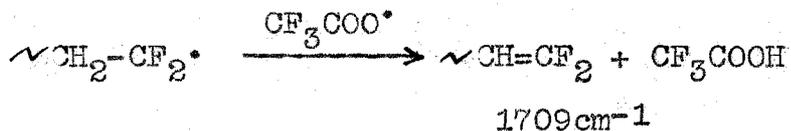
on standing in moist air, nor on hydrolysis with dilute acid.

### Mechanism of formation and hydrolysis

In the case of the product from the large-scale reaction, there could be no trifluoroacetate fragment in the structure, as seen by hydrolysis; thus chain termination, rather than by say:



is more likely to be:



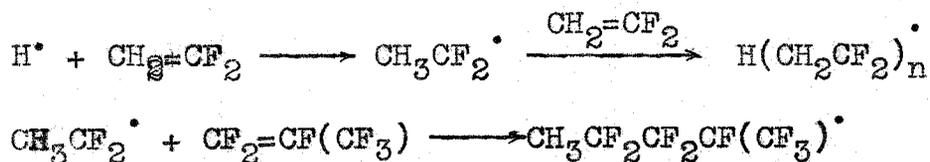
Concerning the small-scale reaction a trifluoroacetate was apparently formed as an end-group. On hydrolysis several possibilities arise according to which olefin has the trifluoroacetate residue attached to it. These possibilities are summarised below:

END GROUP	ON HYDROLYSIS	LEADING TO	
$\cdot\text{CF}_2\cdot\text{O}\cdot\text{COCF}_3$	$-\text{CF}_2\text{OH}$ HF, $\text{CF}_3\text{COOH}$	$-\text{COOH}$	a
$-\text{CH}_2\text{O}\cdot\text{COCF}_3$	$-\text{CH}_2\text{OH}$ HF, $\text{CF}_3\text{COOH}$	$-\text{CH}_2\text{OH}$	b
$-\text{CF}(\text{CF}_3)\text{O}\cdot\text{COCF}_3$	$-\text{CF}(\text{CF}_3)\text{OH}$ HF, $\text{CF}_3\text{COOH}$	$-\text{CO}\cdot\text{CF}_3$	c

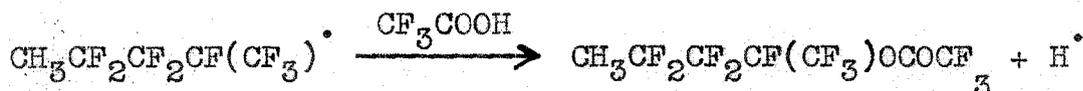
As pointed out before, it is unfortunate that the  $\text{-C=O}$  stretching frequency in the infra-red spectrum coincides with the region assigned to unsaturation. ( $5\mu$ - $6.5\mu$ ). Thus it is difficult to say conclusively just what structure is present due to hydrolysis. Obviously HF has been eliminated, thus we can assume a certain amount of unsaturation to be present in the copolymer chain. Examination of the spectrum of the hydrolysed co-telomer at  $2.91\mu$  shows no O-H group to be present, hence the terminal group cannot be of the type a or b. It should follow therefore that the peak at  $1739\text{cm}^{-1}$  is due to C=O stretching<sup>168</sup> in  $\text{-COCF}_3$  as shown in scheme C. Although  $1800\text{cm}^{-1}$  is quoted<sup>199</sup> as being C=O absorption in  $\text{RfCORf}$ .

#### Telomer formation

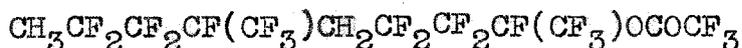
The above argument indicating that the end group is  $\sim\text{CF}(\text{CF}_3)\cdot\text{O}\cdot\text{COCF}_3$ , leads to the conclusion that this is a terminal group not an initial group, since if initiation was by  $\text{CF}_3\text{COO}\cdot$  attack on  $\text{C}_3\text{F}_6$ , the radical formed would be  $\text{CF}_3\text{COOCF}_2\dot{\text{C}}\text{F}(\text{CF}_3)$  (i.e. end-group a, in table). It follows that initial attack is by  $\text{H}\cdot$  on vinylidene fluoride



Consider the formation of the n=1 co-telomer:

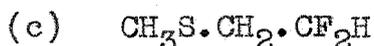
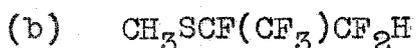
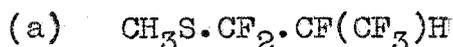


Hydrolysis of this telomer by scheme c, leads to the formation of  $\text{CH}_3\text{CF}_2\text{CF}_2\text{COCF}_3$ -: for the n=2 co-telomer:

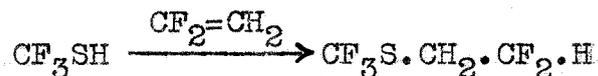


hydrolysis leads to the formation of an unsaturated structure by HF elimination  $\text{CH}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)=\text{CHCF}_2\text{CF}_2\text{COCF}_3$ .

System two with methyl mercaptan as telogen, led to the formation of simple, liquid, one-to-one adducts with the individual fluoro-olefins. This was proved by comparative analytical gas-liquid chromatography (on tricresyl phosphate 60°C.) with authentic samples of the two isomeric adducts (a) and (b) from the addition of mercaptan to hexafluoropropene. The third component was thought to be compound (c) since in a



similar reaction with  $\text{CF}_2=\text{CH}_2$ , Harris et al<sup>42</sup> formed only one of the possible isomers using  $\text{CF}_3\text{SH}$  i.e.



none of these compounds were isolated or characterised.

SYSTEM THREE    Perfluorocyclobutene and vinylidene fluoride

This system has not been co-polymerised before, although the literature reports a perfluorocyclobutene co-polymer with ethylene,<sup>100,151</sup> and tetrafluoroethylene.<sup>100</sup> Perfluorocyclobutene does not homopolymerise under the reaction conditions, but on irradiating the liquid phase of a cyclobutene-vinylidene fluoride mixture an elastomer was obtained containing equimolar proportions of the olefin monomers. Molecular weight determination indicated a chain length of three units (one unit being  $\{C_4F_6\}(CF_2.CH_2)$ ). The infra-red spectrum showed some unsaturation at  $5.50 \mu$  ( $1818 \text{ cm}^{-1}$ ). Conversion of olefins to this elastomer was not complete, since as cyclobutene was removed as co-polymer, the co-polymer tended to contain more vinylidene fluoride, making it a more crystalline, saturated structure. It follows that to prepare the elastomeric co-polymer in good yield, a molar excess of the cyclobutene must be used.

The co-polymer chain was shortened by using methanol as a telogen, this was shown by molecular weight determination. The telomer mixture produced was a semi-solid in poor yield. A by-product was the simple one-to-one adduct of the butene and methanol. It could be concluded by a wide band at  $3436 \text{ cm}^{-1}$  that hydroxyl groups were present in

the telomer mixture. The yield of telomer alcohols could possibly be improved by longer irradiation. This system was not reacted with trifluoroacetic acid in view of the results obtained with cyclobutene and trifluoroacetic acid (page 66).

SYSTEM FOUR    Decafluorocyclohexene and vinylidene fluoride

An attempt was made to co-polymerise this cyclic olefin with vinylidene fluoride, and with tetrafluoroethylene. In both cases, an excess of the  $C_6F_{10}$  was used, and irradiation was carried out of the liquid phase only. This led to formation of the homopolymer of the linear olefin in each case, and recovery of the  $C_6F_{10}$ . With methanol as telogen, the decafluorocyclohexene, vinylidene fluoride mixture yielded (a) homo-polymer of the vinylidene fluoride and (b) the one-to-one adduct of the decafluorocyclohexene in quantitative yield.

Trifluoroacetic acid was not used as a telogen with system four.

SYSTEM FIVE    Octafluorocyclohexa-1,4-diene and vinylidene fluoride

Hopkin<sup>104</sup> investigated this diene in its co-polymerisation reactions with hydrocarbon, and some fluorocarbon olefins (including vinylidene fluoride) and found it unwilling to enter into a co-polymerisation reaction. One exception was with vinyl-n-butyl ether which co-polymerised

with the diene as discussed earlier (p.37 Chapter 1) forming a fully saturated co-polymer i.e. both double bonds of the diene taking part in the process. Work carried out in this laboratory has led to the discovery that, with vinylidene fluoride, this diene forms a white crystalline low-melting, short chain co-polymer. Excess diene was used, to deter homo-polymerisation of the vinylidene fluoride, and 100% conversion of vinylidene fluoride to co-polymer occurred, the composition of which was an equimolar ratio of olefins.

The infra-red spectrum showed an unsaturation peak at  $1724 \text{ cm}^{-1}$  corresponding to only one double bond of the diene being used in the co-polymerisation reaction.

Methanol was a successful telogen with this system. Liquid telomers were produced, with a wide band at  $3436 \text{ cm}^{-1}$  in their infra-red spectra, from which it could be deduced that an hydroxyl group was present. These co-telomer alcohols could be distilled at reduced pressure, giving a yellow distillate, and leaving a black residue. The distillate developed an acidic odour of halogen on standing.

This reaction was repeated on a large scale, with approximately the same results. The by-products were homopolymer of vinylidene fluoride, and the one-to-one adduct of diene and the one-to-one adduct of diene and

methanol, as described previously.

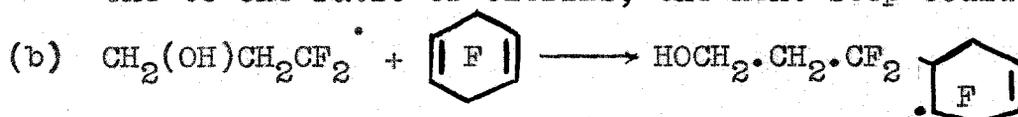
The heating, during distillation of these co-telomers into crude fractions led to the formation of unsaturation in the distillates, the degree of which increased as the temperature increased. Again a large amount of brittle black residue remained after distillation had ceased indicating that HF had been eliminated.

### Mechanism

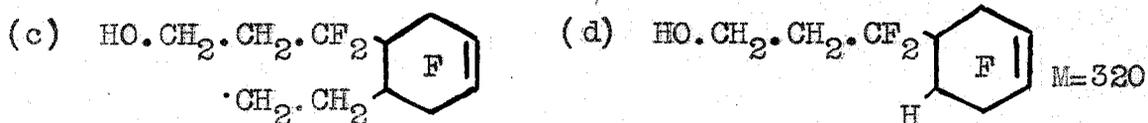
The mechanism visualised for the formation of these mixed co-telomers is as follows:

- (a) Radical attack on vinylidene fluoride, (radical from methanol)  $\dot{\text{C}}\text{H}_2\text{OH} + \text{CH}_2=\text{CF}_2 \longrightarrow \text{CH}_2(\text{OH})\dot{\text{C}}\text{H}_2\cdot\text{CF}_2$ .

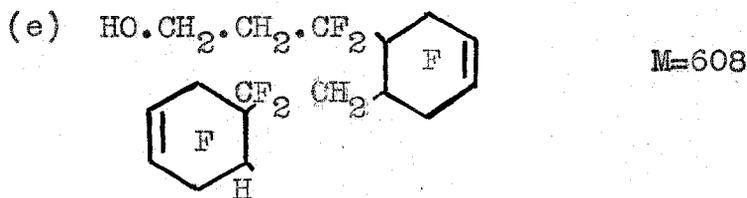
This radical can attack either olefin present, but considering the final structure to contain almost a one-to-one ratio of olefins, the next step could be



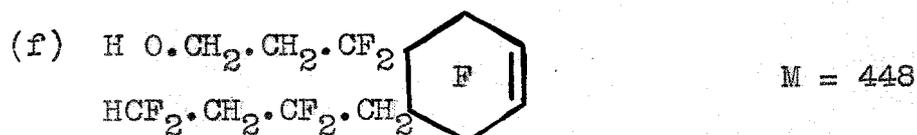
followed by attack exclusively on the vinylidene fluoride, or chain transfer i.e. (c) or (d) respectively:



Thus the final co-telomer formed is probably:

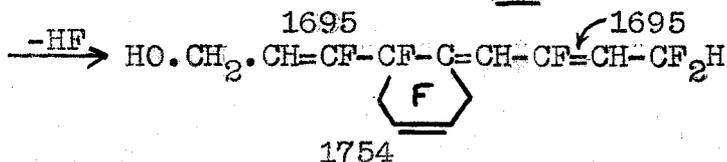
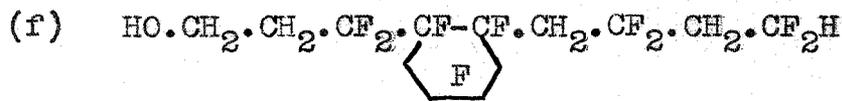
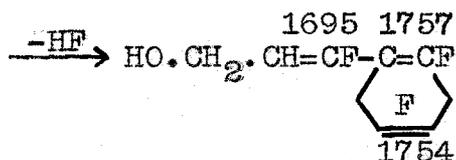
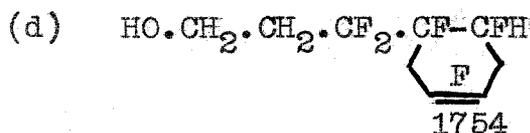


or



The product would in fact be a mixture of (d); (e); (f) based on molecular weight values obtained.

The evolution of acid gases during the distillation process continued after distillation had ceased; one crude fraction for instance (distilled at ca.  $110^\circ\text{C}/.03$  mm)  $\text{M} = 375$  changed colour on standing in air over a period of six months, from yellow to blood-red, with the evolution of acid gases. This elimination of HF can be considered as follows, considering structures (d) and (f)



The infra-red spectrum of the crude fraction mentioned contains sharp peaks in the unsaturation range at the following wavenumbers :

1754	cyclic -CF=CF-	correlation 57, 63,68,69,77
1757	" CF=CF	69A
1695	linear -CH=CF-	21C
	" -CH=CH-	1A,1B,21B
	cyclic -CH=CH-	66,85A,29,83,86A

A small peak at 1618 could be due to conjugation of side chain and ring, since the red colouration of the product indicates a high degree of conjugation. The structure indicated by infra-red spectrum investigation, is therefore the 1,4-diene, cyclic type.

These co-telomers, and the co-telomers from the isomeric 1,3-dienes, are compared later with regard to their tendency to eliminate HF on heating (see p.104).

Trifluoroacetic acid was not a successful telogen with system five in the small-scale carius tube reaction, giving mainly a polymeric material resembling polyvinylidene fluoride, which was not investigated further. On a large scale, however, using excess acid, a viscous liquid co-telomer mixture was obtained which did not liberate trifluoroacetic acid on hydrolysis with dilute acid. The yield of this co-telomer mixture was not high, but could probably be improved by longer irradiation.

The infra-red spectrum of this co-telomer mixture showed several peaks in the region usually assigned to

unsaturation ( $5\mu$ - $6.5\mu$ ). This unsaturation must have been brought about by irradiation, since at no time was the mixture heated excessively.

SYSTEM SIX      Octafluorocyclohexa-1,3-diene; vinylidene fluoride

Unlike its 1,4-isomer, this diene readily co-polymerises with hydrocarbon olefins.<sup>104</sup> We have found that only poor yields of liquid adducts form, in the reaction of this diene with tetrafluoroethylene, or vinylidene fluoride. However, with 1,1-dichloro-2,2-difluoroethylene a simple adduct forms in fairly good yield (see later). It was also seen that radical attack from methanol did not proceed readily, thus indicating the radical additions to this diene are not easily performed.

This system, with methanol as telogen, formed a short-chain co-telomers (inferred by molecular weight determination) in poor yield whose infra-red spectra contained a wide band at  $2.91\mu$  indicating an hydroxyl group to be present.

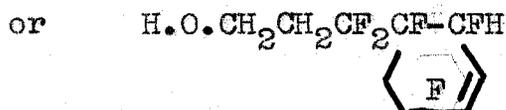
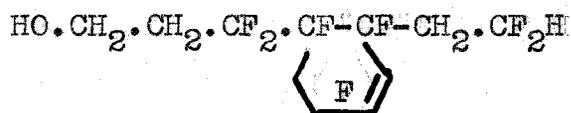
This mixture of co-telomers could be distilled at reduced pressure into a yellow distillate, and leaving a black residue. The distillate did not liberate acid fumes on standing and remained yellow in colour (unlike the  $110^\circ/0.003$  mm crude fraction from system 5). The infra-red spectra of the distillate showed peaks in the region

5-6.5 indicating the presence of unsaturation brought about by the distillation process.

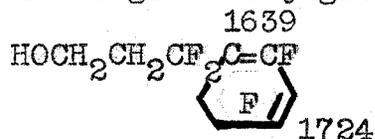
Repetition of this experiment on a large scale duplicated the above observations.

Stability of the co-telomer mixture

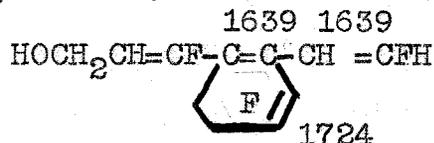
On the grounds that the distillate is unsaturated and does not liberate acid gases on standing, it can be postulated that HF is eliminated during the course of the distillation, to produce a structure from which no further HF elimination occurs. Assuming a reaction mechanism as described earlier, the products would be of the form:



losing HF to give conjugated systems



or by elimination of fluorine (unlikely)



to give a highly unsaturated system, having a similar structure to the original diene stabilised by conjugation. The peaks observed in the infra-red spectrum of the distillate

correspond to the following:

cm	unsaturation	correlation
1724	cyclic -CF=CF-	76,65,85,86
	linear -CF=CF-	14
1639	cyclic -C=C-	29,66
	linear -CH=CFH	6
	linear -CF=CH-	1

When progressive crude fractions are taken as the temperature of distillation rises, the unsaturation in the distillate does not alter appreciably (this is the opposite of what is observed in system 5) hence the structures formed by this initial HF loss must be fairly stable.

#### Aromatic character

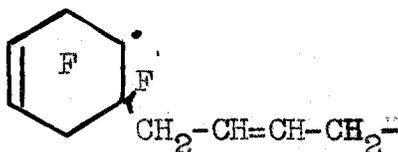
Small peaks arise in the infra-red spectrum of the distillate at  $1526\text{ cm}^{-1}$  and  $1504\text{ cm}^{-1}$ ; from which it could be deduced that the structures contain some aromatic character, similar to the 1,3-diene; methanol polymer (p. 61).

Trifluoroacetic acid did not act as a telogen with system six; only polyvinylidene fluoride, and a trace of viscous residue were produced. This reaction was not investigated further.

#### SYSTEM SEVEN Octafluorocyclohexa-1,3-diene; butadiene

An elastomeric co-polymer containing approximately

equimolar amounts of olefins was produced in quantitative yield. On standing for a long period of time, this material became brittle—having lost hydrogen fluoride. This inherent instability probably arises due to the presence of a tertiary fluorine atom adjacent to a methylene group at the point of attachment to the ring system, i.e.



a situation which always appears to lead to HF elimination.

This system with trifluoroacetic acid, co-polymerised even without irradiation forming products similar to those formed by irradiation.

Styrene is known to homopolymerise instantaneously in the presence of a strong acid such as the chloroacetic acids<sup>171</sup>, and trifluoroacetic acid<sup>172</sup>, and it is thought that a similar process occurs in this case with butadiene. The products were in the form of a yellow elastomer and a black tar.

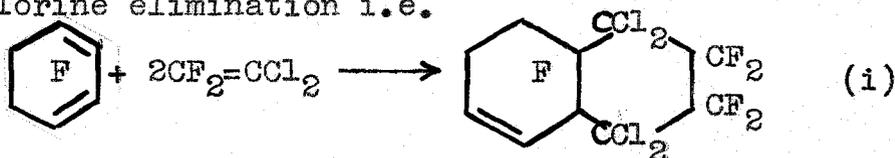
Methanol as a telogen gave a white fibrous co-polymer containing fluorine whether the reaction mixture was irradiated or not.

These reactions were not investigated further.

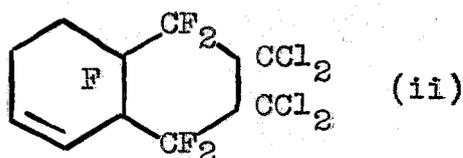
Octafluorocyclohexa-1,3-diene with 1,1-dichlorodifluoroethylene

Complete conversion of the linear olefin to give a viscous mixture of products occurred. Halogen analysis indicated a structure of the form  $C_6F_8(CF_2 \cdot CCl_2)_n$  where  $n=2$  or 3.

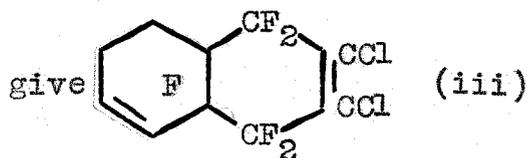
Distillation of this product at reduced pressure yielded the  $n=2$  compound as shown by molecular weight (504), leaving a clear yellow residue. The distillate, on standing developed a halogen-like odour, possibly by chlorine elimination i.e.



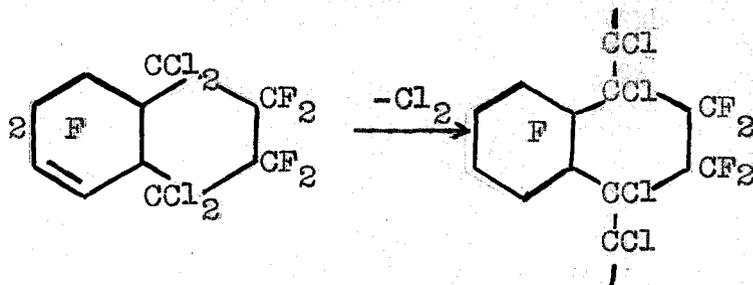
or



losing  $\text{Cl}_2$  to



The residue could be a polymer formed by inter-elimination of chlorine, i.e.



Neither olefin homo-polymerises under the reaction conditions, thus cyclisation is the alternative reaction as indicated.

Observation of the infra-red spectrum of the n=2 compound (the distillate) in the region assigned to unsaturation, shows peaks as follows.

cm <sup>-1</sup>	unsaturation type
1754 s	cyclic -CF=CF- correlation 31, 32, 33
1538	aromatic character correlation 39-54.
1515 w	

indicating structures of the type (i), (ii), (iii) which have eliminated Cl<sub>2</sub> or ClF on heating at 100°/.005 during distillation.

