Perfluoroalkylene oxide derivatives as potential elastomer precursors

Sage, Ian

For J.D. and D.E.

UNIVERSITY OF DURHAM

A THESIS

entitled

PERFLUOROALKYLENE OXIDE DERIVATIVES AS POTENTIAL ELASTOMER PRECURSORS

Submitted by

Ian Sage B.Sc.

(St. Cuthberts Society)

A Candidate for the Degree of Doctor of Philosophy

1978

Acknowledgements

The author is indebted to Dr. W.J. Feast for his continual help and encouragement, and to Professor W.K.R. Musgrave for his advice and interest during their supervision of this work. Thanks are due to members of the technical staff for their assistance in the provision of starting materials.

The help of Mrs. E. Sage in the preparation of this thesis is greatly appreciated, and the provision of a maintenance grant by the Ministry of Defense is gratefully acknowledged.

Memorandum

The work described in this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1973 and November 1976. This work is the original work of the author except where acknowledged by reference. This work has not been submitted for any other degree and is previously unpublished.

Abstract

The synthesis of octadecafluoro-3,9-dioxa-1,11-bis(3-methoxycarbonyl phenyl) undecane from hexafluoroglutaryl fluoride, via the intermediate octadecafluoro-1,11-diiodo-3,9-dioxaundecane has been examined. Each stage of this sequence proceeds in poor yield, and no substantial improvement could be obtained by variation of conditions. The physical properties of the product lead to handling difficulties, and an attempt to derive a polymer from the system failed.

A synthesis of difluoromalonyl chloride from perfluorocyclohexa-1,4-diene is described. Difluoromalonyl fluoride could not be obtained pure, either by fluorination of the chloride, or by direct oxidation of the diene.

The addition reaction of hexafluoropropene epoxide with hexafluoroglutaryl fluoride, catalysed by caesium fluoride, provides a route to a mixture of fluorinated bifunctional ethers. By appropriate choice of reaction conditions, the isomeric distribution in the products may be restricted; a mechanism is suggested to account for the observed product distribution. Separation and purification of the reaction products provided a series of ether-containing bifunctional compounds, which on reduction yielded a corresponding series of ether diols.

Polycondensation of the diols obtained as above with isophthaloyl chloride gave a series of polyesters, which were compared with analogous polyesters derived from other systems. The thermal stability of polyesters having an ether link situated β to the ester group is significantly lower than that of polyesters lacking this feature, but no simple relation was found between structure and the activation energy for degradation.

The glass transition temperatures of non-ether containing polyesters correlate moderately well with predicted values. A knowledge of the glass temperatures of ether containing polyesters allows the calculation of the glass temperature of the hypothetical high molecular weight homopolymer of hexafluoropropene epoxide; a value of ca.-57°C was obtained.

Contents | Page

Note to the Reader

The nomenclature of many of the compounds discussed in this thesis becomes cumbersome in use; an attempt has been made to follow the practice of earlier workers in this field. Where appropriate, compounds are denoted in the text by numerals, and for the reader's convenience the correspondance between numerals and the most important compounds is indicated on endpapers at the back of the thesis.

Characterisation data of important products and intermediates is presented as an appendix to this thesis. All n.m.r. chemical shift data presented both in the appendix and text are in ppm referred to $CFCl_3$. Where necessary, data taken from the literature have been converted to this scale by use of the equation:

$$\text{Shift from } CFCl_3 = \text{Shift from } CF_3CO_2H + 76.5$$

without further note.

CHAPTER 1

General Introduction

In recent years, advances in aerospace technology have increasingly led to a need for new materials capable of service under extreme conditions.[1] One of the most acutely felt requirements has been for elastomeric polymers for use at high temperatures, which maintain their mechanical properties at sub-ambient temperatures. The work described in this thesis forms part of a long term research project directed toward the development of such materials. The upper and lower limits on the service temperature range of an elastomer are set by the thermal stability of the polymer chain, and by its glass transition temperature, respectively. It is therefore appropriate to examine the factors in a polymeric structure which influence these properties.

The Glass Transition Temperature

1. Phenomenology

When any liquid which does not readily crystallize is cooled below its melting point (T_m), the liquid phase persists as a metastable state, and the normal discontinuities in physical properties associated with T_m are not observed. On further cooling, however, a temperature range is encountered in which the liquid viscosity (η) changes dramatically. In the same region of temperature, plots of other physical properties of the liquid, such as the volume (V), enthalpy (H), and entropy (S) against temperature, exhibit discontinuities of slope.

These observations are commonly used in one of several ways to define a temperature T_g, called the glass transition temperature.[2] It will be clear from this discussion that T_g is not in any way so clearly defined as T_m or other phase transition temperatures, which are characteristic of a thermodynamic equilibrium in the system. On the contrary, T_g is characteristic of a non-equilibrium situation. Physical changes in the region of T_g take place over a range of temperature, which moreover varies according to heating rate, and the prior thermal history of the sample. The variations in some of these properties are represented in figures 1.1 to 1.4.

Variation of Liquid Properties in the Region of T_g

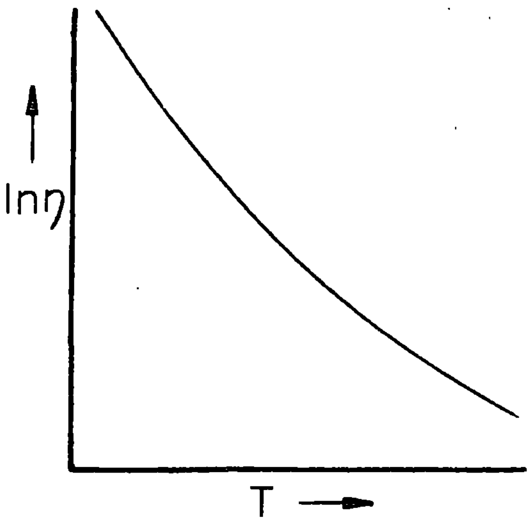


Figure 1.1

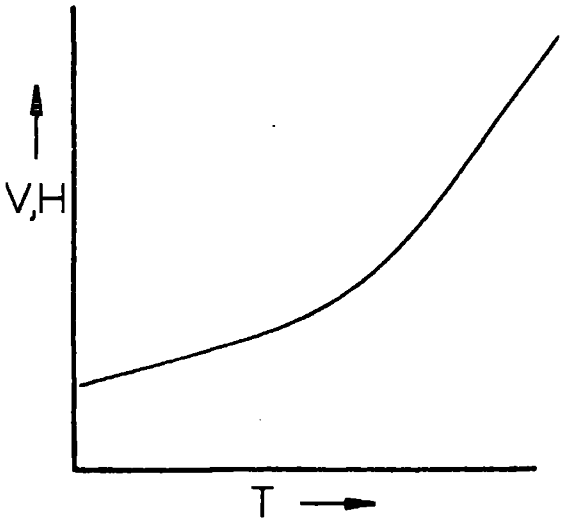


Figure 1.2

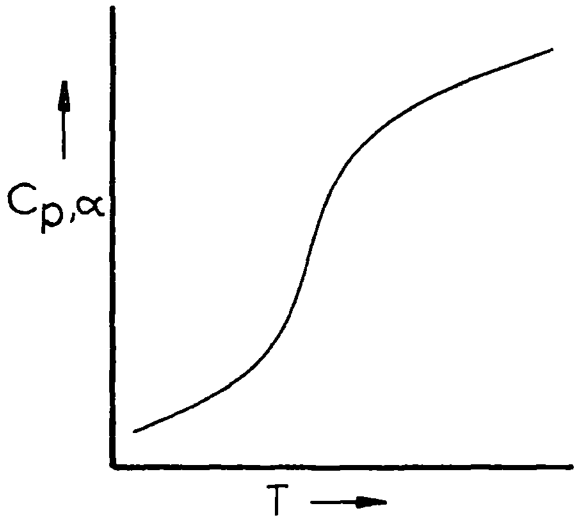


Figure 1.3

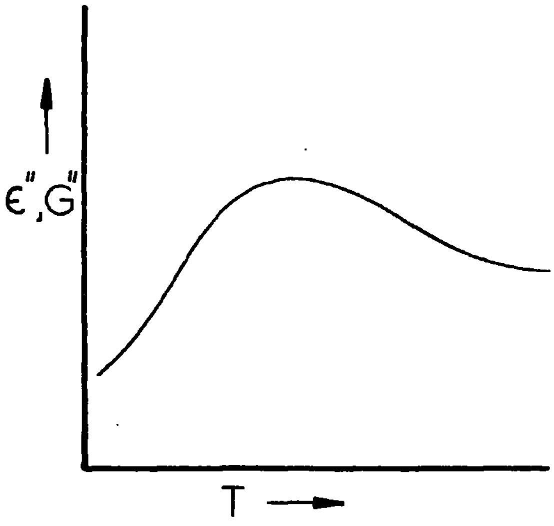


Figure 1.4

The variation of viscosity with temperature has already been referred to; typically η changes by several orders of magnitude over a range of ca.20°C. In the past, T_g has often been defined as the temperature at which η reaches some arbitrary value. Volume and enthalpy do not change sharply in the region of T_g, i.e., there is no expansion or latent heat effect; the changes in these properties above and below the T_g range approximate to straight lines of differing slope, and extrapolation of these lines gives an intersection point which provides a convenient criterion of T_g. The volume coefficient of thermal expansion α , and the specific heat, C_p, vary in the matter anticipated for first derivatives of V and H. The symbols ϵ'' and G'' represent the energy dissipated in the sample under conditions of varying dielectric and mechanical stress respectively. The peaks in these curves correspond to the point at which the applied stress varies at a rate equal to the rate of molecular motion in the sample. The position of the peak on the temperature scale is therefore a function of the frequency of application of stress, and may be used as a criterion of T_g, either by specifying a standard frequency, or by extrapolation to zero frequency.

2. The Glass Transition in Linear Polymers

The glass transition is a characteristic of the amorphous state. Almost all polymers, including those which show a marked tendency to crystallization, contain substantial proportions of amorphous material, consequently it is to be expected that the majority of polymers should show a marked glass transition. This is at once true, and an over-simplification of the observed phenomena. When a polymer is cooled from the melt, crystallization may occur at T_m and below, to give a tough, or hard and brittle material; some polymers however, do not show any observable crystallization under normal experimental conditions. Below T_m, polymers of different crystallinity show different behaviour. Those which are not crystalline display a glass transition similar to a low molecular weight liquid, but with the possibility of more than one transition being present: in such cases, T_g is taken as the temperature of either the major, or the highest temperature amorphous transition. In polymers possessing an appreciable crystallinity, the glass transition occurs over a wider temperature range and is less marked in its effect on physical properties, while for highly crystalline materials, the glass transition can become very difficult to detect, even though a substantial proportion of the sample may still be in the amorphous state.