The residue was also unsaturated having peaks at

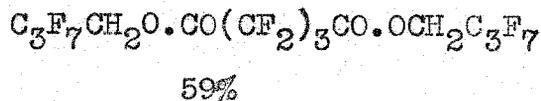
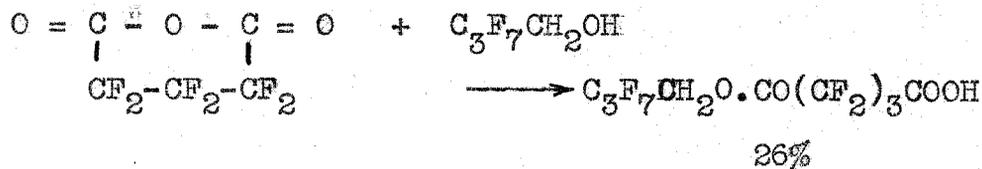
cm <sup>-1</sup>	
1754 s	-CF=CF- cyclic 57, 63, 68 correlation
1770 sh	-CF=CF <sub>2</sub> , 10, 11 -CF=CF- 63
1835 s	
1869 s	
1527	} aromatic character correlation 39-54
1504	

Fluorinated esters

Esterification is normally carried out in the presence of a promoter, usually a mineral acid, such as sulphuric acid. However, Hauptschein<sup>87</sup> found that esters of perfluoromonocarboxylic acids and dicarboxylic acids with 1,1-dihydroperfluoroalcohols, formed in good yield, if the acid chloride was used. In the case of the perfluoromonocarboxylic acid, no promoter being necessary:

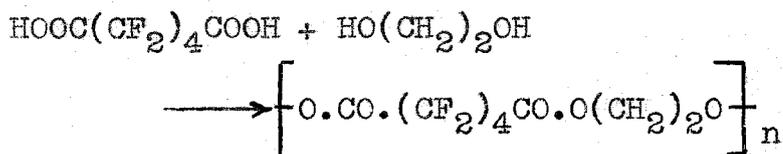


Using dibasic acids, the reaction proceeded rapidly if the dibasic acid anhydride was used: a diester and a mono-ester being formed in this case.

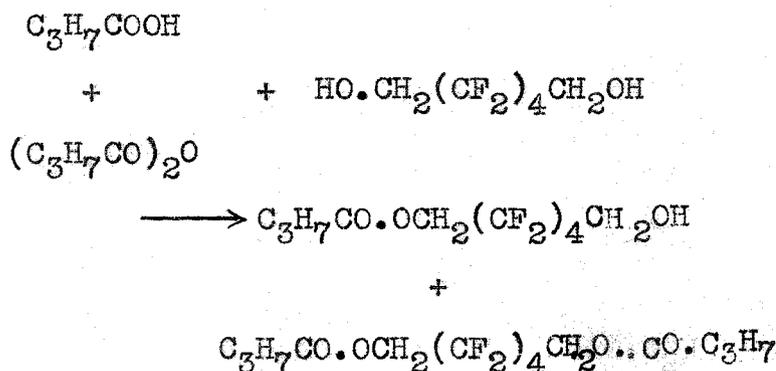


The half-ester could be converted to the diester by treating its acid chloride with alcohol. Hauptschein<sup>163</sup> has also prepared esters of perfluorocarboxylic acids with alcohols and glycols, and found that mineral acid promoters were unnecessary, due to the high acidity of the perfluoro acids, an observation supported by Clark<sup>165</sup>. He found that a polyester formed when dimethylene glycol

was esterified with perfluoroadipic acid:

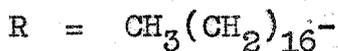
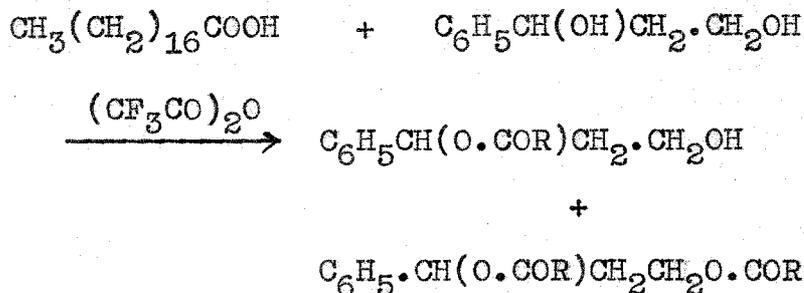


Filler et al<sup>160</sup> have prepared some diesters of fluorine containing alcohols and di-carboxylic acids, using the dicarboxylic acid chlorides, since mineral acid did not catalyse the esterification. They also found, that if a mixture of the dicarboxylic acid and its anhydride were esterified with a 1,1-dihydroperfluoroalcohol, a mixture of mono- and di-ester was produced in equal yield<sup>160</sup>

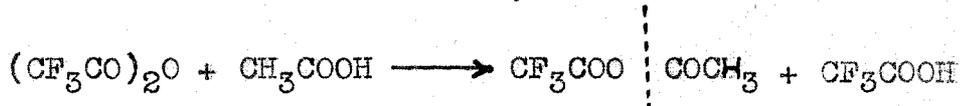


The formation of a monoester when acid anhydride was used in conjunction with its acid, and a dihydric alcohol, was supported by the work of Almirante,<sup>66</sup> who prepared an equimolar mixture of monoester and diester, on esterification of 1,phenyl-1,3-propane diol with stearic acid, using trifluoroacetic acid anhydride as a promoter





Tedder<sup>146</sup> in his review on trifluoroacetic anhydride states that it is an excellent promoter of esterification processes under mild conditions, especially applicable in carbohydrate chemistry. He refers to Tatlow's<sup>166</sup> theory that carboxylic acids are converted to mixed anhydrides with trifluoroacetic acid i.e.,



Because of the acidity of the trifluoroacetic acid being much greater than that of the common organic acids, these mixed anhydrides tend to split off trifluoroacetate anion,  $\text{CF}_3\text{COO}^-$  and an acyl cation  $\text{CH}_3\text{CO}^+$ <sup>167</sup> which reacts readily with alcohols



Faurote<sup>164</sup> has prepared diesters from 1,1-dihydroperfluoroalcohols and dibasic carboxylic acids using p-toluenesulphonic acid monohydrate as a promoter, but there

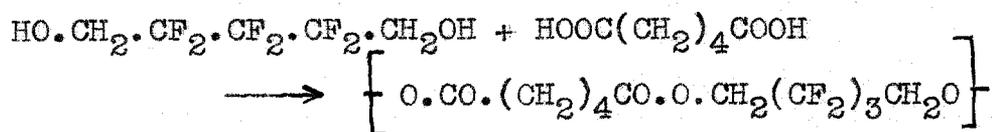
appears to be no reference to ester formation using trifluoroacetic acid anhydride as promoter with fluoro alcohols.

This has now been carried out using 1,1,3-trihydroperfluorobutanol (prepared by the free-radical addition of methanol to perfluoropropylene) esterifying it with adipic and sebacic acids in the presence of the anhydride. Good yields of mainly mono-esters have been formed as shown by analysis, molecular weight and infra-red investigation. These mono-esters were stable at their boiling points being slightly opaque grey non-viscous liquids.

Hauptschein<sup>159</sup> prepared diesters of adipic and sebacic acids with 1,1-dihydroperfluorobutanol and investigated their infra-red spectra. He found C=O frequency shift from  $5.75\ \mu$  for a normal ester<sup>168</sup> to  $5.66\ \mu$  for his compounds. Radell<sup>151</sup> states that diesters of this type show C=O frequency from  $5.59\ \mu$  to  $5.54\ \mu$ . Our mono-esters showed C=O frequencies at  $5.7\ \mu$  -  $5.75\ \mu$  as well as a band at  $5.82\ \mu$  -  $5.85\ \mu$ .

This esterification technique was extended to the co-telomer alcohols prepared from hexafluoropropylene; vinylidene fluoride and methanol; giving a mixture of liquid and solid esters of adipic acid, smelling of black-currents.

The literature contains a report that a polyester elastomer has been made, by the esterification of 2,2,3,3,4,4,hexafluoro-1,5-pentanediol with adipic acid.<sup>170</sup>



this being similar to the one made by Hauptschein<sup>163</sup> using perfluoroadipic acid (see p.101) and it is likely that the mono-esters prepared in this laboratory can be further reacted with fluoroalcohol to make diesters, if the mono-ester acid chloride is reacted with the alcohol, as described by Hauptschein<sup>87</sup> (p.100.).

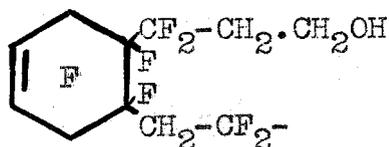
#### Hydrogenation of co-telomer alcohols

The co-telomer alcohols prepared from the octafluorocyclohexadienes, vinylidene fluoride and methanol were hydrogenated\* (palladised carbon at 100 atmospheres, 130°C for 30 hours using ethanol as solvent) in order to remove any labile fluorine atoms, and to saturate any double bonds formed by this process. It had been noted that the perfluorocyclohexa-1,4-diene co-telomer alcohols eliminated hydrogen fluoride, or halogen, on standing in air. This

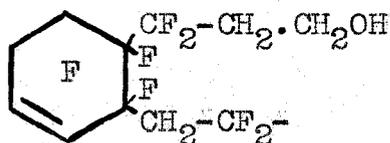
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\* Hydrogenation performed by R.H. MOBBS.

elimination was not so pronounced in the perfluorocyclohexa-1,3-diene co-telomer alcohols however. This fundamental instability was thought to be due to structures containing tertiary fluorine atoms adjacent to each other or to methylene groups such as:



1,4-diene  
co-telomer



1,3-diene  
co-telomer

these tertiary fluorine atoms would seem to be labile, and be removed by heating during distillation.

Hydrogenation of both co-telomer systems, followed by reduced pressure distillation into two "fractions", and molecular weight and fluorine analysis of these "fractions", showed that a decrease in fluorine content and molecular weight had occurred. This was in comparison with similar "fractions" taken from non-hydrogenated samples of the same co-telomers.

Infra-red spectra investigation did not indicate that saturation of double bonds formed by the heating during the hydrogenation process had occurred.

Unfortunately, the hydrogenated "fractions" from the perfluorocyclohexa-1,4-diene co-telomer alcohols still eliminated hydrogen fluoride, or halogen, on standing.

The perfluorocyclohexa-1,3-diene co-telomer alcohols appeared to retain their stability and did not eliminate any acidic gases on standing.

Both co-telomer alcohols were yellow, viscous liquids. The high boiling fractions from the reduced pressure distillation of the 1,4-diene co-telomer alcohols became highly coloured (red) on standing in air for six months, together with the elimination of hydrogen fluoride; the 1,3-diene co-telomer alcohols, however, remained yellow on standing for the same period of time.

This stability of the perfluorocyclohexa-1,3-diene co-telomer alcohols, compared with the perfluorocyclohexa-1,4-diene co-telomer alcohols, is most surprising (with regard to the elimination of hydrogen fluoride on standing). It can only be concluded that on distillation of the primer, at high temperatures, fluorine elimination, either as hydrogen fluoride or elemental fluorine occurs to establish a stable conjugated structure, whereas in the latter case, similar fluorine elimination does not lead to a stable conjugated configuration, hence further HF elimination occurs on standing.

These conclusions are supported by study of the infra-red spectra of the high boiling fractions.

#### Infra-red observations

The region examined was  $5\mu - 7\mu$  (assigned normally to unsaturation). In the case of the 1,3-diene co-telomer

alcohols, two major peaks arose between  $5\mu$ - $6.5\mu$ , plus a doublet at  $1527\text{ cm}^{-1}$ ,  $1504\text{ cm}^{-1}$ . These four peaks were present in both hydrogenated and unhydrogenated "fractions". The first pair ( $1724\text{ cm}^{-1}$  and  $1639\text{ cm}^{-1}$ ) arose with equal intensity in all fractions, and could be assigned as follows:-

$\text{cm}^{-1}$	unsaturation	correlation
1724	cyclic $-\text{CF}=\text{CF}-$	76,65,85,86
	linear $-\text{CF}=\text{CF}-$	14
1639	cyclic $-\text{C}=\text{C}-$	29, 66
	linear $-\text{CH}=\text{CFH}$	6

Structures such as described on p. 95 could thus be postulated. The doublet ( $1527\text{ cm}^{-1}$ ,  $1504\text{ cm}^{-1}$ ) arises close to the doublet in the spectrum of the polymer prepared from 1,3-diene and methanol (p.61) to which an aromatic structure was assigned. The difference in intensity was striking, since in the hydrogenated fractions this doublet was very intense and one could visualise defluorination having occurred, catalysed by the palladised charcoal in the hydrogenation reactions, thus stabilising the structure further.

The 1,4-diene co-telomer alcohol fractions, whether hydrogenated or not, showed a diffuse band between  $5.5\mu$ - $6.5\mu$  (see page 92 for possible structures). There was

no doublet at  $1524\text{ cm}^{-1}$   $1504\text{ cm}^{-1}$ , hence no aromatic character is indicated in these co-telomers. It is to be expected therefore, that this mixture will only attain stability on standing by HF loss, as observed.

The alcohol portion in all co-telomers of this type is retained on hydrogenation (peak in spectrum at  $3436\text{ cm}^{-1}$ ).

#### Cross-linking of co-telomer alcohols

Three general methods are known by which cross-links can be introduced into fluorocarbon co-polymers of the hexafluoropropylene; vinylidene fluoride type (VITON). They are: the action of aliphatic amines, high energy radiation or peroxides. The action of amines is by far the most important one. Smith<sup>91</sup> states that mono-amines cross-link only slowly and require a high temperature cure to cause mutual reaction at the double bonds (formed by the amine) in neighbouring chains without further involvement of the amine. On the basis of infra-red observations<sup>94</sup> he postulates that the action of the amine is to remove hydrogen fluoride to create unsaturated centres. He admits the possibility of amine adding across this unsaturated centre but does not think this to be a major reaction.

Tertiary amines, which could not add across an unsaturated centre, are excellent co-curing agents with dithiols and diamines.<sup>91</sup>



was not complete, however, without further heating the polymer for 24 hours at 200°C. This procedure resulted in the formation of new unsaturation peaks which he attributed to the formation of conjugated double-bonds. He then postulated that these conjugated centres would react with a double bond in an adjacent chain by a Diels-Alder type reaction, leading to formation of a fluorinated cyclohexene which would readily lose hydrogen fluoride to form an aromatic ring.

The co-telomer alcohols prepared by this writer by gamma irradiation show unsaturation similar to that described by Smith which is probably brought about by the irradiation process. Thus our samples are already partially cured.

The co-telomer alcohol mixture was treated with n-butylamine and the product washed with acid to remove excess amine. Decomposition and chain scission occurred to a large extent, indicated by molecular weight determination and fluorine analysis, both of these values falling by large amounts. Infra-red spectrum of the product showed a large amount of unsaturation ( $5.8\mu - 7\mu$ ). Anion-exchange resin, (basic I.R.A. 400) again produced an unsaturated structure, this time having a single infra-red absorption peak at  $5.85\mu$  ( $1709\text{ cm}^{-1}$ ) and a molecular weight higher than the starting material. The fluorine

content of this product was slightly lower than starting material however, thus cross-links must have formed via unsaturation brought about by dehydrofluorination. These base-treated co-telomers still retained their alcohol portion.

They were tested by sodium fusion and ferrous sulphate for nitrogen and gave a negative result, thus the amine does not appear to have added across the double bond formed by the dehydrofluorination. Amine hydrofluoride was precipitated in the reaction with n-butylamine.

The co-telomer alcohol from perfluorocyclohexa-1,4-diene; vinylidene fluoride and methanol on treatment with n-butylamine decomposed completely and could not be extracted from the tar which formed.

#### Scission of perfluoroalkyl iodides by gamma irradiation

Iso-perfluoropropyl iodide, being a liquid, was chosen for this work since it was easily handled in a counting device. A saturated solution of iodine and iodine<sup>131</sup> in the perfluoroalkyl iodide was irradiated by a source of  $6.83 \times 10^4$  rads/hour at room temperature, and exchange between the elemental iodine<sup>131</sup> and the iodine of the perfluoroalkyl iodide occurred to the extent of 1% after  $2\frac{1}{2}$  hours and 6% after  $5\frac{1}{2}$  hours. This works out to a G value of approximately 11 (G = number of mole-

cules of  $C_3F_7I$  exchanging per 100 e.v.).

It was intended that similar exchange reactions be carried out by thermal and ultra-violet means in order to compare G values. This would give a rough idea of the efficiency of this iodide (and other iodides) as a chain transfer agent by comparison of the ease of production of free-radicals by these techniques. Only one iodide was investigated by this worker but other iodides have now been investigated using radioiodine exchange under thermal conditions<sup>169</sup> in this laboratory.

CHAPTER 3: Experimental

## Experimental

Infra-red spectroscopy has been used for purposes of investigation of co-telomers and adducts; the infra-red spectra of all new compounds have been recorded. A Grubb-Parsons, Type G.S.2A double beam grating infra-red spectrometer was used to obtain these spectra. The sample was either in the form of a thin contact film between potassium bromide discs, or as a film left by evaporation of an anhydrous acetone solution on the KBr disc.

Molecular weights. These were determined in the case of gases, by Regnault's method. For this method, a glass bulb (126.4 mls) fitted with a high vacuum tap and a B 10 cone was used; the volume of the bulb being found by weighing the amount of water it contained at a known temperature. The bulb was evacuated using a vacuum line incorporating a mercury diffusion pump, weighed, filled with the unknown vapour to an accurately measured pressure, again using the vacuum line, and weighed again. The weight of vapour occupying the bulb at a known pressure and temperature gives the molecular weight.

The second method had the limitation that the compound used must have (a) a negligible vapour pressure, (b) be soluble in acetone, ether or benzene (most usual - acetone), (c) have a molecular weight below 1000. This instrument was a Gallenkamp semi-micro ebulliometer, suitable for the determination of molecular weights on 200 mg. samples. The samples were injected in the form of weighed pellets, or as liquids (from a weighed dropper), or as semi-solids, or viscous liquids on a looped copper wire.

### Procedure

The apparatus was set up as described in the instruction leaflet. Once the solvent (dry acetone) had reached a condition of steady boiling, a small tablet of naphthalene was dropped into the solvent for stabilisation. The apparatus was now calibrated using a pure solute, such as benzoic acid or naphthalene as follows. Five tablets (approx. 50 mg. each) were weighed accurately, and inserted into the solvent at three minute intervals, noting the resistance change, with every insertion, by bringing the galvanometer deflection back to zero. The results were tabulated as follows

R	$\Delta R$	$\Delta R$	$\Delta Wt$	$\Delta Wt$
1916				
	219	219	1710	1710
1697				
	234	453	1832	3542
1463				
etc.				

Where R = resistance

$\Delta R$  = change in resistance caused by addition of  $\Delta Wt$  gm. solute.

$\Delta Wt$  = the sum of  $\Delta Wt$  corresponding to  $\Delta R$ .

A graph was drawn  $\Delta R$  vs.  $\Delta Wt$ , the slope of which,  $\Delta R / \Delta Wt = S$ , was proportional to the molecular weight of the compound used.

$$\text{i.e. } K = \text{Mol. Wt.} \times S$$

hence for naphthalene standard

$$K = 128.1 \times S$$

K is a constant for the apparatus under these conditions. Thus for any unknown compound, a molecular weight can be determined by repeating the above procedure with the unknown compound in the same solvent, and obtaining a value  $S^*$  for the slope of this graph.

$$\text{Hence} \quad M = \frac{K}{S^*}$$

$$\therefore M = \frac{128.1 \times S}{S^*}$$

### Results

The molecular weights of several standard compounds were determined to calculate the accuracy of this method.

Compound	Mol. Wt.		% Error	
	Found	Theory	+	-
Napthalene	136.6	128.1	6.6	
"	131.2		2.4	
"	135.3		5.6	
Benzoic acid	114.4	122.1		6.3
	119.2			2.3
	109			10.7
Tristerin	869	890		2.3
Squalane	438	423	4.2	

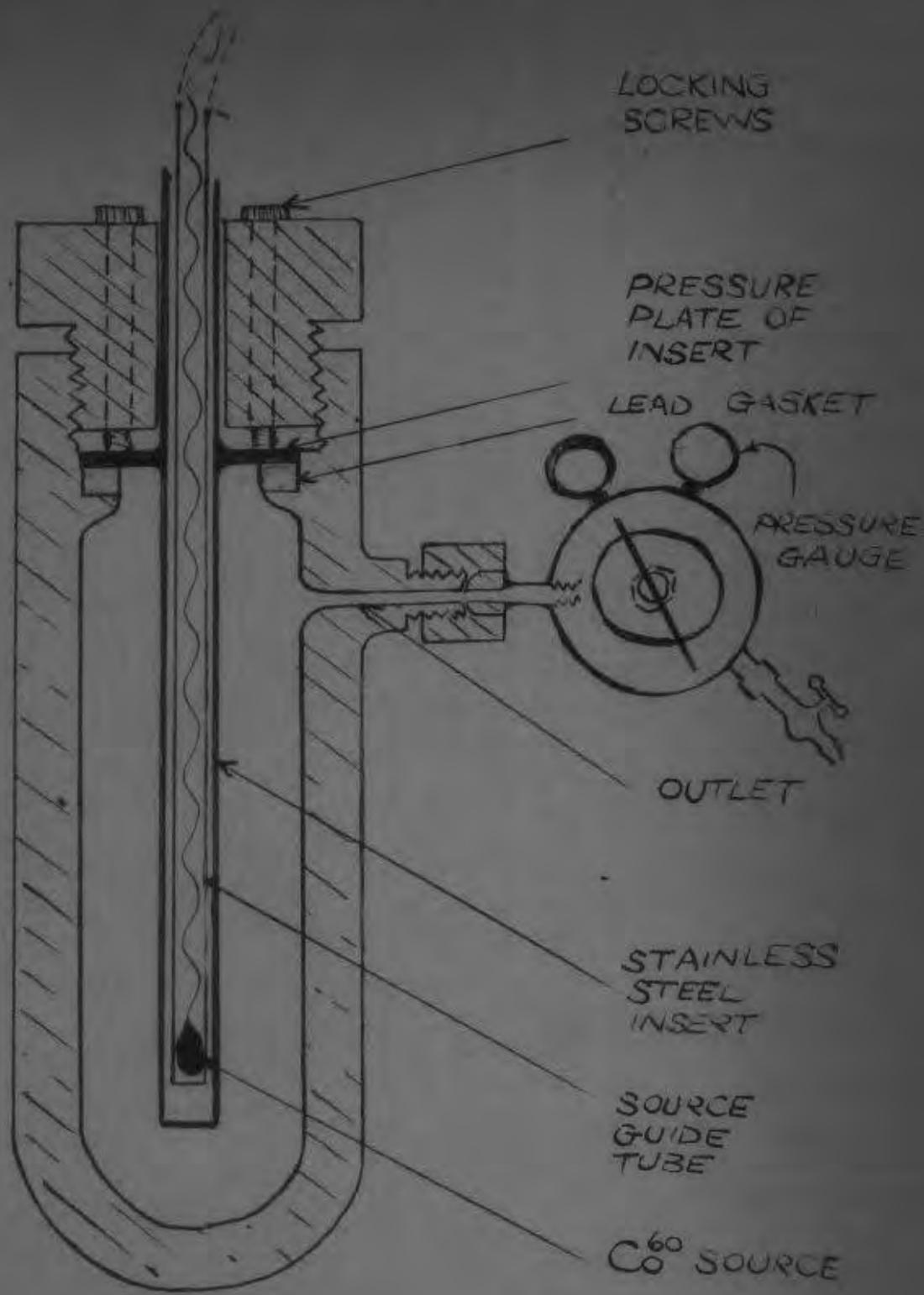
### Pressure Reactions.

Small scale work was carried out in thick-walled, pyrex, carius tubes, and the large-scale reactions were carried out in a stainless-steel autoclave (effective volume 380 ml) fitted with a stainless-steel insert, to accommodate the gamma source guide tube; (see figure)

### General procedure.

1. Carius tubes. The chain transfer agent was weighed directly into the tubes wherever possible, except in the case of evil-smelling, volatile, telogens such as  $\text{CH}_3\text{SH}$ , when vacuum transfer of a weighed sample was employed.

The tube, fitted with a B.14 cone, was attached to a vacuum line incorporating a mercury diffusion pump, and immersed in liquid air. It was evacuated, and whilst isolated from the pumping system, allowed to warm to room temperature, in order that telogen may vapourise. After once more cooling in liquid air, the tube was evacuated again. Thus all oxygen was removed which might otherwise have inhibited the reaction. The olefin monomers were either stored in three-litre bulbs in the line with mercury float valves, or in cylinders. In the former case the required weights of olefins were transferred via a calibrated volume into the carius tube. In the latter case, the cylinders were connected in turn to the vacuum line with pressure tubing, the connecting tube evacuated, and the desired weight of gas passed into a calibrated system, and then into the carius tube. (No condensing of gas was necessary and vacuum transfer was extremely rapid). The cylinders were weighed before



AUTOCLAVE (380 ml.)

and after each sample was removed. Thus the molar ratio of olefins in any one reaction was known exactly, as a ratio of manometer pressures in the same calibrated volume.

Once the tube had been charged with the proportion of olefins required, it was isolated from the line by a tap, and sealed at the constriction previously drawn below the B.14 cone. Thus the tube was removed from the vacuum line, and placed directly next to the gamma source for irradiation.

2. Autoclave. Non-volatile chain transfer agents were weighed directly into the autoclave, the insert fitted, and the pressure head screwed down. The autoclave was cooled in liquid air for half an hour. The outlet from the pressure gauge was connected to the vacuum line with pressure tubing, and, when the autoclave was cooled down, it was evacuated. The olefins were transferred from their cylinders via a three-litre bulb, into the autoclave, and the amount transferred in each case determined by weighing the cylinders before and after the operation. The actual ratio of gases transferred was controlled accurately by noting the manometer pressure of gas in the three-litre bulb, as the gases were transferred. The valve to the autoclave was now closed, and the autoclave allowed to warm to room temperature. The pressure inside the autoclave was noted, and it was irradiated until this pressure ceased to fall. The reactions were followed by,

- (a) looking for a change in the viscosity of the liquids in the carius tube, or formation of a solid. Once either of these are observed the tube was removed.

(b) Watching the pressure drop in the autoclave to a constant value.

In all cases, the duration of irradiation was noted.

Working up.

Carius tubes, after cooling their contents in liquid air, were hot-spotted, but not broken. They were connected to the vacuum system with wide-bore pressure tubing, or by placing the entire tube with the hot-spotted crack broken in a wide necked twelve-inch long trap, and cooling this trap in liquid air whilst attaching it to the vacuum line.

In either case the connections to the vacuum line were evacuated. If the carius tube was connected to the line by rubber pressure tubing (a more common procedure) this was evacuated, and once the hot-spotted crack had been broken by finger pressure through the pressure tubing, the carius tube was allowed to warm up to room temperature, very carefully. All the volatiles at room temperature were expanded into a large volume in the line, to which a vapour density bulb was attached. The average molecular weight of these volatiles was thus determined, and the relative amounts of recovered olefins estimated from this determination.

(Fractionation through a horizontal train of evacuated traps, cooled in various temperature cooling baths, was shown to be inefficient for separating gaseous mixtures; but useful for freeing the telogen from excess gases).

The gas-free liquid remaining in the carius tube (telogen plus products) was pipetted from the carius tube to a 200 ml florentine flask, and the telogen removed by pumping at room temperature, collecting the

telogen in liquid air. This 'fraction' was tested on analytical gas-liquid chromatography for purity and if necessary fractionally distilled at atmospheric pressure using a 6" vigreux column to isolate any product (such as an adduct).

The telogen-free telomer mixture remained in the florentine flask, and was usually transferred to a simple one-piece distillation apparatus, for distillation at 0.003 mm (pirani) up to 200°C.

The distillate b.p. 60° - 200°C at 0.003 mm was re-distilled at 0.003 mm, collecting crude fractions at approximately 50°C intervals. Each fraction was investigated by molecular weight determination (ebullioscopic), fluorine analysis, and infra-red spectrum observation.

The autoclave was worked up similarly, but, if excessive amounts of unreacted gas were recovered, the autoclave was vented into the vacuum line in such a manner as to fill the storage space in the line, in several successive operations. Each operation being accompanied by a vapour density determination, and followed by storing each portion of gas in liquid air, isolated from the storage system. If a volatile telogen was used, it was often impossible to fractionate it from recovered gas, hence the amount of telogen recovered must either be estimated by vapour density determination on the mixture, or using analytical gas-liquid chromatography as described below. Telogens such as  $\text{CH}_3\text{SH}$ , or  $\text{C}_2\text{F}_5\text{I}$  must be handled in this manner when the reaction mixture contains  $\text{CF}_3\text{COOH}$ , this is estimated by titration as described below.

If a volatile, liquid, olefin was used, and was recovered along with

telogen, the amount recovered was estimated using analytical-gas-liquid chromatography described below.

In both cases the telogen ( $\text{CF}_3\text{COOH}$ ) or olefin ( $\text{C}_6\text{F}_8$ ) was pumped from the reaction vessel, and collected in liquid air in the vacuum line.

### Gas-liquid Chromatography

#### Analytical.

A Griffin and George Mark IIB model, with two U-shaped columns (3 ft. x  $\frac{1}{4}$  in.) has been used for analytical work. The packing of the columns consisting of kieselguhr as an inert support with 40% stationary phase of either tricresyl phosphate or silicone elastomer. This apparatus has been used for:

- (a) Determination of purity of samples.
- (b) For identification of unknowns using comparison of retention times with authentic samples.
- (c) To establish the composition of a mixture containing two components, inseparable by distillation or preparative gas-liquid chromatography, such as  $\text{CH}_3\text{OH}$ ; 1,3- $\text{C}_6\text{F}_8$ .

This was done by preparing a set of samples containing various molar ratios of the mixture concerned, and injecting a standard amount of each sample i.e. 3 drops into the apparatus in turn under identical conditions. Each injection results in a pattern of two peaks of different peak areas. If the ratio of these peak areas is plotted graphically against the molar ratio of the corresponding injected sample, a graph results, from which the composition of any unknown molar ratio of this particular mixture can be

read directly, knowing the ratio of the peak areas of this unknown.

This procedure must be repeated each time a mixture of unknown molar composition is investigated, since the conditions of column temperature, flow-rate, pressure difference across the column, and bridge current, must be exactly the same for each injection.

Estimation of mixtures containing two components, one of which is  $\text{CF}_3\text{COOH}$

$\text{CF}_3\text{COOH}$  cannot be estimated using analytical gas-liquid chromatography, since it seems to attack the column packing to give a series of peaks. Thus the composition of a mixture of  $\text{CF}_3\text{COOH}$  and, say,  $1,3\text{-C}_6\text{F}_8$  must be determined in the following manner:

The mixture was extracted with distilled water, and the aqueous layer titrated, first with 2N NaOH and then, nearer the end-point, with N/10 NaOH using phenol phthalein as indicator.

Large-scale polymerisation of tetrafluoroethylene

Tetrafluoroethylene was prepared by the pyrolysis of Teflon waste. A steel tube (3 ft. long x 1 inch internal diameter) blocked at one end, and connected at the other to a system consisting of a large cooled trap ( $-183^\circ\text{C}$ ), a monometer, and an oil pump, was charged with teflon shavings (100 gm) which were held in the central region of the tube by a packing of steel wool at either end. This central part of the tube was then heated in an electric furnace at  $550 - 600^\circ\text{C}$  for one hour, the pressure being set at 5 - 10 min. by a needle valve. Exit gas was collected in the cooled trap. Analytical gas-liquid chromatography show impurity of hexafluoropropene, the proportion of which in the mixture was determined by vapour density

determination. A crude, low temperature distillation through a series of evacuated traps removed some, but not all, of the impurity.

Reaction vessel.

380 ml capacity autoclave, which after charging with gas was irradiated on the 500 curie source.

Results.

Run	Source of Starting Material	Purity by V.D. Analysis	Irrad <sup>n</sup> . Time Hours	Final Pressure Atm.	Weight		Product
					In Gas	Out Polymer	
1	Pyrolysis of teflon at 550°C	80% C <sub>2</sub> F <sub>4</sub> 20% C <sub>3</sub> F <sub>6</sub>	70	4	17	10.5	White powder having electrostatic properties
2	ditto; but fractionated	97% C <sub>2</sub> F <sub>4</sub> 3% C <sub>3</sub> F <sub>6</sub>	130	2	18.3	16.8	
3	Supplied by I.C.I.	100% C <sub>2</sub> F <sub>4</sub>	25.7	1	19.8	18.9	
4	Supplied by I.C.I.	100% C <sub>2</sub> F <sub>4</sub>	49	1	22.1	20.9	

The following results were supplied by I.C.I. (Plastics) Ltd., on these samples.

Run	1	2	3	4	Teflon Commercial
Composition of Starting Material	80% $C_2F_4$ 20% $C_3F_6$	97% $C_2F_4$ 3% $C_3F_6$	100% $C_2F_4$	100% $C_2F_4$	100% $C_2F_4$
Composition of Polymer by Infra-red Measurement	6% $C_3F_6$	0.9% $C_3F_6$	100% $C_2F_4$	100% $C_2F_4$	100% $C_2F_4$
X-ray Crystallinity	70%	85%	85-90%	85-90%	85-90%
Crystalline Melting Point	315.6	326.6	327	327	327

Unless otherwise stated, all the following reactions have been carried out in pyrex carius tubing.

ADDITION OF TELOGENS TO NON-HOMOPOLYMERISABLE OLEFINS  
OF TYPE A

Additions to Hexafluoropropene

<u>Telogen</u>		CH <sub>3</sub> OH
<u>Reagents</u>		CH <sub>3</sub> OH (14.8 gm., 0.46 mol) C <sub>3</sub> F <sub>6</sub> (36.9 gm., 0.24 mol)
<u>Irradiation</u>		51 days 17 hours
<u>Source</u>		100 curie
<u>Recovered</u>		CH <sub>3</sub> OH 6.5 gm. C <sub>3</sub> F <sub>6</sub> Nil
<u>Reacted</u>		CH <sub>3</sub> OH (8.3 gm., 0.25 mol) C <sub>3</sub> F <sub>6</sub> (36.9 gm., 0.24 mol)
<u>Product</u>	(a)	Colourless mobile liquid, 37 gm., 82% yield; Found F, 61.9%, M, 186, n <sub>D</sub> <sup>18</sup> 1.32918, b.p. 114°C., Calc. for CH <sub>2</sub> OH(C <sub>3</sub> F <sub>6</sub> )H, F, 62.6%, M, 182.
<u>Infra-red</u>	(a)	Peaks at 3436 cm <sup>-1</sup> (broad) O-H, 2985 cm <sup>-1</sup> (s) C-H, no unsaturation.
	(b)	A black residue 7.8 gm. (18% yield) remained after distillation at atmospheric pressure; Found F, 58.6%. Calc. for H(C <sub>3</sub> F <sub>6</sub> )CH <sub>2</sub> OH, less IH, F, 58.6%.
<u>Infra-red</u>	(b)	Unsaturation peak 1770 cm <sup>-1</sup> (s) and O-H stretch at 3436 cm <sup>-1</sup> (broad).
<u>Telogen</u>		H(C <sub>3</sub> F <sub>6</sub> )CH <sub>2</sub> OH

<u>Reagents</u>	H(C <sub>3</sub> F <sub>6</sub> )CH <sub>2</sub> OH (11.5 g., 0.063 mol) C <sub>3</sub> F <sub>6</sub> (4.4 g., 0.029 mol)
<u>Irradiation</u>	32 days 2 hours
<u>Source</u>	100 curie
<u>Recovered</u>	H(C <sub>3</sub> F <sub>6</sub> )CH <sub>2</sub> OH 10.6 gm. C <sub>3</sub> F <sub>6</sub> 4.4 gm.
<u>Reacted</u>	Negligible amounts.
<u>Product</u>	A viscous brown residue from distillation at atmospheric pressure, 0.92 gm; Found F, 60.9%. Calc. for CF <sub>3</sub> CF=CF <sub>2</sub> CH <sub>2</sub> OH, F, 58.6%.
<u>Infra-red</u>	OH stretching at 3436 cm <sup>-1</sup> (broad) unsaturation at 1770 cm <sup>-1</sup> (s).
<u>Telogen</u>	CF <sub>3</sub> COOH
<u>Reagents</u>	CF <sub>3</sub> COOH (9.95 gm., 0.087 mol) C <sub>3</sub> F <sub>6</sub> (6.35 gm., 0.042 mol)
<u>Irradiation</u>	12 days 1 hour
<u>Source</u>	500 curie
<u>Recovered</u>	CF <sub>3</sub> COOH 9.8 gm. C <sub>3</sub> F <sub>6</sub> 6.3 gm.
<u>Reacted</u>	Negligible amounts
<u>Product</u>	0.4 gm. black residue remained after distillation at atmospheric pressure.

<u>Telogen</u>		$C_6H_5CH_2OH$
<u>Reagents</u>		$C_3F_6$ (12 gm., 0.08 mol)
		$C_6H_5CH_2OH$ (15 gm., 0.13 mol)
<u>Irradiation</u>		50 days 4 hours
<u>Source</u>		100 curie
<u>Recovered</u>		$C_3F_6$ 11.63 gm.
		$C_6H_5CH_2OH$ 14.5 gm.
<u>Reacted</u>		$C_3F_6$ (0.37 gm., 0.0024 mol)
		$C_6H_5CH_2OH$ (0.5 gm., 0.0046 mol)
<u>Product</u>	(a)	0.89 gm. clear, yellow, viscous liquid, b.p. 100 - 145°C/0.05 mm; Found F, 17.2%.
	(b)	A black residue from reduced pressure distillation, 0.01 gm.
<u>Infra-red</u>	(a)	Unsaturation peaks at 1763 $cm^{-1}$ (sh), 1733 (vs), 1613, 1600 (doublet, s) 1526 (vs), 1460 (vs), O-H stretching at 3436 $cm^{-1}$ (broad). C-H stretching at 3106, 3072 (doublet), 2907 $cm^{-1}$

Since the reagents were immiscible it was decided to repeat this reaction using an inert, halogenated, solvent  $CF_2Cl \cdot CFC l_2$ .

<u>Telogen</u>	$C_6H_5CH_2OH$ in solvent
<u>Reagents</u>	$C_6H_5CH_2OH$ (23.1 gm., 0.21 mol)
	$C_3F_6$ (17.5 g., 0.12 mol)
	$CF_2ClCFC l_2$ solvent 30.7 gm.

<u>Irradiation</u>	8 days 5 hours
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{CF}_2\text{ClCFCl}_2$ 30.7 gm. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ 18.2 gm. $\text{C}_3\text{F}_6$ 15.0 gm.
<u>Reacted</u>	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (4.9 gm., 0.016 mol) $\text{C}_3\text{F}_6$ (2.5 gm., 0.045 mol)
<u>Product</u>	<p>(a) 3.2 gm. clear yellow viscous liquid, b.p. 100 - 145°/0.05 mm; Found F, 14.4%; Cl, 0%, M, 230</p> <p>Calc. for <math>\text{H}(\text{C}_3\text{F}_6)\text{C}_6\text{H}_5\text{CH}(\text{OH})</math>, F, 44%, M, 258  for <math>\text{H}(\text{C}_3\text{F}_6)\text{C}_6\text{H}_5\text{CH}(\text{OH})</math> less IHF: F, 39.9%, M, 238.</p> <p>(b) brittle black residue from reduced pressure distillation 3.5 gm.</p>
<u>Infra-red</u>	Identical to product obtained from reaction carried out without a solvent.
<u>Telogen</u>	$\text{CHCl}_3$
<u>Reagents</u>	$\text{CHCl}_3$ (33.3 g., 0.27 mol) $\text{C}_3\text{F}_6$ (20.6 gm., 0.14 mol)
<u>Irradiation</u>	14 days 21 hours
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{C}_3\text{F}_6$ 20.3 gm. $\text{CHCl}_3$ 33 gm.

<u>Reacted</u>	$\text{CHCl}_3$ (0.3 gm., 0.0025 mol)
	$\text{C}_3\text{F}_6$ (0.3 gm., 0.0020 mol)
<u>Product</u>	0.6 gm. clear white, mobile liquid, b.p. $70^\circ/0.05$ mm.; Found: F, 36.8%; Cl, 38.4%
	This gave two peaks on analytical V.P.C. (silicone elastomer at $200^\circ\text{C}$ ). Calc. for $\text{CCl}_3(\text{C}_3\text{F}_6)\text{H}$ , F, 42.3%, Cl, 39.5%.

Additions to Octafluorocyclohexa-1,4-Diene

<u>Telogen</u>	$\text{CH}_3\text{OH}$ (I)
<u>Reagents</u>	$1,4\text{-C}_6\text{F}_8$ (12.6 gm., 0.056 mol)
	$\text{CH}_3\text{OH}$ (13.6 gm., 0.42 mol)
<u>Irradiation</u>	27 days 15 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$1,4\text{-C}_6\text{F}_8$ Nil
	$\text{CH}_3\text{OH}$ 8.9 gm.
<u>Reacted</u>	$1,4\text{-C}_6\text{F}_8$ (12.6 gm., 0.056 mol)
	$\text{CH}_3\text{OH}$ (4.7 gm., 0.15 mol)
<u>Product</u>	(a) 9.4 gm. colourless mobile liquid, b.p. $163^\circ\text{C}$ ; Found F, 58.7%; M, 254, $n_D^{21}$ 1.36781. Yield 66%. Calc. for $\text{H}(\text{C}_6\text{F}_8)\text{CH}_2\text{OH}$ F, 59.4%; M, 256; $\text{H}_2[(\text{C}_6\text{F}_8)(\text{CH}_2\text{OH})_2]$ F, 52.8%; M, 288.
	(b) 7.3 gm. viscous brown residue from atmospheric pressure distillation; Found F, 52.95%; M, 265

<u>Infra-red</u>	(a)	Unsaturation region:- 1754 $\text{cm}^{-1}$ (vs); 1640 $\text{cm}^{-1}$ (w) Third order:- 3704 (shoulder); 3436 $\text{cm}^{-1}$ (broad); 2958 (s)
	(b)	Unsaturation region no peaks. Third order:- 3704 (vs); 3436 (v. broad); 2958 (vs).
<u>Telogen</u>		$\text{CH}_3\text{OH}$ (II)
<u>Reagents</u>		1,4- $\text{C}_6\text{F}_8$ (7.4 gm., 0.033 mol) $\text{CH}_3\text{OH}$ (26 gm., 0.81 mol)
<u>Irradiation</u>		64 days
<u>Source</u>		500 curie
<u>Recovered</u>		1,4- $\text{C}_6\text{F}_8$ Nil $\text{CH}_3\text{OH}$ 22.4 gm.
<u>Reacted</u>		1,4- $\text{C}_6\text{F}_8$ (7.4 gm., 0.033 mol) $\text{CH}_3\text{OH}$ (3.6 gm., 0.12 mol)
<u>Product</u>	(a)	3.2 gm. colourless mobile liquid, b.p. $100^\circ\text{C}/0.05$ mm; Found F, 18.6% (sodium fusion): M, 195.
	(b)	7.3 gm. pale yellow viscous liquid, b.p. $110^\circ - 180^\circ/0.05$ mm; Found F, 43.6% (sodium fusion): M, 264; Calc. for $(\text{C}_6\text{F}_8\text{H}_3)\text{CH}_2\text{OH}$ F, 58.9%: M, 258. (See previous experiment for other ratios).