The physical state of the polymer melt is also a variable, which is principally dependant on the molecular weight ($\bar{M}$) of the polymer. Just above T_g, an amorphous polymer of low molecular weight behaves as a viscous liquid, whilst samples of higher $\bar{M}$ behave as leathery solids in this temperature range. On raising the temperature further, these leathery materials often show an elastic behaviour before becoming highly viscous liquids; polymers of the highest molecular weight, and those which are lightly cross-linked, maintain their elastic properties up to their decomposition temperature. Polymers which are crystalline may show onset of elastic behaviour above T_m, but it may be noted at this point, that as T_m is generally substantially above T_g, it is highly desirable that an elastomer designed for low temperature applicability should show negligible tendency to crystallize. Furthermore, because a polymer just above its T_g is leathery rather than elastic, T_g must be some 50°C lower than the minimum envisaged service temperature of the elastomer.

The T_g of a polymer is strongly dependant on the parameters of the molecular chain. The first of these is the molecular weight, which corresponds with the physical length of the chain; the glass transition temperature rises with increasing $\bar{M}$, until a plateau is reached, where T_g is independant of $\bar{M}$. (Fig. 1.5)

Variation of T_g with $\bar{M}$ in Polymers

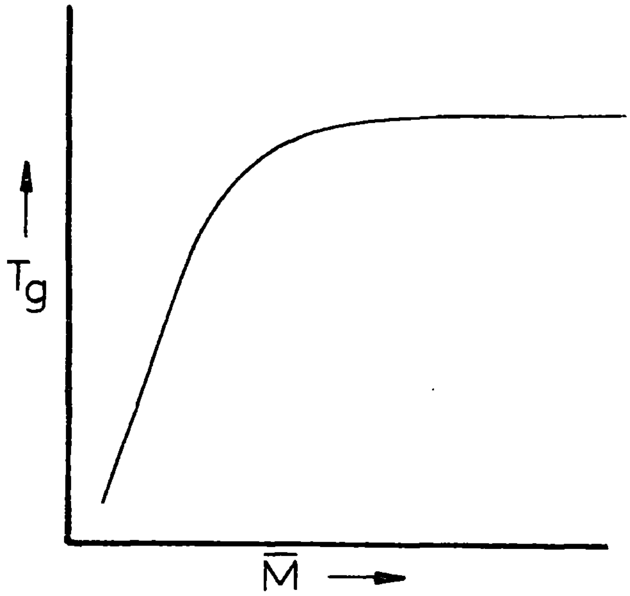


Figure 1.5

The T_g of a polymer, as commonly referred to in the literature, refers to this plateau value. As the optimum mechanical properties of a polymer are generally only developed in a high molecular weight material, it is obviously this figure which is of practical significance, and where data on T_g have been derived from samples of poorly characterised molecular weight, they must be regarded with caution.

The factors which relate the T_g of a polymer to its molecular structure form a series of empirical correlations[3] which are, to a certain extent, mutually complementary. It is in general difficult to distinguish the differing effects that a group has on a polymer chain, but within these limits, such correlations form a basis for the qualitative prediction and interpretation of T_g trends within a polymer series.

a) Bond Flexibility. The flexibility of covalent bonds in a polymer may be quantified in terms of the barrier to rotation about the bond. The inclusion of flexible bonds in a polymer leads to greater chain mobility at low temperature, and to a reduction of T_g. This trend is plainly observed in practise. Table 1.1 lists the glass transition temperatures of some polymers, together with the barrier to bond rotation in the ethane formed by replacing the polymer chain bonds with hydrogen atoms.

Variation of Polymer T_g with Bond Flexibility

Polymer	T_g (°C)	Rotation Barrier in Ethane (kcals/mole)
$(CH_2\ CH_2)_n$	- 125	2.9[5]
$(Si(CH_3)_2\ O)_n$	- 123	~0[4]
$(CH_2\ CF_2)_n$	- 40	3.2[4]
$(CH_2\ CCl_2)_n$	- 18	3.6[5]

Table 1.1

b) Inter-chain Forces. Division of the (theoretical) latent heat of vapourisation of a polymer, after subtraction of an RT term, by the volume in the condensed state, gives the cohesive energy density (c.e.d.). This is a measure of the inter-chain attractive forces in the polymer. The c.e.d. can be obtained from swelling measurements on the polymer in a solvent, or estimated from a set of additive parameters. A high c.e.d. is found to promote high values of T_g, which may be correlated in turn with bond polarity, symmetry, and shielding effects.[6] (Table 1.2).

Variation of Polymer T_g with Cohesive Energy Density

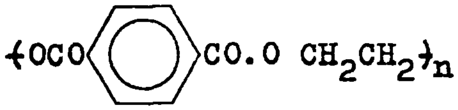
Polymer	c.e.d. (cals/cc)	T_g (°C)
$\left(CH_2CH_2 \right)_n$	65	- 125
$\left(CH_2CHCl \right)_n$	91	81
$\left(CH\text{-}(CO_2CH_3)\text{-}CH_2 \right)_n$	103	6
	114	69

Table 1.2

The inclusion of polyvinyl chloride in the table serves to illustrate a general principle, that no single correlation forms an adequate basis for T_g estimation, but that a number of conflicting factors are involved. A similar effect may be observed in Table 1.1.

c) Disordering of Main-chain Packing. Features which inhibit the close packing of polymer chains exhibit a strong effect in reducing T_g.[3] Among the most important factors in this respect are the inclusion of non-linear and bulky groups in the main chain, and the presence of long and flexible side chain substituents. (Table 1.3).