<u>Infra-red</u>	(a)	$3436 \text{ cm}^{-1}$ (broad), OH stretch, otherwise no peaks, just a high 'background'.
	(b)	3704 (vs); 3436 (broad) OH; 2958 (vs); 2890 (w) CH. No unsaturation.
<u>Telogen</u>		$\text{CF}_3\text{CH}_2\text{OH}$
<u>Reagents</u>		$\text{CF}_3\text{CH}_2\text{OH}$ (9.35 gm., 0.09 mol) 1,4- $\text{C}_6\text{F}_8$ (9.35 gm., 0.04 mol)
<u>Irradiation</u>		12 days 14 hours
<u>Source</u>		500 curie
<u>Recovered</u>		1,4- $\text{C}_6\text{F}_8$ 6.6 gm. $\text{CF}_3\text{CH}_2\text{OH}$ 6.8 gm.
<u>Reacted</u>		1,4- $\text{C}_6\text{F}_8$ (2.7 gm., 0.013 mol) $\text{CF}_3\text{CH}_2\text{OH}$ (1.5 gm., 0.015 mol)
<u>Product</u>	(a)	1.8 gm. colourless, mobile liquid, b.p. $75^\circ\text{C}/0.01 \text{ mm}$ ; Found F, 52.2% F
	(b)	2.8 gm. brown semi-solid residue from reduced pressure distillation; Found F, 51.8%: M, 578; Calc. for $1\text{C}_6\text{F}_8$ : $1\text{CF}_3\text{CH}_2\text{OH}$ F, 64.5%: M, 324  for $2\text{C}_6\text{F}_8$ : $2\text{CF}_3\text{CH}_2\text{OH}$ less 4HF: F, 60.2%: M, 568  for $1\text{C}_6\text{F}_8$ : $1\text{CF}_3\text{CH}_2\text{OH}$ less 1HF: F, 62.5%: M, 304

<u>Infra-red</u>	(a)	$3436 \text{ cm}^{-1}$ (broad) OH; 1770, 1754, 1724 triplet (s), unsaturation.
	(b)	$3436 \text{ cm}^{-1}$ (broad) OH; $1739 \text{ cm}^{-1}$ broad diffuse unsaturation; $1527 \text{ cm}^{-1}$ , $1504 \text{ cm}^{-1}$ (w) aromatic.
<u>Telogen</u>		$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ in $\text{CF}_2\text{ClCFCl}_2$
<u>Reagents</u>		$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (10.9 gm., 0.09 mol) 1,4- $\text{C}_6\text{F}_8$ (15.2 gm., 0.07 mol)
<u>Irradiation</u>		8 days 5 hours
<u>Source</u>		500 curie
<u>Recovered</u>		$\text{CF}_2\text{ClCFCl}_2$ all $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ 10.1 gm. 1,4- $\text{C}_6\text{F}_8$ 14.3 gm.
<u>Reacted</u>		$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (0.8 gm., 0.007 mol) 1,4- $\text{C}_6\text{F}_8$ (0.9 gm., 0.004 mol)
<u>Product</u>		1.7 gm. brown residue from reduced pressure distillation; Found F, 20.7%; Cl, 0%; M, 325. Calc. for $10\text{C}_6\text{F}_8$ : $10\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ F, 45.7%; M, 332 less 1HF; F, 42.6%; M, 312.
<u>Infra-red</u>		$3436 \text{ cm}^{-1}$ (broad) OH; $3086 \text{ cm}^{-1}$ ; $3058 \text{ cm}^{-1}$ CH; 1754, 1727, 1709 (s), unsaturation.
<u>Telogen</u>		$\text{CF}_3\text{COOH}$

<u>Reagents</u>	$\text{CF}_3\text{COOH}$ (10.6 gm., 0.093 mol)
	1,4- $\text{C}_6\text{F}_8$ (5.2 gm., 0.023 mol)
<u>Irradiation</u>	12 days 14 hours
<u>Source</u>	500 curie
<u>Recovered</u>	1,4- $\text{C}_6\text{F}_8$ 4.3 gm.
	$\text{CF}_3\text{COOH}$ 10.1 gm.
<u>Product</u>	0.75 gm., red/yellow viscous residue from atmospheric distillation; Found F, 63.5%.

Additions to Octafluorocyclohexa-1,3-diene.

<u>Telogen</u>	$\text{CH}_3\text{OH}$ (I)
<u>Reagents</u>	1,3- $\text{C}_6\text{F}_8$ (10.4 gm., 0.046 mol)
	$\text{CH}_3\text{OH}$ (13 gm., 0.04 mol)
<u>Irradiation</u>	25 days 13 hours
<u>Source</u>	100 curie
<u>Recovered</u>	1,3- $\text{C}_6\text{F}_8$ 8 gm.
	$\text{CH}_3\text{OH}$ 12.6 gm.
<u>Reacted</u>	1,3- $\text{C}_6\text{F}_8$ (2.4 gm., 0.010 mol)
	$\text{CH}_3\text{OH}$ (0.4 gm., 0.012 mol)
<u>Product</u>	2.4 gm. residue, a brown viscous semi-solid; Found F, 53.7%.

<u>Telogen</u>	$\text{CH}_3\text{OH}$ (II)
<u>Reagents</u>	1,3- $\text{C}_6\text{F}_8$ (29.2 gm., 0.13 mol)
	$\text{CH}_3\text{OH}$ (101.1 gm., 3.1 mol)

<u>Irradiation</u>		7 months
<u>Source</u>		500 curie
<u>Recovered</u>		1,3-C <sub>6</sub> F <sub>8</sub> Nil
		CH <sub>3</sub> OH 96.9 gm.
<u>Reacted</u>		1,3-C <sub>6</sub> F <sub>8</sub> (29.2 gm., 0.13 mol)
		CH <sub>3</sub> OH (4.2 gm., 0.13 mol)
<u>Product</u>	(a)	20.1 gm. red/brown viscous liquid, b.p. 100 - 180°C/0.005 mm.; Found F, 56.9%; M, 477; Calc. for 1C <sub>6</sub> F <sub>8</sub> : 1CH <sub>3</sub> OH F, 59.4; M, 256; 2C <sub>6</sub> F <sub>8</sub> : 2CH <sub>3</sub> OH less 1HF; F, 57.9; M, 492 less 2HF; F, 56.3%; M, 472.  See discussion for possible structures.
	(b)	Brittle black residue, 13.2 gm.
<u>Infra-red</u>	(a)	3436 (broad) O-H; 2958 (s) C-H; 1724 (vs); 1650 (s), unsaturation.  1524, 1504 aromatic.
<u>Telogen</u>		CF <sub>3</sub> COOH
<u>Reagents</u>		CF <sub>3</sub> COOH (10.4 g., 0.91 mol) 1,3-C <sub>6</sub> F <sub>8</sub> (4 g., 0.018 mol)
<u>Irradiation</u>		12 days 14 hours
<u>Source</u>		500 curie
<u>Recovered</u>		1,3-C <sub>6</sub> F <sub>8</sub> 2.85 gm. CF <sub>3</sub> COOH 10 gm.

Reacted 1,3-C<sub>6</sub>F<sub>8</sub> (1.15 gm., 0.004 mol)  
 CF<sub>3</sub>COOH (0.4 gm., 0.003 mol)

Product (a) 0.7 gm. red/yellow mobile liquid, b.p. 80-90°C/  
 0.02 mm.

(b) Residue from reduced pressure distillation 0.45 pale  
 yellow semi-solid; Found: F, 63.6%.

Addition of telogens to perfluorocyclobutene.

Telogen CH<sub>3</sub>OH

Reagents (9) C<sub>4</sub>F<sub>6</sub> (8.6 g., 0.056 mol)  
 CH<sub>3</sub>OH (18.5 g., 0.56 mol)

Irradiation 20 days 2 hours

Source 500 curie

Recovered CH<sub>3</sub>OH 17.6 gm.  
 C<sub>4</sub>F<sub>6</sub> 3.8 gm.

Reacted CH<sub>3</sub>OH (4.8 gm., 0.029 mol)  
 C<sub>4</sub>F<sub>6</sub> (0.9 gm., 0.028 mol)

Product 5.5 gm. colourless, mobile liquid, b.p. 138°C;  
 Found: F, 58.5%; M, 188, n<sub>D</sub><sup>20</sup> 1.34596; Calc. for  
 H(C<sub>4</sub>F<sub>6</sub>)CH<sub>2</sub>OH; F, 58.7%; M, 194.

Infra-red 3436 (broad) O-H; 2958 (s) C-H; 1639 (s),  
 unsaturation.

Telogen CF<sub>3</sub>COOH

Several reactions were carried out with this mixture.

<u>Reagents</u>	$\underline{c}$ $C_4F_6$ (18.3 gm., 0.11 mol) $CF_3COOH$ (4.9 gm., 0.42 mol)
<u>Irradiation</u>	24 days 1 hour
<u>Source</u>	500 curie
<u>Recovered</u>	$\underline{c}$ $C_4F_6$ 15.2 gm. $CF_3COOH$ 4.9 gm.
<u>Reacted</u>	$\underline{c}$ $C_4F_6$ (3.1 gm., 0.019 mol) $CF_3COOH$ (Nil)
<u>Product</u>	3.1 gm. brown viscous liquid smelling of $CF_3COOH$ . This was combined with a product similar in appearance (5 gm.) from a reaction using $C_4F_6$ (27.8 gm., 0.17 mol) $CF_3COOH$ (34.5 gm., 0.3 mol) and hydrolysed using dilute $H_2SO_4$ . The hydrolysed product no longer liberated $CF_3COOH$ on standing.  Found: $M = 1506$ ; Calc. for $(C_4F_6)_{10}$ 1620, Found $F, 56\%$ Calc. for $(C_4F_6)_{12}$ less $22\frac{1}{2} HF$ , $F, 62\%$ . $M, 1504$ 3436 $cm^{-1}$ (broad band) O-H stretch; 3003 $cm^{-1}$ (s) C-H stretch; 1754 $cm^{-1}$ (s), 1639 $cm^{-1}$ (w) either C=O stretch or unsaturation.
<u>Infra-red</u>	

Addition of telogens to decafluorocyclohexene

<u>Telogen</u>	$CH_3OH$
<u>Reagents</u>	$\underline{c}$ $C_6F_{10}$ (2.5 gm., 0.0095 mol) $CH_3OH$ (3.2 gm., 0.1 mol)
<u>Irradiation</u>	12 days 7 hours

<u>Source</u>	500 curie
<u>Recovered</u>	$C_6F_{10}$ Nil $CH_3OH$ 2.85 gm.
<u>Reacted</u>	$C_6F_{10}$ (2.5 gm., 0.0095 mol) $CH_3OH$ (0.35 gm., 0.01 mol)
<u>Product</u>	2.7 gm. colourless, mobile, liquid, b.p. $145^{\circ}C$ , 96% yield; Found: F, 64.7%; M, 290, $n_D^{21}$ 1.34087; Calc. for $H(C_6F_{10})CH_2OH$ F, 64.6%; M, 294.
<u>Infra-red</u>	$3436\text{ cm}^{-1}$ (broad) O-H; 2985 (s) C-H.
<u>Telogen</u>	$CF_3COOH$
<u>Reagents</u>	$C_6F_{10}$ (14.2 gm., 0.054 mol) $CF_3COOH$ (12.0 gm., 0.105 mol)
<u>Irradiation</u>	25 days 14 hours 100 curie 29 days 1 hour 500 curie
<u>Source</u>	See above
<u>Recovered</u>	$C_6F_{10}$ (14.2 gm.) $CF_3COOH$ (12.0 gm.)
<u>Reacted</u>	$C_6F_{10}$ (Nil) $CF_3COOH$ (Nil)
<u>Product</u>	Nil

ADDITION OF TELOGENS TO HOMOPOLYMERISABLEOLEFINS OF THE TYPE BAdditions to vinylidene fluoride

<u>Telogen</u>	$\text{CH}_2\text{OH}(\text{C}_3\text{F}_6)\text{H}$
<u>Reagents</u>	$\text{CH}_2\text{OH}(\text{C}_3\text{F}_6)\text{H}$ (9.5 gm., 0.05 mol)
	$\text{CF}_2=\text{CH}_2$ (3.8 gm., 0.06 mol)
<u>Irradiation</u>	11 days 17 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$\text{CF}_2=\text{CH}_2$ (Nil)
	$\text{CH}_2\text{OH}(\text{C}_3\text{F}_6)\text{H}$ (9.3 gm.)
<u>Reacted</u>	$\text{CF}_2=\text{CH}_2$ (3.8 gm., 0.06 mol)
	$\text{CH}_2\text{OH}(\text{C}_3\text{F}_6)\text{H}$ (Nil)
<u>Product</u>	3.8 gm. white, crystalline polymeric material; Found: F, 60.6% (sodium fusion); Calc. for poly- vinylidene fluoride: F, 59.4%.
<u>Infra-red</u>	Strong peaks at the following wave-numbers: 1408, 1282, 1212, 1190, 1075, 980, 877, 840, 800, 763, 613.
<u>Telogen</u>	$\text{CH}_3\text{OH}$
<u>Reagents</u>	$\text{CH}_3\text{OH}$ (8.2 g., 0.26 mol)
	$\text{CF}_2=\text{CH}_2$ (1.66 g., 0.025 mol)
<u>Irradiation</u>	59 days 20 hours
<u>Source</u>	100 curie

Recovered  $\text{CH}_3\text{OH}$  8.1 gm.  
 $\text{CF}_2=\text{CH}_2$  0.24 gm.

Reacted  $\text{CH}_3\text{OH}$  (negligible)  
 $\text{CF}_2=\text{CH}_2$  (1.42 gm.)

Product 1.4 gm. polymeric white material; Found: F, 58.9%  
(sodium fusion); Calc. for polyvinylidene fluoride  
F, 59.4%. Infra-red spectrum of this material identical  
to polyvinylidene fluoride.

Telogen  $\text{CF}_3\text{COOH}$

Reagents  $\text{CF}_3\text{COOH}$  (31 gm., 0.43 mol)  
 $\text{CF}_2=\text{CH}_2$  (8.5 gm., 0.12 mol)

Irradiation 4 days 5 hours with vapour phase shielded.

Source 500 curie

Recovered  $\text{CF}_2=\text{CH}_2$  1.6 gm.  
 $\text{CF}_3\text{COOH}$  31 gm.

Product 6.9 gm. homopolymer of vinylidene fluoride (by  
comparison of infrared spectra).

Telogen  $\text{CF}_3\text{COOH}$

Reagents  $\text{CF}_3\text{COOH}$  (90 g., 0.78 mol)  
 $\text{CF}_2=\text{CH}_2$  (8.5 gm., 0.13 mol)

Irradiation In autoclave with no irradiation

Source

<u>Recovered</u>	All starting material
<u>Product</u>	Nil
<u>Telogen</u>	$\text{CF}_2\text{Cl}\cdot\text{CFCl}_2$
<u>Reagents</u>	$\text{CF}_2\text{Cl}\cdot\text{CFCl}_2$ (31 gm., 0.16 mol) $\text{CF}_2=\text{CH}_2$ (2.5 gm., 0.04 mol)
<u>Irradiation</u>	1 day 23 hours with vapour phase shielded.
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{CF}_2\text{ClCFCl}_2$ 31 gm. $\text{CF}_2=\text{CH}_2$ Nil
<u>Product</u>	2.5 gm. homopolymer of vinylidene fluoride
<u>Telogen</u>	$\text{H}(\text{C}_6\text{F}_{10})\text{CH}_2\text{OH}$
<u>Reagents</u>	$\text{H}(\text{C}_6\text{F}_{10})\text{CH}_2\text{OH}$ (13.5 gm., 0.045 mol) $\text{CF}_2=\text{CH}_2$ (7 gm., 0.09 mol)
<u>Irradiation</u>	63 days 2 hours with vapour phase shielded.
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{H}(\text{C}_6\text{F}_{10})\text{CH}_2\text{OH}$ (13.5 gm.) $\text{CF}_2=\text{CH}_2$ (4 gm.)
<u>Product</u>	3 gm. homopolymer of vinylidene fluoride, by comparison of infra-red spectra.

Addition to chlorotrifluoroethylene.

Telogen  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$

<u>Reagents</u>	$\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$ (19.2 gm., 0.105 mol)
	$\text{CF}_2=\text{CFCl}$ (13.6 gm., 0.116 mol)
<u>Irradiation</u>	Unknown, since the tube cracked after two days
<u>Source</u>	100 curie
<u>Recovered</u>	$\text{CF}_2=\text{CFCl}$ Nil
	$\text{CH}_2\text{OH}(\text{C}_3\text{F}_6)\text{H}$ 12.1 gm.
<u>Product</u>	6 gm. white polymeric material; Found: F, 48.9%; Cl, 29.1%; Calc. for polychlorotrifluoroethylene: F, 48.9%; Cl, 30.5%.

CO-TELOMERISATION REACTIONS - SYSTEM ONE

Hexafluoropropylene and tetrafluoroethylene

<u>Telogen</u>	Nil
<u>Reagents</u>	$\text{C}_2\text{F}_4$ (3.57 gm., 0.035 mol)
	$\text{C}_3\text{F}_6$ (4.9 gm., 0.033 mol)
<u>Irradiation</u>	13 days 17 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$\text{C}_2\text{F}_4$ Nil
	$\text{C}_3\text{F}_6$ 4.27
<u>Reacted</u>	$\text{C}_2\text{F}_4$ (3.57 gm., 0.035 mol)
	$\text{C}_3\text{F}_6$ (0.63 gm., 0.005 mol)
<u>Product</u>	4.2 gm. white polymeric solid; Found: F, 75% (by sodium fusion); Calc. for $(\text{CF}_2)_n$ F, 76%.

<u>Infra-red</u>	Strong bands at $1219\text{ cm}^{-1}$ , $1156\text{ cm}^{-1}$ , $990\text{ cm}^{-1}$
<u>Telogen</u>	$\text{CH}_3\text{OH}$
<u>Reagents</u>	$\text{C}_2\text{F}_4$ (2.5 gm., 0.025 mol) $\text{C}_3\text{F}_6$ (4.0 gm., 0.026 mol) $\text{CH}_3\text{OH}$ (5.4 gm., 0.17 mol)
<u>Irradiation</u>	30 days 7 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$\text{C}_2\text{F}_4$ Nil $\text{C}_3\text{F}_6$ Nil $\text{CH}_3\text{OH}$ 4.7 gm.
<u>Reacted</u>	$\text{C}_2\text{F}_4$ (2.5 gm., 0.025 mol) $\text{C}_3\text{F}_6$ (4.0 gm., 0.026 mol) $\text{CH}_3\text{OH}$ (0.7 gm., 0.022 mol)
<u>Product</u>	(a) 3.3 gm. white polymeric solid, shown to be the telogen free co-polymer of $\text{C}_2\text{F}_4$ with $\text{C}_3\text{F}_6$ by comparison of infra-red spectra. (b) 3.9 gm. $\text{CF}_3\cdot\text{CFH}\cdot\text{CF}_2\cdot\text{CH}_2\text{OH}$ shown by comparison of infra-red spectra, and comparative gas-liquid chromatography with an authentic sample (silicone elastomer at $110^\circ\text{C}$ ).
<u>Telogen</u>	acetone
<u>Reagents</u>	$\text{CH}_3\text{COCH}_3$ (4 gm., 0.069 mol) $\text{C}_2\text{F}_4$ (2 gm., 0.02 mol) $\text{C}_3\text{F}_6$ (2.2 gm., 0.015 mol)

Irradiation 14 days 18 hours

Source 100 curie

Recovered  $C_2F_4$  Nil  
 $C_3F_6$  1.0 gm.  
 $(CH_3)_2CO$  3.7 gm.

Reacted  $C_2F_4$  (2 gm., 0.02 mol)  
 $C_3F_6$  (1.2 gm., 0.008 mol)  
 $(CH_3)_2CO$  (0.3 gm., 0.005 mol)

Product 3.3 gm. white polymeric solid; Found: F, 74.3% (by sodium fusion); Calc. for  $(CF_2)_n$  F, 76%.

Telogen  $CH_3CHO$

Reagents  $C_2F_4$  (4.9 gm., 0.049 mol)  
 $C_3F_6$  (7.4 gm., 0.049 mol)  
 $CH_3CHO$  (9 gm., 0.2 mol)

Irradiation 32 days 2 hours

Source 100 curie

Recovered  $C_2F_4$  Nil  
 $C_3F_6$  Nil  
 $CH_3CHO$  7 gm.

Reacted  $C_2F_4$  (4.9 gm., 0.049 mol)  
 $C_3F_6$  (7.4 gm., 0.049 mol)  
 $CH_3CHO$  (2 gm., 0.045 mol)

- Product separated by V.P.C. (silicone elastomer 100°C).
- (a) 4.7 gm. colourless, mobile liquid, Found: F, 60.4%;  
Calc. for  $\text{H}(\text{C}_3\text{F}_6)\text{COCH}_3$ , F, 59%.
- (b) 1.8 gm. colourless, mobile liquid; Found: F, 63.4%;  
Calc. for  $\text{H}[(\text{C}_3\text{F}_6)(\text{C}_2\text{F}_4)]\text{COCH}_3$  F, 64.6%.
- (c) Residue from atmospheric pressure distillation 3.8 gms.  
black semi-solid; Found: F, 56.9%.

Telogen  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$

Reagents  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$  (10 gm., 0.085 mol)

$\text{C}_2\text{F}_4$  (2 gm., 0.02 mol)

$\text{C}_3\text{F}_6$  (3.3 gm., 0.02 mol)

Irradiation 10 days 3 hours

Source 100 curie

Recovered  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$  9.7 gm.

$\text{C}_2\text{F}_4$  Nil

$\text{C}_3\text{F}_6$  2.7 gm.

Reacted  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$  (0.3 gm., 0.0026 mol)

$\text{C}_3\text{F}_6$  (0.6 gm., 0.004 mol)

$\text{C}_2\text{F}_4$  (2 gm., 0.02 mol)

Product 2.5 gm. white, polymeric, nitrogen-containing material;  
Found: F, 72.3% (by sodium fusion).

Telogen  $\text{C}_2\text{F}_5\text{I}$

<u>Reagents</u>	$C_2F_5I$	(15.5 gm., 0.063 mol)
	$C_2F_4$	(1.9 gm., 0.019 mol)
	$C_3F_6$	(1.9 gm., 0.012 mol)
<u>Irradiation</u>		30 days
<u>Source</u>		100 curie
<u>Recovered</u>	$C_2F_5I$	approx. 8 gm.
	$C_2F_4$	Nil
	$C_3F_6$	Nil
<u>Reacted</u>	$C_2F_5I$	(approx. 7.5 gm.)
	$C_2F_4$	(1.9 gm., 0.019 mol)
	$C_3F_6$	(1.9 gm., 0.012 mol)
<u>Product</u>		9.1 gm. sticky pink semi-solid. Found: F, 56.9% ; I, 37.2%; m.p. 170°C; Calc. for $I[(C_2F_4)(C_3F_6)]_n C_2F_5$ ; n = 1; F, 56.7%; I, 26%.

<u>Telogen</u>	$CF_3COOH$	
<u>Reagents</u>	$CF_3COOH$	(10.3 gm., 0.903 mol)
	$C_2F_4$	(1.75 gm., 0.017 mol)
	$C_3F_6$	(2.25 gm., 0.015 mol)
<u>Irradiation</u>		10 days 16 hours
<u>Source</u>		100 curie
<u>Recovered</u>	$CF_3COOH$	10.2 gm.
	$C_2F_4$	Nil
	$C_3F_6$	0.7 gm.