The Effect of Disordering Groups on Polymer T_g

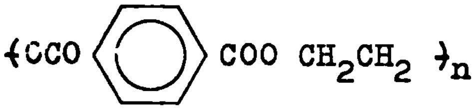
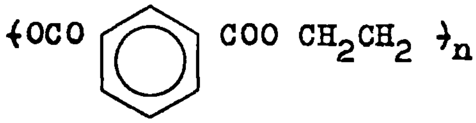
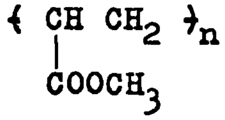
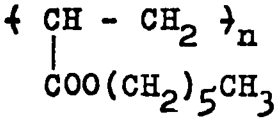
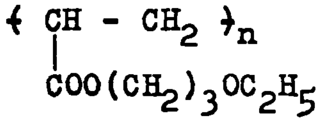
Polymer	T_g (°C)
	69
	51
 $(\!-CH(COOCH_3)\,CH_2-)_n$	6
 $(\!-CH(COO(CH_2)_5CH_3)-CH_2-)_n$	- 57
 $(\!-CH(COO(CH_2)_3OC_2H_5)-CH_2-)_n$	- 68

Table 1.3

Rules-of-thumb other than these may be introduced to further rationalise trends in T_g among a set of polymers.[3] However, the point is reached where it becomes impossible to decide whether, for example, the influence of a bulky group on the T_g of a polymer in which it is substituted will be due primarily to its disordering effect, its polarity or polarisability increasing c.e.d., to steric hindrance of rotation of adjacent bonds, or any other factors. The predictive power of relations such as these is therefore limited, though valuable, so far as it goes. It will therefore prove instructive to examine current views on the fundamental nature of the glass transition with the principal objective of assessing the predictive power of different theories.

3. The Molecular Nature of the Glass Transition

The technological importance of the glass transition, as well as its inherent scientific interest, has led to considerable research on the nature of the processes involved. Certain characteristics of the glass transition show analogy with a thermodynamic second order process. These transitions, such as the onset of methyl group rotation in methyl cyclohexane, or the transformation between the two forms of liquid helium, are characterised by discontinuities in plots of C_p or α against T. As in the glass transition, no volume change or latent heat effect is observed. However, in a typical second order thermodynamic transition C_p and α fall as T rises, in contrast to the behaviour of materials at T_g.[7] Furthermore, as has been pointed out, T_g is observed at different temperatures according to the rate of temperature rise, and the prior thermal treatment of the sample. A true thermodynamic transition occurs at a particular well defined temperature under standard conditions. Above and below the transition temperature, the sample is in thermodynamic equilibrium, whereas the glass to liquid transition has a non-equilibrium state on one side. The attainment of thermodynamic equilibrium in a liquid is dependant on the free motion of molecules in response to the constantly changing local force field. When this motion is impeded by the increasing viscosity of the liquid, the system begins to deviate from thermodynamic equilibrium to a degree which is greater, the greater the rate of cooling. In this light, there appears little justification for regarding the glass transition as a typical thermodynamic equilibrium.

The nature of the glassy state leads to great difficulty in the experimental investigation of the glass transition. In the region of T_g, the time which a sample takes to respond to a change of temperature becomes comparable with the time scale of the experiment. At lower temperatures, the response or relaxation time becomes inconveniently long, and this problem has led to the wide use of extrapolations based on a limited range of data. The validity of such extrapolations is questionable, and their conclusions cannot usually be checked by independant means. Kauzmann extrapolated the thermodynamic functions of glycerol from above its T_g toward absolute zero.[8] He found that H, S and V fell rapidly to such a degree that they should fall below the corresponding values for the crystalline state at very low temperatures. (Fig. 1.6) The figure is diagrammatic, and the dotted line represents the extrapolated

Kauzmann's Extrapolation

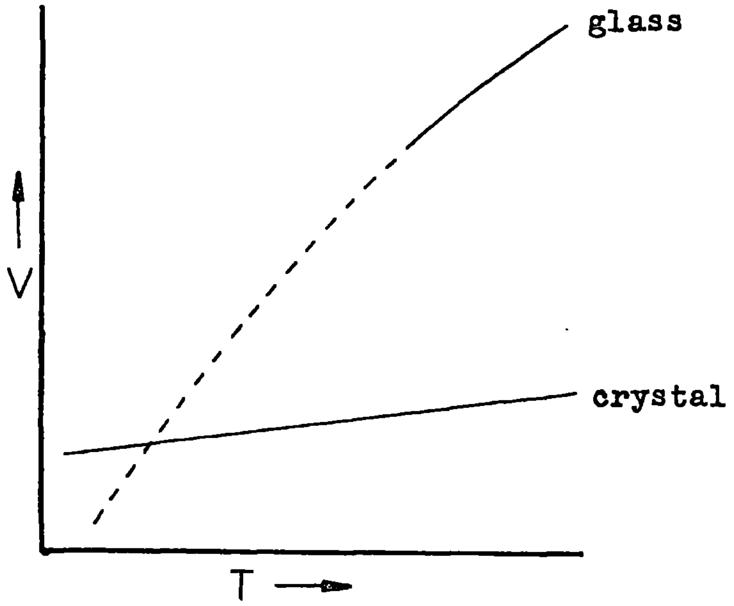


Figure 1.6

portion of the curve. Kauzmann realised that this extrapolation presented a paradox, which he resolved by assuming a smooth transition from glass to crystal at the crossover point of the two curves. Gibbs and di Marzio, however, interpreted the problem in a different way, on which they built their theory of the glass transition.[9] They assumed a true thermodynamic second-order transition should occur at some temperature T_2, below T_g. (Fig. 1.7) In practise, the region of T_2 is not accessible to experiment, but Gibbs and di Marzio reasoned that analogous