<u>Reacted</u>	CF <sub>3</sub> COOH (negligible)
	C <sub>2</sub> F <sub>4</sub> (1.75 gm., 0.017 mol)
	C <sub>3</sub> F <sub>6</sub> (1.55 gm., 0.01 mol)
<u>Product</u>	3.3 gm. white polymeric material, having the same infra-red spectrum as the parent co-polymer; Found: F, 74.4% (sodium fusion). Calc. for (CF <sub>2</sub> ) <sub>n</sub> F, 76%; for H[(C <sub>2</sub> F <sub>4</sub> )(C <sub>3</sub> F <sub>6</sub> )] <sub>n</sub> OCOCF <sub>3</sub> ; n = 1; F, 68%; for H[(C <sub>3</sub> F <sub>6</sub> )(C <sub>2</sub> F <sub>4</sub> ) <sub>3</sub> ]OCOCF <sub>3</sub> ; F, 73.3%.
<u>Telogen</u>	CF <sub>3</sub> COOH
<u>Reagents</u>	CF <sub>3</sub> COOH (114 gm., 1.0 mol)
	C <sub>3</sub> F <sub>6</sub> (101 gm., 0.6 mol)
	C <sub>2</sub> F <sub>4</sub> (9.5 gm., 0.095 mol)
<u>Irradiation</u>	<u>AUTOCLAVE</u> 10 days 23 hours, final pressure 5 atm.
<u>Source</u>	500 curie
<u>Recovered</u>	CF <sub>3</sub> COOH 114 gm.
	C <sub>3</sub> F <sub>6</sub> 85.3 gm.
	C <sub>2</sub> F <sub>4</sub> Nil
<u>Reacted</u>	CF <sub>3</sub> COOH (nil)
	C <sub>3</sub> F <sub>6</sub> (16.3 gm., 0.11 mol)
	C <sub>2</sub> F <sub>4</sub> (9.5 gm., 0.095 mol)
<u>Product</u>	22.6 gm. greenish solid; m.p. 210°C; Found: F, 73.5%; Calc. for 1C <sub>3</sub> F <sub>6</sub> : 3C <sub>2</sub> F <sub>4</sub> : 1CF <sub>3</sub> COOH; F, 73.3% and for (CF <sub>2</sub> ) <sub>n</sub> , F, 76%.

Infra-red Similar to that of parent co-polymer, but the consistency of the solid indicates that chain shortening has occurred.

SYSTEM TWO Hexafluoropropylene with vinylidene fluoride

<u>Telogen</u>	Nil
<u>Reagents</u>	$C_3F_6$ (2.16 gm., 0.014 mol) $CF_2=CH_2$ (0.89 gm., 0.014 mol)
<u>Irradiation</u>	33 days 18 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$C_3F_6$ 1.14 gm. $CF_2=CH_2$ Nil
<u>Reacted</u>	$C_3F_6$ (1.02 gm., 0.006 mol) $CF_2=CH_2$ (0.89 gm., 0.014 mol)
<u>Product</u>	1.9 gm. sticky, off-white elastomer.
<u>Infra-red</u>	C-H peaks at 3058, 3030 $cm^{-1}$ (s), unsaturation peaks at 1802, 1757, and 1739 $cm^{-1}$ (s).
<u>Telogen</u>	Nil
<u>Reagents</u>	$C_3F_6$ (14.4 gm., 0.096 mol) $CF_2=CH_2$ (2.29 gm., 0.036 mol)
<u>Irradiation</u>	26 days
<u>Source</u>	100 curie
<u>Recovered</u>	$C_3F_6$ 7.7 gm. $CF_2=CH_2$ Nil

<u>Reacted</u>	$C_3F_6$	(6.7 gm., 0.045 mol)
	$CF_2=CH_2$	(2.29 gm., 0.036 mol)
<u>Product</u>	8.9 gms. sticky pink elastomer; Found: F, 69.7% (sodium fusion); Calc. for 1:1 co-polymer, 71% F	
<u>Telogen</u>	$CH_3OH$	
<u>Reagents</u>	$CH_3OH$	(4.2 gm., 0.13 mol)
	$C_3F_6$	(3.6 gm., 0.024 mol)
	$CF_2=CH_2$	(1.2 gm., 0.019 mol)
<u>Irradiation</u>	33 days 20 hours	
<u>Source</u>	100 curie	
<u>Recovered</u>	$CH_3OH$	3.6 gm.
	$CF_2=CH_2$	Nil
	$C_3F_6$	Nil
<u>Reacted</u>	$CH_3OH$	(0.6 gm., 0.013 mol)
	$CF_2=CH_2$	(1.2 gm., 0.019 mol)
	$C_3F_6$	(3.6 gm., 0.024 mol)
<u>Product</u>	(a)	1.5 gm. colourless mobile liquid, b.p. 114°C; Found: F, 61.9; $CF_3 \cdot CFH \cdot CF_2 \cdot CH_2OH$ requires 62.6% F. Infra-red spectrum same as an authentic sample of this adduct.
	(b)	Residue, 3.6 gm. from atmospheric pressure distillation, b.p. greater than 180°C; Found: F, 61.4%; Calc. for $1C_3F_6: 1CF_2=CH_2: 1CH_3OH$ F, 61.8% and for $1C_3F_6: 2CF_2=CH_2: 1CH_3OH$ F, 61.3%.

Infra-red (b) O-H stretch at  $3436\text{ cm}^{-1}$  (broad); C-H stretch at  $2985\text{ cm}^{-1}$ , unsaturation at  $1770\text{ cm}^{-1}$ ,  $1709\text{ cm}^{-1}$  (s).

Telogen  $\text{CH}_3\text{OH}$

Reagents  $\text{CH}_3\text{OH}$  (51 gm., 1.6 mol)

$\text{C}_3\text{F}_6$  (55.8 gm., 0.37 mol)

$\text{CF}_2=\text{CH}_2$  (26 gm., 0.4 mol)

Irradiation in AUTOCLAVE: 12 days 19 hours

Source 500 curie

Recovered  $\text{CH}_3\text{OH}$  46.4 gm.

$\text{C}_3\text{F}_6$  3 gm.

$\text{CF}_2=\text{CH}_2$  Nil

Reacted  $\text{C}_3\text{F}_6$  (52.5 gm., 0.29 mol)

$\text{CF}_2=\text{CH}_2$  (26 gm., 0.4 mol)

$\text{CH}_3\text{OH}$  (4.6 gm., 0.13 mol)

Product (a) 11.6 gm. colourless, mobile liquid, shown by infra-red spectrum and comparative gas chromatography to be  $\text{CF}_3\cdot\text{CFH}\cdot\text{CF}_2\text{CH}_2\text{OH}$ , b.p.  $114^\circ\text{C}$ .

(b) 60 gms. viscous green liquid residue. After removal of volatiles at  $30^\circ/0.05\text{ mm}$ . Found: F, 59.1%.

Fractionation (I) of (b) gave

(c) Yellow/white viscous liquid 21.9 gm., b.p.  $100-160^\circ/0.05\text{ mm}$ ; Found: F, 59.4%; M, 366.

(d) Brown viscous residue 37.6 gm.; Found: F, 62.5; M, 1041.

Fractionation (II) of (c) gave

- (e) 5 gm., colourless mobile liquid, b.p. 50-80°C/0.003 mm;  
 Found: F, 56%; M, 234; Calc. for  $10C_3F_6: 10CF_2=CH_2:$   
 $1CH_3OH$ : F, 61.8; M, 246 less 1HF F, 58.8%; M, 226.
- (f) 5.5 gm. colourless mobile liquid, b.p. 80 - 100°C/  
 0.003 mm; Found F, 38%; M, 318; Calc. for  $10C_3F_6:$   
 $2CF_2=CH_2: 1CH_3OH$ ; F, 61.2%; M, 310.
- (g) 5.2 gm. colourless mobile liquid, b.p. 100-130°C/  
 0.003 mm; Found: F, 46%; M, 610; Calc. for  $3C_3F_6:$   
 $3CF_2=CH_2: 1CH_3OH$  less 3HF; F, 65%; M, 614.
- (h) 6.3 gm. residual yellow viscous liquid, b.p. greater  
 than 160°C/0.003 mm; Found: F, 62.5%; M, 940; Calc.  
 for  $5C_3F_6: 5CF_2=CH_2: 1CH_3OH$ ; F, 69%; M, 1102.

Infra-red data

- (e) 3690 (s), 3436  $cm^{-1}$  (broad) O-H stretching; 2985  $cm^{-1}$   
 (s) C-H stretching; 1757  $cm^{-1}$ , 1724  $cm^{-1}$ , 1639  $cm^{-1}$   
 (w) unsaturation.
- (f) 3690 (s); 3436  $cm^{-1}$  (broad) O-H stretch; 2985 (s)  
 C-H stretch; 1757  $cm^{-1}$  (w) unsaturation.
- (g) 3690, 3436, 2985, 1757  $cm^{-1}$  (all s)
- (h) 3690 (vs); 3436; 2985 (s doublet); 1754 (w)

TelogenCF<sub>3</sub>COOH

<u>Reagents</u>	$\text{CF}_3\text{COOH}$ (4 gm., 0.035 mol)
	$\text{C}_3\text{F}_6$ (2.9 gm., 0.02 mol)
	$\text{CF}_2=\text{CH}_2$ (0.91 gm., 0.014 mol)
<u>Irradiation</u>	44 days 21 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$\text{CF}_3\text{COOH}$ 3.3 gm.
	$\text{C}_3\text{F}_6$ 0.99 gm.
	$\text{CF}_2=\text{CH}_2$ 0.42 gm.
<u>Reacted</u>	$\text{CF}_3\text{COOH}$ (0.7 gm., 0.006 mol)
	$\text{C}_3\text{F}_6$ (1.91 gm., 0.012 mol)
	$\text{CF}_2=\text{CH}_2$ (0.49 gm., 0.009 mol)
<u>Product</u>	3.1 gm. white viscous liquid free from telogen; Found: F, 65%; Calc. for $1\text{C}_3\text{F}_6: 1\text{CF}_2=\text{CH}_2: 1\text{CF}_3\text{COOH}$ ; F, 63.7, for $2\text{C}_3\text{F}_6: 2\text{CF}_2=\text{CH}_2: 1\text{CF}_3\text{COOH}$ ; F, 66.6%.
<u>Telogen</u>	$\text{CF}_3\text{COOH}$
<u>Reagents</u>	$\text{CF}_3\text{COOH}$ (87.8 gm., 0.77 mol)
	$\text{C}_3\text{F}_6$ (79.1 gm., 0.53 mol)
	$\text{CF}_2=\text{CH}_2$ (7.4 gm., 0.12 mol)
<u>Irradiation</u>	in <u>AUTOCCLAVE</u> , 7 days 20 hours, final pressure 5 atm.
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{CF}_3\text{COOH}$ 87.8 gm.
	$\text{C}_3\text{F}_6$ 61.8 gm.
	$\text{CF}_2=\text{CH}_2$ Nil

<u>Reacted</u>	$\text{CF}_3\text{COOH}$	(Nil)
	$\text{C}_3\text{F}_6$	(17.1 gm., 0.115 mol)
	$\text{CF}_2=\text{CH}_2$	(7.4 gm., 0.12 mol)
<u>Product</u>	23 gm. off-white viscous liquid which on hydrolysis with dilute acid produced no $\text{CF}_3\text{COOH}$ .	

There were several attempts to make this co-telomer on a large scale in an autoclave, but only when a large molar excess of  $\text{C}_3\text{F}_6$  was used was this successful. All other attempts led to the formation of the co-polymer.

Hydrolysis of the co-telomer from hexafluoropropylene;  
vinylidene fluoride and trifluoroacetic acid

The co-telomer (3.4 gm.) was dissolved in the minimum volume of acetone and 10 ml. of 0.106 N  $\text{H}_2\text{SO}_4$  added, followed by more acetone to prevent precipitation of the co-telomer. The mixture was refluxed on an oil-bath at  $80^\circ\text{C}$  for three hours, cooled, and titrated with 0.096 N NaOH using phenol phthalein as indicator. The acetone was then distilled off at atmospheric pressure.

The residual mass was triturated with water, and the washings, containing  $\text{Na}_2\text{SO}_4$ ,  $\text{CF}_3\text{COONa}$  and NaF, decanted into the distillation flask of a steam distillation apparatus, where they were acidified with 5 N  $\text{H}_2\text{SO}_4$ . The  $\text{CF}_3\text{COOH}$  was then steam distilled and the distillate titrated with 0.096 N NaOH.

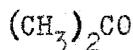
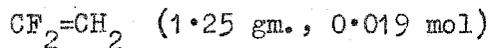
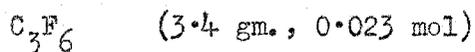
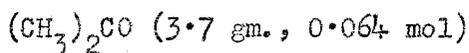
The hydrolysed co-telomer was dissolved in acetone, dried over  $\text{MgSO}_4$ , filtered, and the acetone removed under vacuum. The product was a very

viscous brown semi-solid, which no longer liberated acid fumes on standing. Recovered: 2.4 gm.; Found: M, 1566; F, 50.5%

Vol. NaOH for titration				
Wt. of co-telomer taken	After hydrolysis $H_2SO_4:HF:CF_3COOH$	$CF_3COOH$ + HF	After steam distillation	
			$CF_3COOH$	HF
3.4	48.2	32.3	4.7	27.6
2.0	34.4	23.8	3.5	20.3
1.3	27.9	17.3	0.4	16.9

Infra-red

Doublet at  $3030\text{ cm}^{-1}$  (vs) C-H stretching:  
peaks in the unsaturation region at 1739 (vs),  
1709 (vs).

TelogenReagentsIrradiation

46 days 16 hours

Source

100 curie

Recovered

<u>Reacted</u>	$(\text{CH}_3)_2\text{CO}$ (0.15 gm., 0.002 mol)
	$\text{C}_3\text{F}_6$ (2.5 gm., 0.016 mol)
	$\text{CF}_2=\text{CH}_2$ (0.85 gm., 0.014 mol)
<u>Product</u>	2.8 gm. residue from atmospheric pressure distillation; Found: F, 57.6%; Calc. for $\text{H}[(\text{C}_3\text{F}_6)(\text{CF}_2\cdot\text{CH}_2)]_n\text{CH}_2\text{OCH}_3$ ; $n = 1$ ; F, 56%; $n = 2$ ; F, 62.6%.
<u>Telegen</u>	$\text{CH}_3\text{CHO}$
<u>Reagents</u>	$\text{CH}_3\text{CHO}$ (3 gm., 0.068 mol)
	$\text{C}_3\text{F}_6$ (3.1 gm., 0.021 mol)
	$\text{CF}_2=\text{CH}_2$ (1.2 gm., 0.019 mol)
<u>Irradiation</u>	47 days 14 hours
<u>Source</u>	100 curie
<u>Recovered</u>	$\text{CH}_3\text{CHO}$ 2 gm.
	$\text{C}_3\text{F}_6$ Nil
	$\text{CF}_2=\text{CH}_2$ 0.43 gm.
<u>Reacted</u>	$\text{CH}_3\text{CHO}$ (0.93 gm., 0.021 mol)
	$\text{C}_3\text{F}_6$ (3.1 gm., 0.021 mol)
	$\text{CF}_2=\text{CH}_2$ (0.77 gm., 0.012 mol)
<u>Product</u>	(a) 0.3 gm. colourless, mobile liquid, b.p. 70-80°C; Found: F, 59%; Calc. for $\text{H}(\text{C}_3\text{F}_6)\text{COCH}_3$ F, 58.8%: $\text{CH}_3\text{CO}(\text{CH}_2\text{CF}_2)_n\text{H}$ F, 50.3%; $\text{CH}_3\text{CO}[(\text{C}_3\text{F}_6)(\text{CF}_2\cdot\text{CH}_2)]_n\text{H}$ F, 58.9%.

- (b) 0.7 gm., b.p. 100-115°C; Found F, 54.6%.
- (c) 5.5 gm., residue from distillation at atmospheric pressure; Found: F, 48%.

<u>Telogen</u>	CH <sub>3</sub> SH	
<u>Reagents</u>	CH <sub>3</sub> SH	(16.9 gm., 0.35 mol)
	C <sub>3</sub> F <sub>6</sub>	(29.1 gm., 0.19 mol)
	CF <sub>2</sub> =CH <sub>2</sub>	(10.3 gm., 0.16 mol)
<u>Irradiation</u>	6 days 16 hours in <u>AUTOCLAVE</u>	
<u>Source</u>	500 curie	
<u>Recovered</u>	CH <sub>3</sub> SH	Nil
	C <sub>3</sub> F <sub>6</sub>	Nil
	CH <sub>2</sub> =CF <sub>2</sub>	Nil
<u>Reacted</u>	CH <sub>3</sub> SH	(16.9 gm., 0.35 mol)
	C <sub>3</sub> F <sub>6</sub>	(29.1 gm., 0.19 mol)
	CF <sub>2</sub> =CH <sub>2</sub>	(10.3 gm., 0.16 mol)
<u>Product</u>	Composition found by analytical gas-liquid chromatography (silicone elastomer at 110°C)	
	(a)	37.6 gm. CH <sub>3</sub> S·CF <sub>2</sub> ·CFH·CF <sub>3</sub>
	(b)	0.5 gm. CH <sub>3</sub> S·CF(CF <sub>3</sub> )CF <sub>2</sub> H
	(c)	18.0 gm. probably CH <sub>3</sub> S·CH <sub>2</sub> ·CF <sub>2</sub> H.
	None of these compounds was isolated.	

SYSTEM THREE     Hexafluorocyclobutene with vinylidene fluoride.

<u>Telogen</u>	Nil
<u>Reagents</u>	C <sub>4</sub> F <sub>6</sub> (20 gm., 0.12 mol)
	CF <sub>2</sub> =CH <sub>2</sub> (8.9 gm., 0.14 mol)

Irradiation 4 days 2 hours with vapour phase shielded.

Source 100 curie

Recovered  $C_4F_6$  18.8 gm.  
 $CF_2=CH_2$  7.5 gm.

Reacted  $C_4F_6$  (1.2 gm., 0.0074 mol)  
 $CF_2=CH_2$  (1.4 gm., 0.021 mol)

Product 2.6 gm. pink, elastomeric material; Found: F, 62%;  
M, 681; Calc. for:  $6CF_2=CH_2$ :  $2C_4F_6$ ; F, 64.4%;  
M, 708.

Infra-red Doublet at 3058, 3175  $cm^{-1}$  (vs) C-H stretching;  
Unsaturation at 1812, 1764  $cm^{-1}$  (w).

Telogen  $CH_3OH$

Reagents  $CH_3OH$  (16 gm., 0.5 mol)  
 $C_4F_6$  (14 gm., 0.08 mol)  
 $CF_2=CH_2$  (4.5 gm., 0.07 mol)

Irradiation 2 days 7 hours

Source 500 curie

Recovered  $CH_3OH$  13.4 gm.  
 $C_4F_6$  5.5 gm.  
 $CF_2=CH_2$  2.3 gm.

Reacted  $CH_3OH$  (2.6 gm., 0.08 mol)  
 $C_4F_6$  (8.5 gm., 0.052 mol)  
 $CF_2=CH_2$  (2.2 gm., 0.034 mol)

<u>Product</u>	(a) 8 gm. colourless mobile liquid, shown to <sup>be</sup> $\text{H}(\text{C}_4\text{F}_6)\text{CH}_2\text{OH}$ by comparative analytical g.l.c. (silicone elastomer $130^\circ\text{C}$ ).
	(b) 4 gm. brown, very viscous liquid, residue, after removal of volatiles at $30^\circ/0.05$ mm; Found: F, 58.3%; M, 472; Calc. for $1\text{CH}_3\text{OH}: 1\text{C}_4\text{F}_6: 4\text{CF}_2=\text{CH}_2$ ; F, 59.1%; M, 450. For $2\text{CF}_2=\text{CH}_2: 2\text{C}_4\text{F}_6: 1\text{CH}_3\text{OH}$ ; F, 62.8; M, 484.
<u>Infra-red</u>	$3650\text{ cm}^{-1}$ (vs), $3436$ (broad) O-H stretching. Doublet at $3058, 3175\text{ cm}^{-1}$ (vs) C-H.

SYSTEM FOUR.      Decafluorocyclohexene with vinylidene fluoride

<u>Telogen</u>	Nil
<u>Reagents</u>	$\text{C}_6\text{F}_{10}$ (46.5 gm., 0.177 mol) $\text{CF}_2=\text{CH}_2$ (2.6 gm., 0.04 mol)
<u>Irradiation</u>	5 days 2 hours with vapour phase shielded.
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{C}_6\text{F}_{10}$ 45.9 gm. $\text{CF}_2=\text{CH}_2$ 0.2 gm.
<u>Reacted</u>	$\text{C}_6\text{F}_{10}$ (0.6 gm. negligible) $\text{CF}_2=\text{CH}_2$ (2.4 gm., 0.037 mol)
<u>Product</u>	2.3 gm. white polymeric; Found: F, 58.9%. material identified as polyvinylidene fluoride by its infra-red spectrum; Calc. for P.V.F. 59.4% F.
<u>Telogen</u>	$\text{CH}_3\text{OH}$

<u>Reagents</u>	CH <sub>3</sub> OH	(16 gm., 0.5 mol)
	C <sub>6</sub> F <sub>10</sub>	(13.5 gm., 0.05 mol)
	CF <sub>2</sub> =CH <sub>2</sub>	(3.8 gm., 0.059 mol)
<u>Irradiation</u>	24 days 3 hours	
<u>Source</u>	500 curie	
<u>Recovered</u>	CH <sub>3</sub> OH	14.5 gm.
	C <sub>6</sub> F <sub>10</sub>	Nil
	CF <sub>2</sub> =CH <sub>2</sub>	2.1 gm.
<u>Reacted</u>	CH <sub>3</sub> OH	(1.5 gm., 0.05 mol)
	C <sub>6</sub> F <sub>10</sub>	(13.5 gm., 0.05 mol)
	CF <sub>2</sub> =CH <sub>2</sub>	(1.7 gm., 0.026 mol)
<u>Product</u>	(a)	Polyvinylidene fluoride 1.7 gm.
	(b)	11.3 gm. colourless mobile liquid, found to be H(C <sub>6</sub> F <sub>10</sub> )CH <sub>2</sub> OH by comparative retention times on analytical g-l-c (silicone elastomer at 130°C).
	(c)	3.6 gm. brittle black residue from reduced pressure distillation.

SYSTEM FIVE      Octafluorocyclohexa-1,4-diene with vinylidene fluoride

<u>Telogen</u>	Nil	
<u>Reagents</u>	1,4-C <sub>6</sub> F <sub>8</sub>	(33 gm., 0.147 mol)
	CF <sub>2</sub> =CH <sub>2</sub>	(2.4 gm., 0.037 mol)
<u>Irradiation</u>	8 weeks	
<u>Source</u>	100 curie	

<u>Recovered</u>	$1,4\text{-C}_6\text{F}_8$	24.5 gm.
	$\text{CF}_2=\text{CH}_2$	Nil
<u>Reacted</u>	$1,4\text{-C}_6\text{F}_8$	(8.5 gm., 0.037 mol)
	$\text{CF}_2=\text{CH}_2$	(2.4 gm., 0.037 mol)
<u>Product</u>	10.8 gm. white, crystalline co-polymer; Found: F, 62.3% (sodium fusion); M, 1385, m.p. 75°C; Calc. for $5\text{C}_6\text{F}_8$ : $5\text{CF}_2=\text{CH}_2$ ; F, 65.9%; M, 1440.	
<u>Infra-red</u>	Unsaturation 1724 cm (w) C-H peaks at 2985 $\text{cm}^{-1}$ (vw).	
<u>Telogen</u>	$\text{CH}_3\text{OH}$	(I)
<u>Reagents</u>	$\text{CH}_3\text{OH}$	(7.8 gm., 0.24 mol)
	$1,4\text{-C}_6\text{F}_8$	(14 gm., 0.062 mol)
	$\text{CF}_2=\text{CH}_2$	(2.8 gm., 0.044 mol)
<u>Irradiation</u>	40 days 30 hours	
<u>Source</u>	100 curie	
<u>Recovered</u>	$\text{CH}_3\text{OH}$	5.4 gm.
	$1,4\text{-C}_6\text{F}_8$	Nil
	$\text{CF}_2=\text{CH}_2$	Nil
<u>Reacted</u>	$\text{CH}_3\text{OH}$	(2.4 gm., 0.075 mol)
	$1,4\text{-C}_6\text{F}_8$	(14 gm., 0.062 mol)
	$\text{CF}_2=\text{CH}_2$	(2.8 gm., 0.044 mol)
<u>Product</u>	19 gm. viscous liquid residue from an attempted distillation at atmospheric pressure. HF was eliminated on standing; Found: F, 58.9%; Calc. for $1\text{C}_6\text{F}_8$ : $n\text{CF}_2=\text{CH}_2$ : $1\text{CH}_3\text{OH}$ , F, 59.3.	

<u>Telogen</u>	$\text{CH}_3\text{OH}$	
<u>Reagents</u>	$\text{CH}_3\text{OH}$	(101.3 gm., 3.2 mol)
	1,4- $\text{C}_6\text{F}_8$	(83.9 gm., 0.37 mol)
	$\text{CF}_2=\text{CH}_2$	(37.2 gm., 0.58 mol)
<u>Irradiation</u>	in <u>AUTOCLAVE</u> , 13 days 1 hour, final pressure: zero.	
<u>Source</u>	500 curie	
<u>Recovered</u>	$\text{CH}_3\text{OH}$	57.6 gm.
	1,4- $\text{C}_6\text{F}_8$	48.7 gm.
	$\text{CF}_2=\text{CH}_2$	Nil
<u>Reacted</u>	$\text{CF}_2=\text{CH}_2$	(37.2 gm., 0.58 mol)
	1,4- $\text{C}_6\text{F}_8$	(35.2 gm., 0.16 mol)
	$\text{CH}_3\text{OH}$	(43.7 gm., 1.36 mol)
<u>Product</u>	(a)	22.6 gm. colourless, mobile liquid, b.p. $164^\circ\text{C}$ shown to be $\text{H}(\text{C}_6\text{F}_8)\text{CH}_2\text{OH}$ by comparative g-l-chromatography with an authentic sample.
	(b)	43.1 gm. viscous, yellow liquid, b.p. $60-200^\circ\text{C}/0.002$ mm.
	(c)	50.4 gm. black, brittle residue from distillation at reduced pressure; Found: F, 50.5%; M, 1280.

The fraction (b) was re-fractionated giving:

- (d) 4.5 gm. colourless, mobile liquid, b.p.  $19^\circ\text{C}/0.002$  mm., which separated into two layers. Top layer; Found: F, 36%; M, 181. Lower layer; Found: F, 54.5%; M, 359; Calc. for  $1\text{C}_6\text{F}_8: 2\text{CF}_2=\text{CH}_2: 1\text{CH}_3\text{OH}$  less  $1\text{HF}$ . F, 57.4%; M, 364 less  $2\text{HF}$ . F, 55.2%; M, 344.

- (e) 21.7 gm. colourless mobile liquid, b.p. 40-70°C/0.002 mm;  
 Found, F, 54.6%; M, 216; Calc. for  $10C_6F_8$ :  $1CH_3OH$  less  
 1HF: F, 56.2%; M, 236, less 2HF; F, 52.7; M, 216.
- (f) 6.3 gm., yellow viscous liquid, b.p. 70-110°C; Found:  
 F, 55.7%; M, 375; Calc. for  $10C_6F_8$ :  $2CF_2=CH_2$ :  $1CH_3OH$ :  
 F, 59.4%; M, 384; for  $10C_6F_8$ :  $2CF_2=CH_2$ :  $1CH_3OH$  less 1HF  
 F, 57.4; M, 364.
- (g) 6.8 gm., yellow, viscous liquid, b.p. 110-160°C; Found:  
 F, 51.9%; M, 350; Calc. for  $10C_6F_8$ :  $2CF_2=CH_2$ :  $1CH_3OH$ ,  
 less 2HF: F, 55.2%; M, 344.

Infra-red data of the above fractions (d) - (g)

- (d) Top layer: gave a high background, and no peaks could  
 be observed.
- (d) Lower layer: 3436 (broad) O-H; 2985 (s) C-H; 1757 (vs),  
 1721 (vs), 1536 (s) unsaturation.
- (e) 3436 (broad) O-H; 2985 (w) C-H; 1757 (vs) unsaturation.
- (f) 3436 (broad) O-H; 2985 (s) C-H; 1757  $cm^{-1}$  (s), 1748 (vs),  
 1695 (vs), 1618 (vs) unsaturation.
- (g) 3436 (broad) O-H; 2985 (vs) C-H; 1764 (vs), 1626 (vs)  
 diffuse unsaturation.

The peak at 1757  $cm^{-1}$  occurs in 1,4- $C_6F_8$ . All fractions  
 continued to lose HF on standing in moist air.

Hydrogenation of fraction (e): This was carried out as follows.

Fraction (e), (3.3 gm.), 5% palladised charcoal (1.0 gm.) and absolute ethanol (10 mls.) were placed in a 50 ml. stainless steel autoclave which was then sealed and cooled in liquid air.

After pumping down, and admitting hydrogen several times to ensure removal of air, the vessel was filled with hydrogen at 135 atmospheres pressure.

On warming to room temperature, an initial pressure of 145 atm. being obtained, the vessel was heated, with rocking, to 100°C in two hours, and kept at that temperature for 11 hours, the pressure remaining steady at 200 atm. On cooling, the final pressure being 145 atm., the hydrogen was vented, the vessel unsealed, and the pale yellow liquid contents filtered through a charcoal bed to remove Pd/C, and dried over  $MgSO_4$ .

The bulk of ethanol was distilled off at reduced pressure, and the residual brown, viscous liquid heated at 40°C and 1 mm. pressure to remove the last trace of ethanol. The product (1.43 gm.) was transferred to a small flask and distilled at 0.002 mm. Hg. pressure (Pirani) using an oil bath, fractions being taken as follows:-

- |      |         |   |
|------|---------|---|
| (i)  | 20-40°C | 0.35 gm. clear red liquid.                |
| (ii) | 40-70°C | 0.44 gm. clear, more viscous, red liquid. |

Found: F, 52.6%; M, 259.

Having carried out this rather small-scale experiment, a large-scale hydrogenation experiment was carried out, on 50% of the unfractionated product from a large scale autoclave preparation of these mixed co-telomers. After hydrogenation, this portion was fractionated, and compared

with similar fractions from a distillation of the remaining 50% of the product, which had not been hydrogenated. A comparison of physical properties was then possible.

The experiment was carried out to prepare the mixed co-telomers using exactly the same molar ratio of reagents.

Product 149 gm. viscous brown liquid freed from volatile components at  $40^{\circ}/0.05$  mm.

Hydrogenation 75 gms. of this product was hydrogenated following the same procedure as described previously. The product from the hydrogenation (48 gm.) was fractionated as follows:-

- (a) 6.6 gm. colourless mobile liquid, b.p.  $60^{\circ}/0.003$  mm., found F, 27.5%; M, 156.
- (b) 12 gm. yellow, viscous, liquid, b.p.  $60-120^{\circ}C/0.003$  mm., found F, 48.5; M, 307.
- (c) 29.4 gm. brittle black residue.

Not-hydrogenated

This portion (47 gm.) was fractionated under identical conditions as the hydrogenated portion, giving:

- (d) 9.8 gm. colourless, mobile, liquid, b.p.  $60^{\circ}C/0.003$  mm; Found: F, 51.6%; M, 250.
- (e) 8.3 gm. yellow, viscous, liquid, b.p.  $60-120^{\circ}C/0.003$  mm; Found: F, 50%; M, 369.
- (f) 27.1 gm. brittle black residue.

Infra-red data on a, b, d, e

- (a) A high background concealed peaks.
- (b)  $3649\text{ cm}^{-1}$  (s),  $3436\text{ cm}^{-1}$  (broad) O-H,  $2985\text{ cm}^{-1}$  (s) C-H. Broad diffuse weak unsaturation band at  $1724\text{ cm}^{-1}$ .
- (d) A high background, but peaks discernible at  $3436\text{ cm}^{-1}$  (broad),  $1754$  (diffuse) unsaturation.
- (e)  $3649\text{ cm}^{-1}$  (s),  $3436\text{ cm}^{-1}$  (broad),  $2985\text{ cm}^{-1}$  (s),  $1754\text{ cm}^{-1}$  (diffuse).
- Fraction (a), (b), (d) and (e) all eliminated acid fumes on standing.

<u>Telogen</u>	$\text{CF}_3\text{COOH}$	
<u>Reagents</u>	$\text{CF}_3\text{COOH}$	(10.3 gm., 0.09 mol)
	1,4- $\text{C}_6\text{F}_8$	(7.5 gm., 0.033 mol)
	$\text{CF}_2=\text{CH}_2$	(3.7 gm., 0.058 mol)
<u>Irradiation</u>		31 days 15 hours
<u>Source</u>		100 curie
<u>Recovered</u>	$\text{CF}_3\text{COOH}$	9.9 gm.
	1,4- $\text{C}_6\text{F}_8$	4.9 gm.
	$\text{CF}_2=\text{CH}_2$	Nil
<u>Reacted</u>	$\text{CF}_3\text{COOH}$	(0.4 gm., 0.003 mol)
	1,4- $\text{C}_6\text{F}_8$	(2.6 gm., 0.011 mol)
	$\text{CF}_2=\text{CH}_2$	(3.7 gm., 0.058 mol)
<u>Product</u>		6.2 gms. of mixed white solid, and brown elastomeric material, found for the latter: F, 61.2%; Calc. for $10\text{C}_6\text{F}_8: 4\text{CF}_2=\text{CH}_2: 1\text{CF}_3\text{COOH}$ : F, 60.8%.

<u>Telogen</u>	$\text{CF}_3\text{COOH}$
<u>Reagents</u>	$\text{CF}_3\text{COOH}$ (87.4 gm., 0.76 mol) 1,4- $\text{C}_6\text{F}_8$ (60.2 gm., 0.027 mol) $\text{CF}_2=\text{CH}_2$ (16.5 gm., 0.27 mol)
<u>Irradiation</u>	in <u>AUTOCLAVE</u> , 11 days 4 hours, final pressure zero.
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{CF}_3\text{COOH}$ 87 gm. 1,4- $\text{C}_6\text{F}_8$ 47.3 gm. $\text{CF}_2=\text{CH}_2$ Nil
<u>Reacted</u>	$\text{CF}_3\text{COOH}$ (0.4 gm., 0.003 mol) 1,4- $\text{C}_6\text{F}_8$ (12.9 gm., 0.058 mol) $\text{CF}_2=\text{CH}_2$ (16.5 gm., 0.27 mol)
<u>Product</u>	10 gms. off-white, semi-solid; Found: F, 52.8%; M, 754; Calc. for $2\text{C}_6\text{F}_8$ : $5\text{CF}_2=\text{CH}_2$ : F, 64.3%; M, 768.
<u>Hydrolysis</u>	No $\text{CF}_3\text{COOH}$ eliminated on hydrolysis with dilute acid.
<u>Infra-red</u>	$3436\text{ cm}^{-1}$ (broad) O-H, 1835 (vs), 1785, 1727, $1695\text{ cm}^{-1}$ (vs) diffuse unsaturation, $1526\text{ cm}^{-1}$ (w).

SYSTEM SIX      Octafluorocyclohexa-1,3-diene with vinylidene fluoride

<u>Telogen</u>	Nil
<u>Reagents</u>	1,3- $\text{C}_6\text{F}_8$ (29 gm., 0.13 mol) $\text{CF}_2=\text{CH}_2$ (2.3 gm., 0.037 mol)
<u>Irradiation</u>	with vapour phase shielded. 10 days 17 hours.
<u>Source</u>	500 curie.

<u>Recovered</u>	$1,3-C_6F_8$	27.9 gm.
	$CF_2=CH_2$	2 gm.
<u>Reacted</u>	$1,3-C_6F_8$	(1.1 gm., 0.005 mol)
	$CF_2=CH_2$	(0.3 gm., 0.0047 mol)
<u>Product</u>	1.3 gm., viscous, yellow liquid; Found: F, 62.9%; M, 837; Calc. for $3C_6F_8: 3CF_2=CH_2$ : F, 66%; M, 864: for $2C_6F_8: 6CF_2=CH_2$ : F, 63.9%; M, 832.	
<u>Infra-red</u>	Unsaturation peaks at: $1869\text{ cm}^{-1}$ (w), 1769, 1751 (doublet) (s).	
<u>Telogen</u>	$CH_3OH$	
<u>Reagents</u>	$1,3-C_6F_8$	(7.2 gm., 0.032 mol)
	$CF_2=CH_2$	(1.7 gm., 0.025 mol)
	$CH_3OH$	(9.9 gm., 0.3 mol)
<u>Irradiation</u>	25 days 13 hours	
<u>Source</u>	100 curie	
<u>Recovered</u>	$1,3-C_6F_8$	6.6 gm.
	$CF_2=CH_2$	1.3 gm.
	$CH_3OH$	9.7 gm.
<u>Reacted</u>	$1,3-C_6F_8$	(0.6 gm., 0.0026 mol)
	$CF_2=CH_2$	(0.4 gm., 0.0062 mol)
	$CH_3OH$	(0.2 gm., 0.0063 mol)
<u>Product</u>	1.2 gm. yellow viscous liquid residue from distillation at atmospheric pressure; Found: F, 50%; Calc. for $1C_6F_8: 2CF_2=CH_2: 1CH_3OH$ : F, 59.3%.	

<u>Infra-red</u>	3436 $\text{cm}^{-1}$ (broad) O-H; 3030, 2857 $\text{cm}^{-1}$ (s) C-H, 1754, 1724 (s), 1639 $\text{cm}^{-1}$ (s), unsaturation peaks, also 1471 $\text{cm}^{-1}$ (s)
<u>Telogen</u>	$\text{CH}_3\text{OH}$
<u>Reagents</u>	$\text{CH}_3\text{OH}$ (77 gm., 2.4 mol) 1,3- $\text{C}_6\text{F}_8$ (57 gm., 0.25 mol) $\text{CF}_2=\text{CH}_2$ (20 gm., 0.3 mol)
<u>Irradiation</u>	in <u>AUTOCLAVE</u> , 33 days; Final pressure 4 atm.
<u>Source</u>	500 curie
<u>Recovered</u>	$\text{CH}_3\text{OH}$ 68 gm. 1,3- $\text{C}_6\text{F}_8$ 35 gm. $\text{CF}_2=\text{CH}_2$ 14.1 gm.
<u>Reacted</u>	$\text{CH}_3\text{OH}$ (9 gm., 0.028 mol) 1,3- $\text{C}_6\text{F}_8$ (22 gm., 0.098 mol) $\text{CF}_2=\text{CH}_2$ (5.9 gm., 0.092 mol)
<u>Product</u>	28.6 gms. viscous green liquid residue after removal of volatile components at 30°C/0.05 mm.
<u>Hydrogenation</u>	of 15 gms. of this product, using the method described previously, followed by fractionation at reduced pressure gave. (a) 1.3 gm. colourless mobile liquid, b.p. 60°C/0.003 mm; Found: F, 39.4%; M, 291; 1 $\text{C}_6\text{F}_8$ : 1 $\text{CF}_2=\text{CH}_2$ : 1 $\text{CH}_3\text{OH}$ less 2HF: F, 54.2; M, 280.

$1C_6F_8$ :  $2CF_2=CH_2$ :  $1CH_3OH$  less  $4HF$ ; F, 50%; M, 304.

(b) 3 gm. yellow viscous liquid, b.p.  $60-190^{\circ}/0.003$  mm.,

Found: F, 52.9%; M, 409; Calc. for  $1C_6F_8$ :  $3CF_2=CH_2$ :

$1CH_3OH$  less  $2HF$ : F, 55.9; M, 408;  $2C_6F_8$ :  $2CH_3OH$  less

$5HF$ : F, 51; M, 412.

(c) 0.7 gm. brittle black residue.

Not hydrogenated. A 15 gm. portion of product was fractionated under exactly the same conditions as the hydrogenated fraction, in order to compare the molecular weights of similar fractions.

(d) 4.6 gm., colourless, mobile liquid, b.p.  $60^{\circ}C/0.003$  mm.; Found: F, 54.6%; M, 234; Calc. for  $1C_6F_8$ :  $1CH_3OH$

less  $2HF$ : F, 52.7%; M, 216; for  $1C_6F_8$ :  $1CF_2=CH_2$ :

$1CH_3OH$  less  $2HF$ : F, 54.2%; M, 280.

(e) 7.0 gm., yellow, viscous liquid, b.p.  $60-190^{\circ}/0.003$  mm.; Found: F, 57.1%; M, 518; Calc. for  $1C_6F_8$ :

$4CF_2=CH_2$ :  $1CH_3OH$ : F, 59.3%; M, 512;  $2C_6F_8$ :  $1CF_2=CH_2$ :

$1CH_3OH$ : F, 62.8%; M, 544 less  $1HF$ : F, 61.6%; M, 524.

(f) 3 gms. brittle black residue.

Infra-red (a) An extremely high background eliminated any sharp peaks.  $3436\text{ cm}^{-1}$  (broad) O-H;  $2985\text{ cm}^{-1}$  (s) C-H;  $1724, 1640\text{ cm}^{-1}$  (diffuse) unsaturation,  $1526, 1504$  (s. doublet) aromatic character.

(b)  $3436\text{ cm}^{-1}$  (v. weak),  $2985$  (w);  $1731, 1653\text{ cm}^{-1}$  (s) unsaturation;  $1527, 1504$  (s. doublet) aromatic character.

- (d)  $3436\text{ cm}^{-1}$  (broad) O-H;  $2950, 2857\text{ cm}^{-1}$  (s) C-H;  
 $1724$  (vs),  $1639$  (vs),  $1526$  (vw),  $1504$  (s).
- (e)  $3436\text{ cm}^{-1}$  (broad) O-H;  $2950$ , C-H;  $1724$  (vs),  
 $1653$  (w),  $1626$  (w),  $1526$  (w),  $1504$  (s).

TelogenCF<sub>3</sub>COOHReagentsCF<sub>3</sub>COOH (14.8 gm., 0.13 mol)1,3-C<sub>6</sub>F<sub>8</sub> (8.9 gm., 0.039 mol)CF<sub>2</sub>=CH<sub>2</sub> (1.9 gm., 0.03 mol)Irradiation

25 days 14 hours

Source

100 curie

RecoveredCF<sub>3</sub>COOH 14.7 gm.1,3-C<sub>6</sub>F<sub>8</sub> 8 gm.CF<sub>2</sub>=CH<sub>2</sub> 0.7 gm.ReactedCF<sub>3</sub>COOH negligible1,3-C<sub>6</sub>F<sub>8</sub> (0.9 gm., 0.004 mol)CF<sub>2</sub>=CH<sub>2</sub> (1.2 gm., 0.018 mol)Product

2.1 gm. brown residue from distillation at  
 atmospheric pressure; Found: F, 57.6%; Calc. for  
 $1\text{C}_6\text{F}_8 : 4\text{CF}_2=\text{CH}_2$ : F, 63.3%.

SYSTEM SEVENOctafluorocyclohexa-1,3-diene with buta-1,3-dieneTelogen

Nil

Reagents1,3-C<sub>6</sub>F<sub>8</sub> (28.8 gm., 0.127 mol)CH<sub>2</sub>=CH-CH=CH<sub>2</sub> (9.4 gm., 0.174 mol)

<u>Irradiation</u>	10 days	
<u>Source</u>	100 curie	
<u>Recovered</u>	1,3-C <sub>6</sub> F <sub>8</sub>	0.4 gm.
	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	Nil
<u>Reacted</u>	1,3-C <sub>6</sub> F <sub>8</sub>	(28.4 gm., 0.126 mol)
	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	(9.4 gm., 0.174 mol)
<u>Product</u>	37.8 gm., pink elastomeric material insoluble in organic solvents. On standing in air the co-polymer becomes black and brittle, with HF loss.	
<u>Telogen</u>	CH <sub>3</sub> OH	
<u>Reagents</u>	CH <sub>3</sub> OH	(9.9 gm., 0.34 mol)
	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	(0.7 gm., 0.013 mol)
	1,3-C <sub>6</sub> F <sub>8</sub>	(9.2 gm., 0.04 mol)
<u>Irradiation</u>	6 days 23 hours	
<u>Source</u>	100 curie	
<u>Recovered</u>	CH <sub>3</sub> OH	9.9 gm.
	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	Nil
	1,3-C <sub>6</sub> F <sub>8</sub>	7.30 gm.
<u>Reacted</u>	CH <sub>3</sub> OH	(nil)
	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	(0.7 gm., 0.013 mol)
	1,3-C <sub>6</sub> F <sub>8</sub>	(1.9 gm., 0.0085 mol)
<u>Product</u>	2.6 gms. white, fibrous solid plus a trace of viscous liquid residue. After distillation of recovered liquid at atmospheric pressure; Found for solid: F, 40.7% (sodium fusion); Calc. for: 1C <sub>6</sub> F <sub>8</sub> : 3C <sub>4</sub> H <sub>6</sub> : F, 39.4%.	