The Gibbs - di Marzio Extrapolation

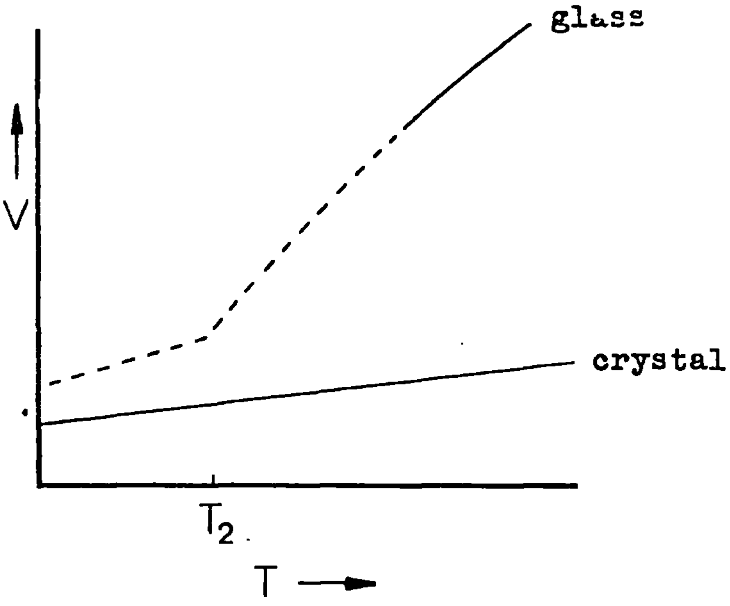


Figure 1.7

molecular processes occurred at T_2 and at T_g. In this way they justified a thermodynamic approach to the interpretation of the glass transition, since although the transition at T_g was not of thermodynamic origin, the temperature at which it occurred should be affected by the same factors as the transition at T_2, which was. The Gibbs - di Marzio theory provides a conceptual basis for understanding the effect of molecular weight and additives on polymer T_g. Furthermore, it may be extended to the theory of polymer viscosity to yield the equation

$$\ln \frac{\eta_2}{\eta_1} = \frac{A\,(T_2 - T_1)}{B + (T_2 - T_1)} \qquad \text{Equ. 1.1}$$

where η_1 and η_2 are the viscosities of the polymer melt at temperatures T_1 and T_2 respectively, and A and B are constants. Equation 1.1 is identical in form to that deduced empirically from experimental data. It is known as the Williams - Landel - Ferry (WLF) relation, and is closely followed by liquids in the range $T_g < T_{exp} < T_g+100$. Although the Gibbs - di Marzio theory does succeed in these ways, many workers regard the introduction of a transition at T_2 to be an artificial solution. Rehage has cast experimental doubt on the reality of this transition by conducting measurements of α over a wide temperature range, on solutions of different concentration.[7] These results he then extrapolates to 100% solute concentration. On the basis of this work he suggests a simple non-linear extrapolation of Kauzmann's data. (Fig. 1.8)

The Rehage Extrapolation

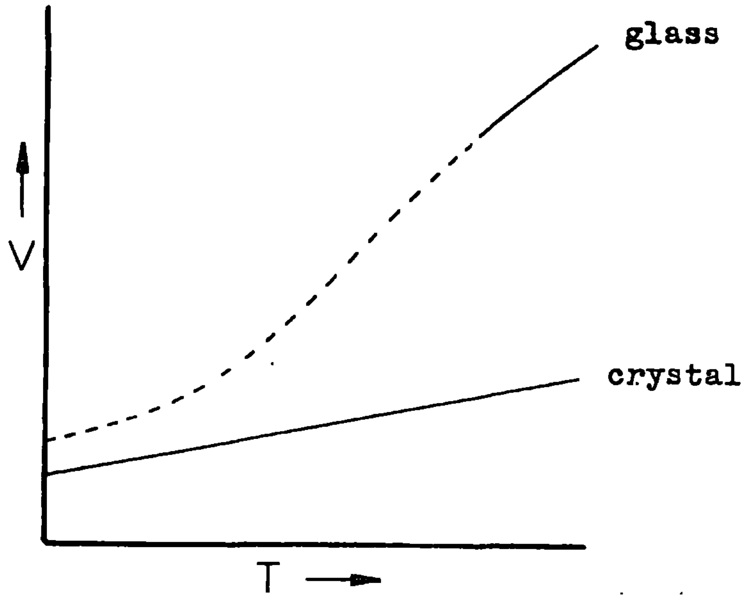


Figure 1.8

The concept of 'free volume' within a liquid or glass has been used in several attempts to rationalise the glass transition.[10] The assumption common to these treatments is that in a liquid or glass, a certain amount of free volume unoccupied by any molecule exists. In the glassy state, this volume is frozen into voids, which lose their individual identity when the molecules gain freedom of motion above T_g. According to the model used, statistical or thermodynamic methods are used to estimate the size of the voids in the glass, which increases with temperature. When this void size becomes comparable to the molecular diameter, the molecules gain an additional degree of freedom of motion, by a 'hopping' mechanism. Because the motion of a molecule leaves a void behind it, the onset of this motion is concerted and cooperative, accounting for the reasonably narrow temperature range over which T_g is observed. The additional degree of freedom which the molecules now possess leads naturally to the increase in C_p and α. Such a model is successful in aiding our understanding of many features of the glass transition, including the effect of molecular weight, additives, and molecular structure in polymers. Like the Gibbs - di Marzio theory, it can be used to derive an equation of the form of the WLF relation. Furthermore, these theories predict that for a liquid at T_g,

$$(V - V_o) / V = \text{Constant} \qquad \text{Equ. 1.2}$$

where V is the volume of the sample at T_g, and V_o is the volume of the liquid extrapolated to 0 K. It has been shown that for some polymers at least, Equation 1.2 does hold, the value of the constant being ca. 0.1 - 0.15. The major shortcoming of these theories at the present time lies in their predictions with regard to certain details of the glass transition, particularly the effect of pressure on T_g.

The approaches outlined above are among the most important theories of the glass transition advanced, but are by no means the only ones. Several other attempts to explain the glass transition have met with partial success, and detailed discussion of these theories, as well as those mentioned above, may be found in references.[2] All these theories have in common the inclusion of approximations and non-calculable parameters which make them unsuitable for the prospective prediction of T_g. It may well be felt that the uncertainty surrounding even the unambiguous definition of T_g leads to a somewhat unsatisfactory situation with regard to its theoretical treatment. This situation appears to be unavoidable while understanding of the liquid and glassy states remains so limited, and it may be expected that the a priori prediction of T_g is not a strong possibility in the near future.

4. Empirical Approaches to T_g Prediction

An oft-quoted relationship[11,12,13] suggests a connection between the melting points and the glass transition temperatures of polymers. As melting points are available for many polymers of which the T_g's have not been determined, such a connection could make a valuable contribution to the extension of T_g data. The relationship is usually given in the form:

For symmetric polymers $T_g/T_m = 0.5$

For asymmetric polymers $T_g/T_m = 0.67$

Both T_g and T_m are expressed in degrees K. Symmetric polymers are those in which no main chain atom carries two different side chain substituents. The relationship has been critically reviewed by Lee and Knight.[14] They found that the ratio T_g/T_m varied between 0.25 and 0.97 in a sample of 132 polymers for which reliable data were available. The standard deviation on the results was 0.11. Some 85% of polymers considered had T_g/T_m values of between 0.5 and 0.8. It was concluded that T_g/T_m was not a constant ratio even within a given class of polymers, and the relation was not useful as a means of predicting T_g.

An approach to T_g prediction based on the use of additive parameters has been explored more recently. It had previously been noted that the glass transition temperature of copolymers can be related to the T_g's of the homopolymers derived from the same monomers by a linear relationship.[15,16] (Fig. 1.9) In practise, deviations are observed from the ideal behaviour

Ideal Variation of T_g with Composition in Copolymers

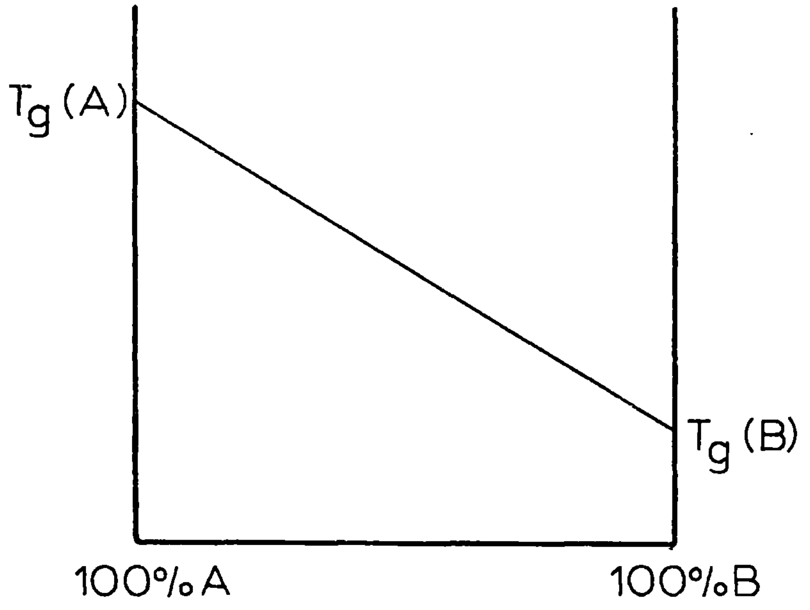


Figure 1.9

illustrated in Fig. 1.9, which may be corrected for by various equations.[17] It seemed reasonable to treat any polymer in this way, as equivalent to a copolymer of the constituent structural groups.[18,19,20] Consider a polymer of structure $(A - B - C)_n$. Then the polymer T_g may be expressed in terms of the glass transition temperatures of homopolymers:[21]

$$T_g = a_A T_{g_A} + a_B T_{g_B} + a_C T_{g_C}$$

T_g is the glass temperature of the polymer under consideration. The parameters T_{g_A}, T_{g_B}, and T_{g_C} are the glass temperatures of the theoretical homopolymers $\leftarrow A \rightarrow_n$, $\leftarrow B \rightarrow_n$

and $\text{-}(C)\text{-}_n$ respectively. The coefficients a_A, a_B and a_C are weighting factors whose function is to take account of the relative importance of different groups in determining the final T_g. These coefficients are normalised, i.e.,

$$a_A + a_B + a_C = 1$$

This simple example will serve to illustrate several important features of the additive temperature parameter method. Firstly, some means of establishing the magnitudes of the coefficients must be defined. Frequently, a_x is taken as the weight fraction or mole fraction of group x in the polymer. Other choices of a_x are mentioned below. Secondly, in order to predict the T_g of a polymer, the additive temperature parameter (ATP) of each constituent group in the polymer must be known. This in turn necessitates the existance of a large body of T_g data covering a variety of polymer types. Moreover, the extraction of ATP values from these data relies on the availability of good computing facilities.