Polymerisation appeared to occur prior to irradiation, hence this mixture was sealed in a carius tube and left, without irradiation, for 10 days. A solid white fibrous co-polymer formed in small yield without total conversion of the butadiene. This co-polymer resembled that produced from the irradiated experiment.

<u>Telogen</u>	$\text{CF}_3\text{COOH}$	
<u>Reagents</u>	$\text{CF}_3\text{COOH}$	(11.9 gm., 0.104 mol)
	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	(2.2 gm., 0.04 mol)
	1,3- $\text{C}_6\text{F}_8$	(8.6 gm., 0.038 mol)
<u>Irradiation</u>		6 days 7 hours
<u>Source</u>		100 curie
<u>Recovered</u>	$\text{CF}_3\text{COOH}$	(11.9 gm.)
	1,3- $\text{C}_6\text{F}_8$	(7.3 gm.)
	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	(Nil)
<u>Reacted</u>	$\text{CF}_3\text{COOH}$	(Nil)
	1,3- $\text{C}_6\text{F}_8$	(1.3 gm., 0.006 mol)
	$\text{C}_4\text{H}_6$	(2.2 gm., 0.04 mol)
<u>Product</u>		3.4 gm. dark brown semi-solid; Found: F, 33.1%;
		Calc. for $1\text{C}_6\text{F}_8: 4\text{C}_4\text{H}_6$ : F, 34.7%; For $1\text{C}_6\text{F}_8: 5\text{C}_4\text{H}_6$ : F, 30.8%.

This mixture polymerised prior to irradiation, and on repeating the reaction without irradiation gave a product in similar yield, and similar in appearance to the semi-solid formed in the irradiated experiment;

Found: F, 34.3%.

FURTHER ADDITION OF OLEFINS TO CYCLIC MONO-ENES  
AND DI-ENES

Additions to octafluorocyclohexa-1,3-diene

<u>Olefin</u>	$\text{CF}_2=\text{CF}_2$	
<u>Reagents</u>	$1,3\text{-C}_6\text{F}_8$	(38.8 gm., 0.173 mol)
	$\text{CF}_2=\text{CF}_2$	(0.6 gm., 0.006 mol)
<u>Irradiation</u>	With vapour phase shielded; 10 days 17 hours.	
<u>Source</u>	500 curie	
<u>Recovered</u>	$1,3\text{-C}_6\text{F}_8$	37.5 gm.
	$\text{CF}_2=\text{CF}_2$	Nil
<u>Reacted</u>	$1,3\text{-C}_6\text{F}_8$	(1.3 gm., 0.006 mol)
	$\text{CF}_2=\text{CF}_2$	(0.6 gm., 0.006 mol)
<u>Product</u>	1.7 gm. viscous grey liquid. A distillation residue at atmospheric pressure found: F, 61.4%; M, 594; Calc. for $1\text{C}_6\text{F}_8$ : $1\text{C}_2\text{F}_4$ : F, 70.4%; M, 324; For $2\text{C}_6\text{F}_8$ : $2\text{C}_2\text{F}_4$ : F, 70.4; M, 648.	
<u>Infra-red</u>	Unsaturation $1739\text{ cm}^{-1}$ (s).	
<u>Olefin</u>	$\text{CF}_2=\text{CCl}_2$	
<u>Reagents</u>	$\text{CF}_2=\text{CCl}_2$	(1.2 gm., 0.0097 mol)
	$1,3\text{-C}_6\text{F}_8$	(17.5 gm., 0.078 mol)
<u>Irradiation</u>	87 days 14 hours	
<u>Source</u>	100 curie	
<u>Recovered</u>	$1,3\text{-C}_6\text{F}_8$	14 gm.
	$\text{CF}_2=\text{CCl}_2$	Nil

Reacted             $1,3-C_6F_8$             (3.5 gm., 0.012 mol)  
                        $CF_2=CCl_2$             (1.29 gm., 0.0097 mol)

Product            4.75 gm. yellow viscous liquid, residue from  
                           distillation  $40^\circ C/0.05$  mm.; Found: F, 47.2%; Cl,  
                           23.3%.

Fractionation of this product gave:

- (a) 1.5 gm. colourless, mobile liquid, b.p.  $60^\circ C/0.003$  mm;  
 Found: M, 504; Calc. for  $1C_6F_8: 2CF_2=CCl_2$ : F, 53.3%;  
 Cl, 19.9%; M, 490.
- (b) 3.25 gm. yellow viscous liquid, b.p. bigger than  $100^\circ C/$   
 $0.003$  mm; Found: M, 693.

Infra-red            (a) Unsaturation  $1754\text{ cm}^{-1}$  (s),  $1538\text{ cm}^{-1}$ ,  $1515\text{ cm}^{-1}$  (vw)  
                           (b) Unsaturation 1869, 1835,  $1754$  (s),  $1527$  (w),  $1504$  (s).

Additions to decafluorocyclohexene

Olefin                 $C_2F_4$

Reagents             $C_2F_4$             (1.85 gm., 0.018 mol)  
                            $C_6F_{10}$             (39.4 gm., 0.15 mol)

Irradiation            With vapour phase shielded; 5 days 2 hours

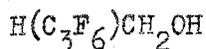
Source                500 curie

Recovered             $C_6F_{10}$             39.1  
                            $CF_2=CF_2$         Nil

Reacted                 $C_6F_{10}$             (0.3 gm. negligible)  
                            $C_2F_4$             (1.85 gm., 0.18 mol)

Product 1.8 gm. white polymeric material, shown to be polytetrafluoroethylene by comparison of infra-red spectra.

Addition of chlorotrifluoroethylene to



<u>Reagents</u>	$\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$	(19.2 gm., 0.105 mol)
	$\text{CF}_2=\text{CFCl}$	(13.6 gm., 0.116 mol)
<u>Irradiation</u>	2-3 days - after which time the tube cracked.	
<u>Source</u>	100 curie	
<u>Recovered</u>	$\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$	19.2 gm.
	$\text{CF}_2=\text{CFCl}$	Nil
<u>Product</u>	6 gm., white, polymeric material; Found: F, 48.9%; Cl, 29.1% (sodium fusion); Calc. for $(\text{CF}_2-\text{CFCl})_n$ : F, 48.9%; Cl, 30.5%	

ESTERIFICATION OF FLUOROALCOHOLS

The esterification process was promoted by trifluoroacetic acid anhydride, prepared in the following manner.

Preparation of  $(\text{CF}_3\text{CO})_2\text{O}$  (J., 1949, 2977)

A three-necked, round-bottomed flask was fitted with a mercury sealed stirrer, dropping funnel and reflux condenser.  $\text{P}_2\text{O}_5$  (59 gm) i.e. 0.87 gm. per gm. of  $\text{CF}_3\text{COOH}$ , was placed in the flask, and  $\text{CF}_3\text{COOH}$  (68 gm., 0.60 mol) added dropwise, with stirring, over a period of half an

hour until the paste formed ~~was~~ too stiff for further stirring. The mixture ~~was~~ then refluxed for 8 hours at  $80^{\circ}\text{C}$  on an oil bath.

Hot water is now run through the reflux condenser, and the contents of the reaction vessel are pumped out and collected in an acetone-drikold bath at  $-70^{\circ}\text{C}$ . The anhydride is fractionated from this mixture up a 6" vigreux column, collecting the fraction, b.p.  $38-42^{\circ}\text{C}$ , yield 47 gm. (69%).

#### Esterification.

Tedder (Chem. Revs., 1955, 55, 767) describes the use of trifluoroacetic acid anhydride to promote esterification hydrocarbon alcohols. This method was adapted for esterification of fluoroalcohols as follows.

A three-necked, round bottomed flask was fitted with a mercury sealed stirrer, dropping funnel and reflux condenser. The dibasic acid (1 mole) is placed in the flask and the trifluoroacetic acid anhydride added (1.2 mole). The acid dissolved in the anhydride. The alcohol (2 moles) was added over a period of 20 minutes, and the mixture refluxed for 24 hours. After this time it was poured carefully into a saturated solution of  $\text{NaHCO}_3$ , extracted with chloroform, dried over  $\text{MgSO}_4$  and the chloroform pumped off at  $40^{\circ}\text{C}/0.05$  mm. The ester was left as a residue from this process, and was distilled at reduced pressure if this was possible.

#### Esterification of $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$ and adipic acid $\text{HOOC}(\text{CH}_2)_4\text{COOH}$

The product from adipic acid (12 gm., 0.08 mol);  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$  (25 gm., 0.14 mol) and  $(\text{CF}_3\text{CO})_2\text{O}$  (15 gm., 0.07 mol) weighed 14 gm. (40% yield). Found b.p.  $130^{\circ}/0.05$  mm; F, 43.1%; M, 311;  $n_D^{20}$  1.38232.

It was an opaque, colourless, mobile, sweet-smelling, liquid; Calc. for  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{O}\cdot\text{CO}\cdot(\text{CH}_2)_4\text{COOH}$ ; F, 36.8%; M, 310.

Infra-red 3436 (broad), 2976 (vs), 1750 (vs), 1709 (s).

Esterification of  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$  and sebacic acid  $\text{HOOC}(\text{CH}_2)_8\text{COOH}$

The product from sebacic acid (30 gm., 0.1 mol);  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$  (36 gm., 0.197 mol) and  $(\text{CF}_3\text{CO})_2\text{O}$  (20 gm., 0.06 mol) weighed 17 gm. (44% yield). Found b.p.  $150^\circ/0.05$  mm; F, 26.5%; M, 326;  $n_D^{20}$  1.41300; Calc. for  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{O}\cdot\text{CO}\cdot(\text{CH}_2)_8\text{COOH}$ : F, 31.1%; M, 366. It was a colourless, mobile liquid.

Infra-red  $3436\text{ cm}^{-1}$  (broad), 2976 (vs), 1750 (sh), 1739 (vs), 1709 (s).

Esterification of mixed co-telomer alcohols from  $\text{C}_3\text{F}_6$ ;  $\text{CF}_2=\text{CH}_2$ ;  $\text{CH}_3\text{OH}$  with adipic acid  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$

The product, from adipic acid (30 gm., 0.2 mol) telomer alcohol mixture (40 gm.) and  $(\text{CF}_3\text{CO})_2\text{O}$  (54 gm., 0.26 mol) weighed 37 gm. A little of it (5 gm.) distilled at  $180^\circ/0.003$  mm; Found: F, 47.4%; M, 409. The remainder (32 gm.) did not distil and contained solid matter; Found: F, 47%; M, 752.

Infra-red (a) distillate: 3436 (broad), 2976 (vs), 1818 (vs), 1750 (wide diffuse band).

(b) remainder: 3436 (broad), 2976 (diffuse), 1750 (wide diffuse band).

DEHYDROFLUORINATION OF CO-TELOMER ALCOHOLS

Anion exchange resin

Anion exchange resin has been successfully employed in the dehydro-

fluorination of cyclic fluorocarbon hydrogen-containing, hexanes (Banks, Bevan, Musgrave, Chem. and Ind., 1959, 296). The resin (I.R.A. 400) was first regenerated as follows.

A slurry of resin (67 gm.) in deionised water was poured into a vertical liquid-chromatography column (50 cm x 2.5 cm). A 4% solution of NaOH in deionised water (2,400 ml.) was passed down the column at a steady rate, followed by 2 litres of deionised water. This procedure should give 100% regeneration of anion exchange resin.

#### Dehydrofluorination.

This was effected by placing 10 gms. of the mixed co-telomers from  $C_3F_6$ ;  $CF_2=CH_2$ ;  $CH_3OH$ , in a conical flask together with excess  $CF_2ClCFCl_2$  (an inert solvent) and adding 20 gm. of regenerated resin. This encourages contact of resin and reagent, and hence an efficient removal of HF.

The mixture was shaken for two days, the resin filtered off and washed with  $CF_2ClCFCl_2$ , and the dehydrofluorinated product recovered by pumping off the solvent at  $30^\circ C/0.05$  mm. The product was a yellow viscous liquid 7.9 gm.; Found: F, 59.9%; M, 592; Original material contained: F, 64.3%; M, 376. Thus 0.046 moles of HF have been removed.

Infra-red of the dehydrofluorinated material,

I.R.A. 400 - 1709  $cm^{-1}$  (s)  
 $\sim C_4H_9NH_2$  - 1724  $cm^{-1}$  (s) 1639  $cm^{-1}$  (broad)

Amine dehydrofluorination.

This work was based on that carried out by Paciorek,<sup>99</sup> using n-butylamine. REACTION A.

The co-telomer alcohol mixture (10 gm.) (from  $C_3F_6$ ;  $CF_2=CH_2$ ;  $CH_2OH$ ) was placed in a three necked flask fitted with a stirrer, reflux condenser and dropping funnel. The apparatus was cooled to  $0^\circ C$  in an ice-bath, and n-butylamine (16.1 gm., 0.2 mol) in 15 ml. anhydrous ether, added dropwise over a period of one hour. The reaction mixture was then allowed to warm up to room temperature and stirred gently for 14 hours. A white precipitate formed (3.5 gm.) which was filtered off and washed with anhydrous ether; Found: F, 20.47%; Calc. for  $C_4H_9NH_3F$ : F, 20.43%.

The dark brown alkaline ethereal solution was filtered through activated charcoal, and the ether and excess amine pumped off at  $40^\circ / 0.05$  mm.

The residue from this process was a dark, red-brown, viscous liquid. After washing with dilute HCl, to remove excess amine, it was extracted with ether, dried over  $MgSO_4$  and the ether pumped off. Product 8 gm. brown, viscous liquid; Found: F, 40.7%; M, 273. (Original contained 64.3% F; M, 376). Thus 0.037 moles of HF have been removed (based on  $C_4H_9NH_3HF$  formed).

REACTION B

Using the co-telomer alcohols from 1,4- $C_6F_8$ ,  $CF_2=CH_2$ ,  $CH_3OH$  and the procedure described above, led to complete degradation of starting material forming a brittle black solid mass.

## DOSIMETRY

### Calibration of sources

These calibrations were performed according to the method of Weiss (Nucleonics, July 1952, p. 28) using a ferrous/ferric oxidation system which makes use of the overall reaction



### Experimental

#### (a) Preparation of dosimeter solution:

0.4 gms. ferrous ammonium sulphate with 0.06 gms. KCl made up to 1 litre with 0.8N  $\text{H}_2\text{SO}_4$  in deionised water.

The addition of potassium chloride makes it unnecessary to use conductivity water since the salt for some unknown reason nullifies the effect of slight impurities which may be present in deionised water.

#### (b) Calibration:

Polythene capsules 3" x 1" diameter with clip tops were washed with deionised water, rinsed with dosimeter solution and then filled with solution. They were placed touching, and at 5 cm, 10 cm, 20 cm, and 30 cm away from the source tube at a level coinciding with the centre of the source (this was determined by placing a length of glass tubing touching the source tube and irradiating for a few hours; the change in colour of the glass tubing i.e. from dark to light brown indicated the intensity of irradiation on the tube).

The sample capsules were irradiated for time intervals which ensured that the conversion  $\text{Fe}^{++} \longrightarrow \text{Fe}^{+++}$  would not go 100% and the optical density of each solution determined using a "Unicam" spectro-

photometer at wavelength setting 305 m $\mu$  and slit width 0.28 mm. A further sample of dosimeter solution was irradiated with the source inlet tube (which normally fits inside the autoclave) between it and the source guide tube, to reproduce the conditions inside the autoclave, and determine the dose rate inside the autoclave.

The G value (the number of molecules which have been changed for 100 ev. of energy absorbed) for this calibration was taken as

$$15.5 \text{ moles/litre/kilo rep.}$$

Thus, the dose could be calculated from the formula:

$$\text{Dose} = \frac{\text{Optical density}}{\text{extinction coefficient}} \times \frac{10^3 \times 0.97}{15.5} \text{ rads.}$$

Graph (I) is a plot of dose/hour against distance from the source and it can be seen that it falls off exponentially, to a steady value.

500 Curie Source

Distance from source tube (cm)	Irradiation time (mins)	O.D.	Dose rate rads/h x 10 <sup>5</sup>
touching	2	0.728	7.51
5	10	0.95	1.96
10	10	0.308	0.636
20	10	0.072	0.148
30	10	0.027	0.056
inside autoclave	2	0.695	7.17

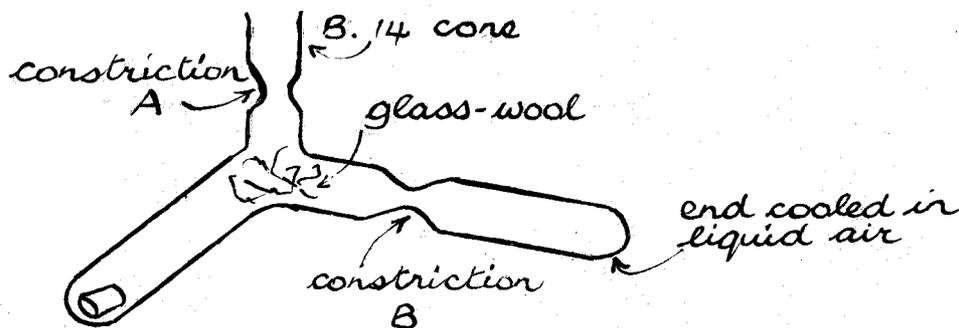
100 curie source

Distance from source tube (cm)	Irradiation time (mins)	Optical density	Dose rate rads/hr.
touching	34	1.1255	$6.83 \times 10^4$
5	34	0.60	$3.64 \times 10^4$
10	34	0.130	$0.789 \times 10^4$
20	34	0.0376	$0.228 \times 10^4$
30	34	-	-

Dosimetry and determination of G value for  $i\text{C}_3\text{F}_7\text{I}$ Preparation of  $\text{I}^{131}$ 

Radioactive iodine was supplied as a solution of potassium iodide in water. Two drops of this (enough for a count of 10,000 per min.) were added to five drops of 10% potassium iodide solution.

Excess of palladous chloride was added to this, and the vessel shaken vigorously to ensure complete precipitation of the palladous iodide. The precipitate was filtered under suction through a weighed glass fibre filter, supported by a plastic disc, dried at  $100^\circ\text{C}$ , and the weight of the palladous iodide determined by difference. The palladous iodide was then transferred to the apparatus shown below.



which was then evacuated and sealed at constriction A. On heating the palladous iodide at about  $300^{\circ}\text{C}$  with a micro-burner it dissociated and the free iodine collected in <sup>the</sup> and cooled in liquid air. The particles of palladium being caught in the glass wool.

That part of the glass on which the ring of iodine had collected was cut out, carefully crushed, and enough  $\text{C}_3\text{F}_7\text{I}$  added to ensure that a saturated solution of iodine was obtained [solubility of  $\text{I}_2$  in  $\text{C}_3\text{F}_7\text{I}$   $0.0048$  g/g].

The mixture was left in the dark overnight to reach saturation.

#### Exchange reaction with $\text{C}_3\text{F}_7\text{I}$

It was first necessary to ensure that no exchange takes place under normal conditions i.e. in the simple solution of iodine in  $\text{C}_3\text{F}_7\text{I}$  and when this solution is dissolved in  $\text{CCl}_4$ . For this purpose, two samples of approximately 2 gm. of solution each were sealed at atmospheric pressure in the presence of air, into small glass ampules and kept in darkness for 68 and 87 hours respectively. The tubes were opened and the contents washed with  $\text{CCl}_4$  through a filter paper into a 12 ml. graduated flask. The solution was made up to exactly 12 ml. with  $\text{CCl}_4$ , 10 ml. were taken after mixing in a pipette and run into a liquid counter. The total activity was determined (a previously determined background count having been taken) and then the solution was poured back into the standard flask. The whole of this solution was treated with Ag powder until it was quite colourless to remove free iodine. After filtration of the AgI, another 10 ml. of the filtrate was pipetted into the clean, dry counter, the

background count of which had again been taken, and any residual activity was determined. It was found that for these solutions the following transfer of  $^{131}\text{I}$  was

<u>Irradiation</u>	<u>Standing Time</u>	<u>Percentage transfer</u>
Nil	68	0.21
Nil	87	0.93

The experiment was repeated with three further samples, sealed this time in vacuo, and irradiated for varying times.