A critical comparison of different relationships capable of use in an ATP approach to T_g prediction has been made by Lee.[22] The equations examined were as follows:

$$T_g = 1 / \sum_i (w_i / T_{g_i}) \qquad \text{Equ. 1.3}$$

$$T_g = \sum_i w_i \, T_{g_i} \qquad \text{Equ. 1.4}$$

$$T_g = \sum_i (n_{H_i} \, T_{g_i}) \, / \sum_i n_{H_i} \qquad \text{Equ. 1.5}$$

$$T_g = \sum_i n_i \, T_{g_i} \qquad \text{Equ. 1.6}$$

In these equations, the summation is taken over the number of discrete groups in the polymer repeating unit. A group is taken as the smallest structural unit capable of independant torsional motion. The symbols w_i and n_i stand for the weight fraction and mole fraction of group i in the repeating unit, respectively, and n_{H_i} is the Hayes constant, a measure of cohesive energy density. In defining groups, the following conventions are used: single atoms substituted on a chain atom are considered together with the chain atom; multiply bonded groups, and ring structures are taken as single groups; chemically identical groups in polymer main chains and side chains are considered independantly. A further convention leads to a significant improvement in the results obtained; this is to consider chemically identical groups having different nearest neighbours, separately; this is termed a 'neighboured group analysis'. The neighboured group analysis therefore takes account explicitly of interactions between adjacent groups, of which the barrier to bond rotation may be expected to be particularly significant. The other conventions take account of the interaction of groups with the 'averaged' polymer chain, and of the inflexibility of multiply bonded groups.

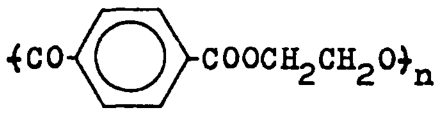
The relationship which gave best results in this study was Eq. 1.6, and this equation will be used to illustrate the procedure necessary to allow prediction of polymers T_g's. The same method may be applied to the other equations with obvious modifications. As stated above, the first requirement is for a substantial body of data on the T_g's of different polymers. The T_g's are then expressed as the sum of parameters based on the structural components of the polymer repeat unit. E.g., for the polymer polyvinylchloride:

$$\{CH_2\text{-}CHCl\}_n$$

$$T_g = n_1\, T_{g_1} + n_2\, T_{g_2}$$

$$354 = 0.5\, T_g\,(-CH_2-) + 0.5\, T_g\,(-CHCl-)$$

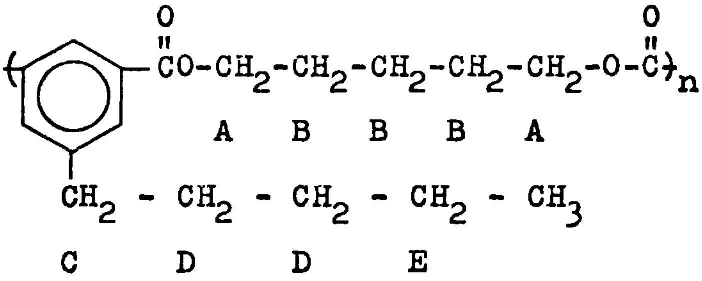
For polyethylene terephthalate



$$T_g = \sum_i n_i\, T_{g_i}$$

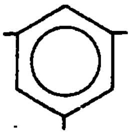
$$294 = \frac{1}{5}\, T_g\,(p-C_6H_4) + \frac{2}{5}\, T_g\,(-\overset{\overset{O}{\|}}{C}O-) + \frac{2}{5}\, T_g\,(-CH_2-)$$

Note that in both these examples, each type of structural group has only one pair of nearest neighbours. In cases where this does not hold, more complex expressions of the same form will result. For example, in the polyester structure shown below, five types of methylene groups must be considered.



In this case,

$$T_g = \sum_i n_i T_{g_i}$$

$T_g = \frac{1}{15} T_g$ () $+ \frac{2}{15} T_g (-\overset{O}{\overset{\|}{C}}-) + \frac{2}{15} T_g (-O-) +$

$$\frac{2}{15} T_g (CH_2)_A + \frac{3}{15} T_g (CH_2)_B + \frac{1}{15} T_g (CH_2)_C + \frac{2}{15} T_g (CH_2)_D +$$

$$\frac{1}{15} T_g (CH_2)_E + \frac{1}{15} T_g (CH_3)$$

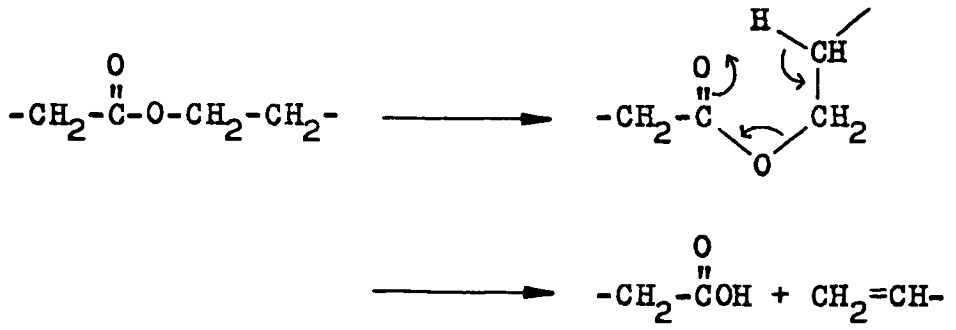
and it is understood that in compiling data for a polymer set, groups other than methylene will also be grouped according to their nearest neighbours. The distinction drawn between main chain and side chain groups is also illustrated by this example.

It is evident that by applying this procedure to a number of polymers, a set of simultaneous linear equations will be obtained. Provided that the number of polymers considered is greater than or equal to the number of structural groups in the polymers, this set of equations can be solved by standard mathematical techniques to yield the additive temperature parameters of the groups. In certain cases (where the equations are not linearly independant), a partial solution is possible which will yield the ATP of a combination of discrete groups. In cases where more polymers are used than there are structural groups, there is a certain redundancy of information, and a least squares fit to the data becomes possible.