<u>Irradiation dose rate</u>	<u>Time (Hours)</u>	<u>% Transfer</u>	<u>G</u>
$6.83 \times 10^4$	2.5	1.14	12.4
rads/hr.	4.05	4.81	12
"	5.66	6.04	11

#### Calculation of G value

Dose rate  $6.83 \times 10^4$  rads/hr/gm.  $\therefore$  energy absorbed in 5.66 hours  
 $= 6.83 \times 10^4 \times 10^2 \times 5.66$  ergs/gm.  $= 38.65 \times 10^6$

In a liquid 32.5 e.v. (i.e.  $5.2 \times 10^{-11}$  ergs.) are required to produce an ion pair  $\therefore$  no. of ion pairs produced in 5.66 hours

$$= \frac{38.65 \times 10^6 \times 10^{11}}{5.2} = 7.43 \times 10^{17}$$

Total wt. of  $\text{I}_2$  taken (normal and radioactive = 0.01219 gm.  
 Exchange 6.04%

$$\therefore \text{C}_3\text{F}_7\text{I}^{\text{III}} \text{ formed} = 0.01219 \times \frac{6.04}{100} \times \frac{296}{127}$$

i.e. No. of molecules of  $C_3F_7I^*$  formed

$$= \frac{0.01219 \times 6.04}{100 \times 127} \times \frac{6 \times 10^{23}}{1}$$

∴ No. of molecules of  $C_3F_7I^*$  per gm. of  $C_3F_7I$  started with

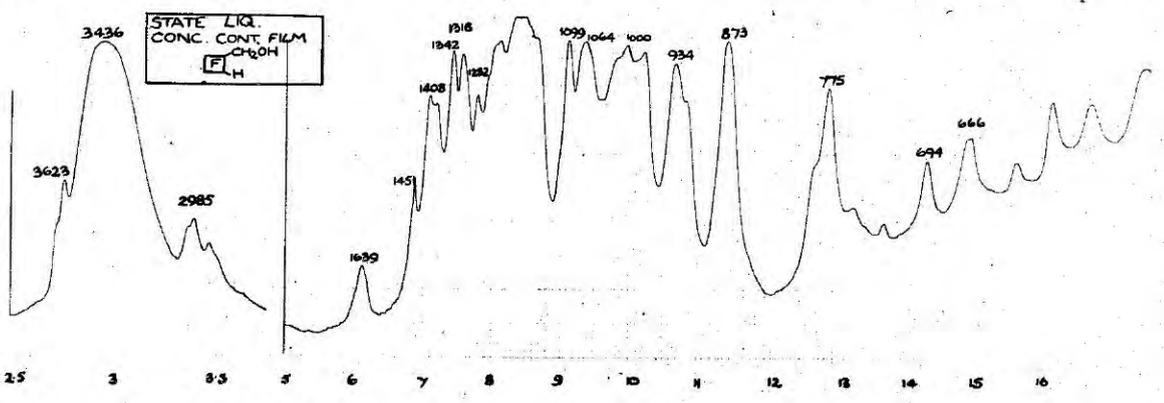
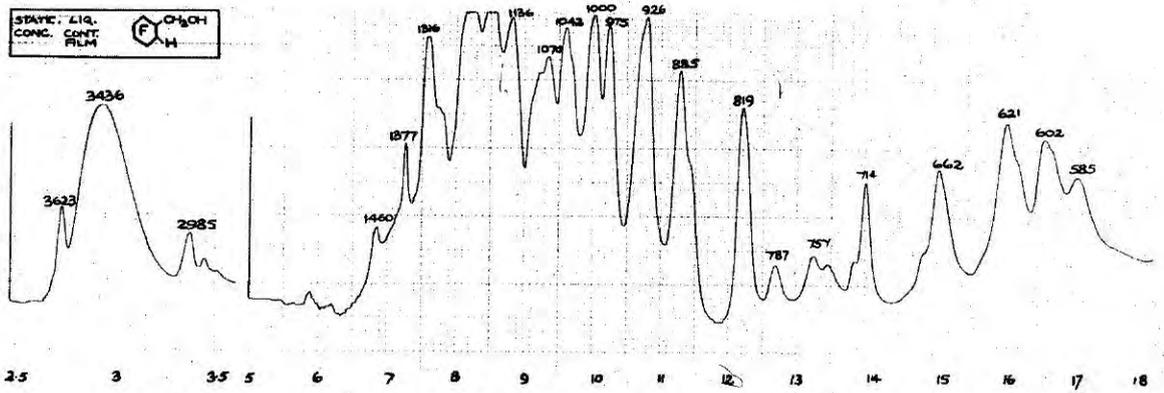
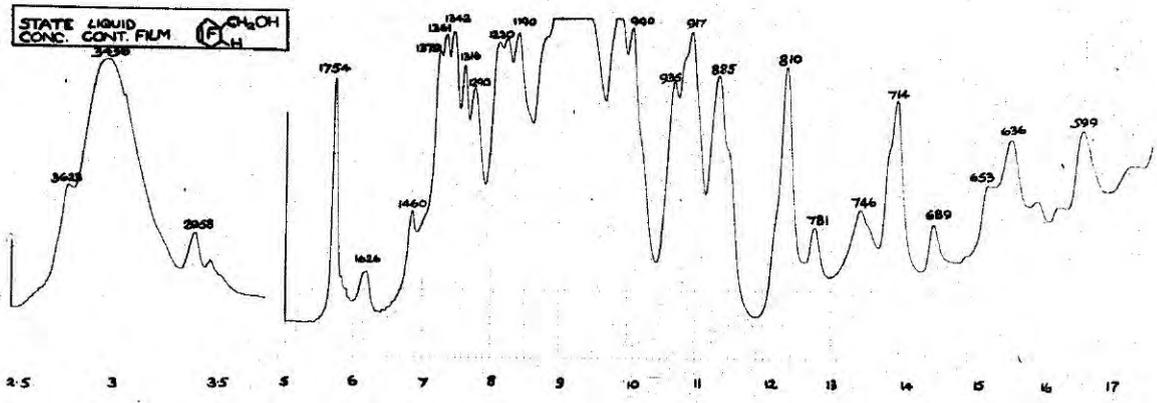
$$= \frac{0.01219 \times 6.04 \times 6 \times 10^{23}}{100 \times 127 \times 1.3165}$$

∴ No. of mols per ion pair

$$= \frac{0.01219 \times 6.04 \times 6 \times 10^{23}}{100 \times 127 \times 1.3165 \times 7.43 \times 10^{17}}$$

∴ G (No. of molecules of  $C_3F_7I$  changed to  $C_3F_7I^*$  per 100 ev. input) =  $\frac{0.01219 \times 6.04 \times 6 \times 10^{23} \times 100}{100 \times 127 \times 1.3165 \times 7.4 \times 10^{17} \times 32.5}$

= 10.98



## FUTURE WORK

### Esterification.

The esterification of the fluoroalcohol  $\text{H}(\text{C}_3\text{F}_6)\text{CH}_2\text{OH}$  with Boronic acids should yield stable diesters, using  $(\text{CF}_3\text{CO})_2\text{O}$  promoter. This could be extended to the telomer alcohols from system two.

### Cross-linking.

The cross-linking of system two, co-telomer alcohols using  $\text{KCNS}$ , or  $\text{Et}_3\text{N}$  with  $\text{HS}(\text{CH}_2)_3\text{SH}$ .

### Free-radical addition.

The free-radical addition of  $\text{HS}(\text{CH}_2)_3\text{SH}$  to  $\text{C}_3\text{F}_6$  could yield an adduct, which could also be dehydrofluorinated and cross-linked.

REFERENCES

1. Musgrave, *Quart. Rev.*, 1954, Vol. 8, No. 4, p. 334.
2. England, Melby, Dietrich, Lindsay, *J. Amer. Chem. Soc.*, 1960, 82, 5116.
3. Lazerte, U.S.P. 2,704,769; C.A. 50, 2654e, 1956.
4. Barr, Rapp, Pruett, *J. Amer. Chem. Soc.*, 1950, 72, 4480.
5. Lazerte, Koshar, *J. Amer. Chem. Soc.*, 1955, 77, 910.
6. Haszeldine, Osborne, J., 1956, 61.
7. Henne, Ruh, *J. Amer. Chem. Soc.*, 1947, 69, 279.
8. Fuller, Tatlow, J., 1961, 3198.
9. Hauptschein, Fainberg, Braid, *J. Amer. Chem. Soc.*, 1958, 80, 842.
10. Brown, H.C., *J. Org. Chem.*, 1957, 22, 1256.
11. Coffman, Barrick, Cramer, Raasch, *J. Amer. Chem. Soc.*, 1949, 71, 490.
12. Barrick, U.S.P. 2,462,345; C.A. 43, 4293g, 1949; U.S.P. 2,462,347; C.A. 43, 4294h, 1949.
13. Barrick, U.S.P. 2,427,116; C.A. 42, 594e, 1948.
14. Haszeldine, J., 1949, 2856.
15. Haszeldine, J., 1953, 3761.
16. Hauptschein, Braid, Lawlor, *J. Amer. Chem. Soc.*, 1957, 79, 2549.
17. Hauptschein, Braid, Fainberg, *J. Amer. Chem. Soc.*, 1958, 82, 851.
18. Hanford, Joyce, Harman, *J. Amer. Chem. Soc.*, 1948, 70, 2529.
19. Hauptschein, Braid, Fainberg, *J. Amer. Chem. Soc.*, 1961, 83, 2495.
20. Haszeldine, J., 1955, 4291.
21. Haszeldine, Steel, J., 1953, 1592.

22. Henne, Kraus, J. Amer. Chem. Soc., 1954, 76, 1175.
23. Park, Lycan, Lacher, J. Amer. Chem. Soc., 1951, 73, 711.
24. Haszeldine, Steele, J., 1954, 3747.
25. Haszeldine, J., 1953, 1764.
26. Haszeldine, Steele, J., 1955, 3005.
27. Haszeldine, Steele, J., 1953, 1199.
28. Haszeldine, J., 1953, 3559.
29. Haszeldine, J., 1952, 2504.
30. Henne, Nager, J. Amer. Chem. Soc., 1951, 73, 5527.
31. Haszeldine, Chem. and Ind., 1951, 684.
32. Haszeldine, Steele, J., 1957, 2193.
33. Tarrant, Lovelace, J. Amer. Chem. Soc., 1955, 77, 768.
34. Tarrant, Lilyquist, J. Amer. Chem. Soc., 1955, 77, 3640.
35. Hauptschein, Braid, Lawlor, J. Amer. Chem. Soc., 1958, 80, 846.
36. Hutchinson, Mobbs, Musgrave, Unpublished Work.
37. Krespan, Harder, Drysdale, J. Amer. Chem. Soc., 1961, 83, 3424.
38. Haszeldine, Steele, J., 1957, 2800.
39. Miller, Fried, J. Amer. Chem. Soc., 1959, 81, 2078.
40. Coscia, J. Org. Chem., 1961, 26, 2995.
41. Tarrant, Lovelace, Lilyquist, J. Amer. Chem. Soc., 1955, 77, 2783.
42. Harris, Stacey, J. Amer. Chem. Soc., 1961, 83, 840.
43. Kroll, U.S.P. 2,750,350, 1956; C.A. 50, 135071, 1956.
44. Moynihan, J. Amer. Chem. Soc., 1959, 81, 1045.
45. Dixon, J. Polymer Sci., 1959, 36, 552.
46. Wheeler, U.S.P. 2,847,391; C.A. 53, 2691e, 1959.

47. Brubaker, U.S.P. 2,393,967; C.A. 40, 3648-4, 1946.
48. Kellogg Co., B.P. 795,513; C.A. 53, 769d, 1959.
49. Hamilton, U.S.P. 2,369,524; C.A. 46, 1299c, 1952.
50. Rearick, U.S.P. 2,600,804, 1952; C.A. 46, 8415h, 1952.
51. Caird, U.S.P. 2,600,202, 1952; C.A. 46, 8415f, 1952.
52. Hanford, U.S.P. 2,820,027; C.A. 52, 5884f, 1958.
53. Padbury, Kropa, U.S.P. 2,602,824; C.A. 46, 8415g, 1952.
54. Borland, Miller, Pearson, U.S.P. 2,865,824; C.A. 53, 5749c, 1959.
55. Hauptschein, Lesser, J. Amer. Chem. Soc., 1956, 78, 676.
56. McBee, Hill, Bachman, Ind. Eng. Chem., 1949, 41, 70.
57. Madorski, Hart, Straus, Sedlak, J. Res. Nat. Bur. Standards, 1953, 51, 327.
58. Madorski, Straus, J. Res. Nat. Bur. Standards, 1959, 63, 261.
59. Coffman, Ford, U.S.P. 2,456,255; C.A. 43, 1608e, 1949.
60. Newkirk, J. Amer. Chem. Soc., 1946, 68, 2467.
61. Kalb, Coffman, Ford, J. Appl. Polymer Sci., 1960, 4, 55.
62. Adams, Bovey, J. Polymer Sci., 1952, 9, 481.
63. Manowitz, Nucleonics, 1953, 11, 18.
64. Eleuterio, U.S.P. 2,958,685, 1960.
65. Miller, U.S.P. 2,598,283; C.A. 46, 7824e, 1952; B.P. 804,561; C.A. 53, 16600i, 1959.
66. Almirante, Tosolini, J. Org. Chem., 1961, 26, 177.
67. Sauer, U.S.P. 2,549,935; C.A. 45, 6874c, 1951.
68. Mallouk, Sandt, Bro., B.P. 829,600, 1957; C.A. 54, 14795g, 1960.
69. Hamlin, C.A. 50, 10442h, 1956.

- 70.a) E.I. Du Pont de Nemours, B.P. 593,605; C.A. 2139d (1948)  
b) and Pearson, B.P. 584,742; C.A. 4007c, 1947.
71. Miller, U.S.P. 2,662,072; C.A. 48, 4253d, 1954.
72. E.I. Du Pont de Nemours, B.P. 606,273; C.A. 43, 5637g, 1949.
73. Conroy, Honn, Robb, Wolf, Rubber Age, 1955, 76, 543.
74. Montermoso, Griffis, Wilson, Oesterling, Proc. Inst. Rubber Ind., 1958, 5, 97.
75. Wilson, Griffis, Montermoso, Rubber Age, 1958, 83, 647.
76. Kellogg and Co., B.P. 742,908; C.A. 50, 13497g, 1956.
77. Kellogg and Co., B.P. 742,907; C.A. 50, 13497b, 1956.
78. Teeters, Passino, Dittman, U.S.P. 2,770,606; C.A. 51, 7752a, 1957.
79. Allied Chemical and Dye, B.P. 783,933; C.A. 52, 4245e, 1958.
80. Ferguson, J. Amer. Chem. Soc., 1960, 82, 2416.
81. Rugg, Stevenson, Rubber Age, 1957, 82, 102.
82. Moran, Rubber World, 1957, 137, 250.
83. Stivers, Honn, Robb, Ind. Eng. Chem., 1959, 51, 1465.
84. Minnesota Mining, B.P. 823,974; C.A. 54, 9368f, 1960.
85. Griffis, Montermoso, Rubber Age, 1958, 83, 118.
86. Baumann, Chem. and Ind., 1959, 1498.
87. Hauptschein, O'Brien, Stokes, J. Amer. Chem. Soc., 1953, 75, 87.
88. Moran, Kane, Smith, J. Chem. Eng. Data, 1959, 4, 276.
89. Moran, Kane, Smith, Ind. Eng. Chem., 1959, 51, 831.
90. Gallagher, Eubank, Rubber World, 1960, 141, 827.
91. Smith, Rubber World, 1959, 140, 263.
92. Dixon, Rexford, Rugg, Ind. Eng. Chem., 1957, 49, 1687.

93. Lenk, Mitchell, Paciorek, J. Polymer Sci., 1960, 45, 405.
94. Smith, Proc. Int. Rubber Conf., 1959.
95. Postlenceck, Ind. Eng. Chem., 1958, 50, 1602.
96. Barbour, Chem. and Ind., 1961, 958.
97. Banks, Haszeldine, J. Oil Colour Chem. Assoc., 1959, 42, 591.
98. Hauptschein, J. Amer. Chem. Soc., 1957, 79, 6248.
99. Paciorek, J. Org. Chem., 1962, 27, 266.
100. Harmon, U.S.P. 2,511,258; C.A. 44, 8166d, 1950.
101. Hauptschein, J. Amer. Chem. Soc., 1959, 81, 2676.
102. Evans, Tatlow, J., 1954, 3779.
103. Chambers, Ph.D. Thesis, Durham, 1959.
104. Hopkin, M.O.A. Conf. on Macromolecules, London, 1961.
105. Ballantine, Nuc. Sci. Abs., 1955, 9, 1781 and 4100.
106. Medvedev, Abkin, Vysokomolekulyarne Soedineniy, 1960, 2, 904.
107. Magat, Coll. Czech. Chem. Comm., 1957, 22, 141, (C.A. 8536k, 1957).
108. Barb, Gerson, Yarseley, B.P. 784,274; C.A. 52, 4240f, 1958.
109. Chapiro, Stannett, J. Chim. Phys., 1959, 56, 830, (C.A. 54, 10468i, 1960).
110. Okamura, Futami, App. Radn. and Isotopes, 1960, 8, 46.
111. El-Ahmadi, Herba, Anderson, J. Amer. Chem. Soc., 1957, 79, 4940.
112. Rabilloud, Traynard, Compt. Rend., 1960, 250, 334.
113. Wiley, Harrell, J. Org. Chem., 1960, 25, 903.
114. Chang, Yang, Wagner, J. Amer. Chem. Soc., 1959, 81, 2060.
115. El-Abbady, Anderson, J. Amer. Chem. Soc., 1958, 80, 1737.
116. Brown, Gewanter, J. Org. Chem., 1960, 25, 2071.

117. Fokin, Volkova, *Khim. Nauka. i Prom.*, 1959, 4, 806.
118. Haszeldine, Steele, J., 1954, 923.
119. Durrell, J. *Org. Chem.*, 1960, 25, 1661.
120. Coffmann, Cramer, Rigby, J. *Amer. Chem. Soc.*, 1949, 71, 979.
121. Henne, Kraus, J. *Amer. Chem. Soc.*, 1951, 73, 1791.
122. Haszeldine, J., 1953, 3565.
123. Haszeldine, J., 1953, 922.
124. Hanford, U.S.P. 2,443,003; C.A. 42, 6841d, 1948.
125. Hanford, Joyce, U.S.P. 2,562,547; C.A. 46, 1578i, 1952.
126. Joyce, U.S.P. 2,559,628; C.A. 46, 3063b, 1952.
127. Skinner W., Skinner E., Tiezen, Johnson, J. *Org. Chem.*, 1958, 23, 1710.
128. E.I. Du Pont de Nemours, B.P. 583,874; C.A. 41, 5141f, 1947.
129. Haszeldine, Marklew, J., 1956, 962.
130. Hoyt, U.S.P. 2,843,575; C.A. 53, 2675b, 1959.
131. Berry, U.S.P. 2,412,960; C.A. 41, 1885c, 1947.
132. Imperial Chemical Industries, B.P. 594,249; C.A. 42, 2473i, 1948.
133. E.I. Du Pont de Nemours, B.P. 596,943; C.A. 42, 5719c, 1948.
134. Harris, McCane, B.P. 812,116; C.A. 53, 14585e, 1959.
135. Ford, U.S.P. 2,468,054; C.A. 43, 5638b, 1949.
136. Pearson, U.S.P. 2631, 998; C.A. 47, 5725c, 1953.
137. Kroncke, U.S.P. 2,770,615; C.A. 52, 797e, 1958.
138. Kropa, Padbury, U.S.P. 2,590,019; C.A. 46, 10197a, 1952.
139. Minnesota Mining, B.P. 840,735, 1956; C.A. 54, 25974c, 1960.
140. Holbrook, Gordon, Pierce, J. *Amer. Chem. Soc.*, 1960, 82, 825.

141. Minnesota Mining, B.P. 823,974, 1956; C.A. 51, 9368f, 1960.
142. Haszeldine, J., 1953, 2193.
143. Hauptschein, J. Amer. Chem. Soc., 1959, 2676.
144. Geyer, Haszeldine, Leedham, Marklew, J., 1957, 4472.
145. McBee, Roberts, J. Amer. Chem. Soc., 1957, 79, 2329.
146. Tedder, Chem. Revs., 1955, 55, 787.
147. Bacq and Alexander, Fundamentals of Radiobiology, Butterworths, 1955.
148. Prober, J. Amer. Chem. Soc., 1950, 72, 1036.
149. Martin, U.S.P. 2,409,948, 1946; C.A. 41, 40059, 1947.
150. Harmon, U.S.P. 2,436,142, 1948; C.A. 42, 3776h, 1948.
151. Radell, Connolly, J. Chem. Eng. Data, 1961, 6, 282.
152. Haszeldine, Young, J., 1960, 4503.
153. Miller, Dittman, Ehrenfeld, Prober, Ind. Eng. Chem., 1947, 39, 333.
154. Koshar, Trott, Lazerte, J. Amer. Chem. Soc., 1953, 75, 4595.
155. Barrick, U.S.P. 2,403,207; C.A. 40, 6497-4, 1946.
156. Minnesota Mining, B.P. 827,308, 1956; C.A. 54, 13711b, 1960.
157. Plunkett, U.S.P. 2,230,654; C.A. 35, 3365-8, 1941.
158. Haszeldine, Osborne, J., 1955, 3880.
159. Hauptschein, J. Amer. Chem. Soc., 1953, 75, 2695.
160. Hauptschein, J. Amer. Chem. Soc., 1953, 75, 2693.
161. Hauptschein, J. Amer. Chem. Soc., 1960, 82, 2868.
162. Anderson, Putnam, Sharkey, J. Amer. Chem. Soc., 1961, 83, 382 and 389.

163. Filler, O'Brien, Fenner, Hauptschein, J. Amer. Chem. Soc., 1953, 75, 966.
164. Faurote, Henderson, Murphy, Ind. Eng. Chem., 1956, 48, 445.
165. Clark, Simons, J. Amer. Chem. Soc., 1953, 75, 6305.
166. Bourne, Stacey, Tatlow, Worrall, J., 1954, 2006.
167. Bourne, Randles, Stacey, Tatlow, J. Amer. Chem. Soc., 1954, 76, 3206.
168. Rasmussen, Brattain, J. Amer. Chem. Soc., 1949, 71, 1073.
169. Hutchinson, Musgrave, Unpublished Work.
170. Schweiker, Robitschek, J. Polymer Sci., 1957, 24, 33.
171. Brown, Mathieson, J., 1957, 3608.
172. Throssell, Sood, Szwarc, J. Amer. Chem. Soc., 1956, 78, 1122.
173. Florin, Wall, J. Res. Nat. Bur. Stand., 1961, 65A, 375.
174. Baxendale Mellows, J. Amer. Chem. Soc., 1961, 83, 4720.
175. Melville, Chem. and Ind., 1957, 1632.
176. Park, Holler, Lacher, J. Org. Chem., 1960, 25, 990.
177. Knunyants, Shokina, Doklady, Akad. Nauk, S.S.S.R., 1959, 129, 328; C.A. 1960, 54, 7528i.
178. S.C.I. Symposium on Thermal Degradation of Polymers, 1961, p.256.
179. Hanford, U.S.P. 2,440,850, 1948.
180. Waters, "Chemistry of Free Radicals", 2nd Ed., Oxford University Press, 1948, p.182.
181. Hauptschein, Chem. Eng. News, 1958, 36, No. 38, 48.
182. Du Pont Information Bulletin, Dyes and Chemicals.

183. Barrick, U.S.P. 2462,346, 1949; C.A., 43, 4294f.
184. Barrick, Coffman, Cramer, J. Amer. Chem. Soc., 1949, 71, 490.
185. Putnam, Anderson, Sharkey, J. Amer. Chem. Soc., 1961, 82, 386.
186. Putnam, Castle, J. Amer. Chem. Soc., 1961, 83, 389.
187. Anderson, Putnam, Sharkey, J. Amer. Chem. Soc., 1961, 83, 382.
188. Birchall, Haszeldine, J., 1959, 13.
189. Bellamy, "Infrared Spectra of Complex Molecules", p.42, 2nd Ed., 1960.
190. Nield, Stephens, Tatlow, J., 1960, 3800.
191. Evans, Tatlow, J., 1955, 1184.
192. Evans, Tatlow, J., 1954, 3779.
193. Stephens, Tatlow, Wiseman, J., 1959, 148.
194. Nield, Stephens, Tatlow, J., 1959, 159.
195. Nield, Stephens, Tatlow, J., 1959, 166.
196. Stephens, Tatlow, Chem. and Ind., 1957, 821.
197. Birchall, Haszeldine, J., 1961, 3719.
198. Brice, Lazerte, Hals, J. Amer. Chem. Soc., 1953, 75, 2698.
199. Haszeldine, Nature, 1951, 168, 1028.
200. Burdon, Whiffen, Spectrochim. Acta, 1958, 12, 139.