By using the method outlined above, the additive temperature parameters corresponding to a wide range of structural units have been obtained. Any hypothetical polymer containing only these structural units can have its T_g estimated by having the ATP's re-substituted in Eq. 1.6. The results obtained from this method of T_g prediction in the original study were sufficiently good to give some confidence in the technique. The greatest difference between predicted and observed T_g was 7K, while the average (r.m.s.) inaccuracy was 3.8K. However, the polymer set used in this study was chosen to some extent factitiously by prior selection of the polymers according to structural criteria, and to the manner in which T_g varied as a homologous series is ascended. In a subsequent study on fluorinated polymers,[23,24] the greatest observed inaccuracy was 21K, while the average was 6K. The reliability in this case is therefore considerably lower, and the T_g's predicted by this method must be regarded with a degree of reservation. Nevertheless, in the absence of any superior method of T_g prediction, the ATP approach provides the best indication of which polymers are likely to show useful mechanical properties at temperatures toward the low end of the service range.

Thermal Stability

The ultimate theoretically attainable thermal stability of a polymer is dependant on the dissociation energy of the weakest chemical bonds in the structure. In practise, however, this is very rarely the limiting factor in polymer stability; much more commonly, a pathway of lower activation energy results in scission of bonds in a specific manner without recourse to a high energy intermediate. Some examples are given below:-



$-CH_2-CHCl- \xrightarrow{-HCl} -CH=CH-$

$\xrightarrow{\qquad}$ crosslinked residue

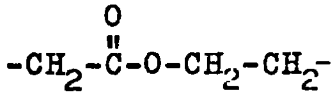
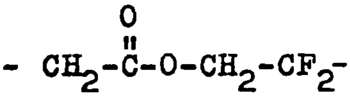
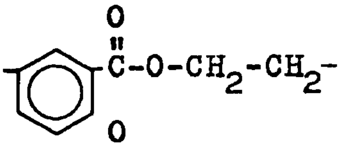
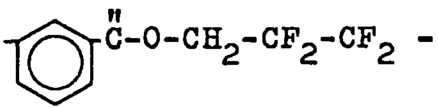
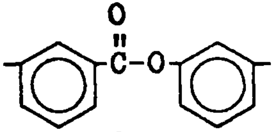
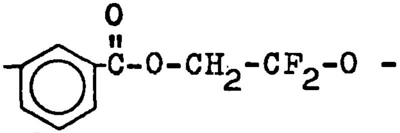
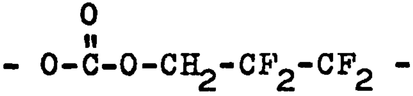
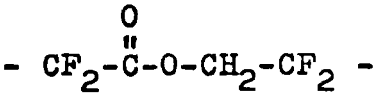
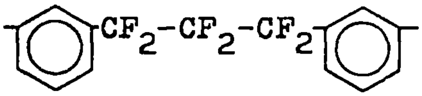
$-CH_2-O-CH_2-O-H \xrightarrow{-CH_2=O}$ 'unzips' from chain end.

In addition to these considerations, the thermal stability of a practical polymer must be considered in the presence of oxygen, moisture and possibly other agents, according to its intended use. Accordingly, a great deal of effort has been devoted to the investigation of which factors in a polymeric structure may lead to favourable stability under service conditions.

The great stability which fluorination may impart to a polymeric structure has been known since the discovery of PTFE. This polymer is in fact stable to a temperature about 100°C[25] higher than polyethylene. The influence of fluorine in this respect, however, is a function of the manner, rather than the amount in which it is substituted, and poly(trifluoroethylene), poly (chlorotrifluoroethylene) and poly(vinylidenefluoride) do not differ significantly from polyethylene in their thermal stability. Furthermore, poly(perfluoro 1-heptene) and poly(hexafluoropropene) are less stable than PTFE, despite the absence of substituents other than fluorine. Clearly, the chemical groups present in the repeat unit of the polymer are a more appropriate basis for the estimation of stability.

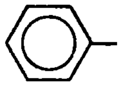
No useful general theory exists for the estimation of thermal stabilities of polymers. However, an extensive series of studies has been made of the decomposition temperatures of various polymers, and a more limited number of polymers have had a more or less complete study made of their decomposition kinetics. It may be assumed with reasonable confidence that the thermal stability of a new polymer containing any particular group will not significantly exceed the thermal stability of the most stable known polymer containing that group. A series of groups, together with their approximate decomposition temperature, is represented in table 1.4. Different authors have used widely varying criteria of stability, such as, in dynamic thermal analysis, the temperature at which the sample has lost 10%, 20% or 50% of its original weight (the heating rates in such tests are not, in general, standardised). Where tests have been carried out at constant temperature, the decomposition temperature is usually chosen as giving some specified half-life to the sample weight. Furthermore, different workers have carried out their tests in vacuum, or in atmospheres of dry or moist nitrogen, argon or helium, so comparison of results compiled from different references becomes very difficult, and some care must be taken in drawing conclusions from such a table. The significance of measurements obtained in these different ways is discussed more fully in the final chapter of this thesis.

Comparative Thermal Stabilities of Some Polymeric Structural Units

Group	Decomposition Temp.[a] (°C.)
$- CF_2-CF_2-CF_2 -$	508[25] 510[28] 509[30]
$- CH_2-CH_2-CH_2 -$	404[30]
$- CF_2-CH_2 -$	410[25] 440[28]
$- CF_2-CHCl -$	355[25]
 $-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-$	280[26]
 $- CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CF_2-$	340[25] 380[26]
	330[26]
	418[25] 480[26]
	525[29]
	380[27]
 $- O-\overset{\overset{O}{\|}}{C}-O-CH_2-CF_2-CF_2 -$	450[26]
 $- CF_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CF_2 -$	380[26]
$—CF_2-CF_2-O-CF_2-CF_2—$	515[31]
	548[32]

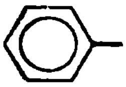
a) See script or reference

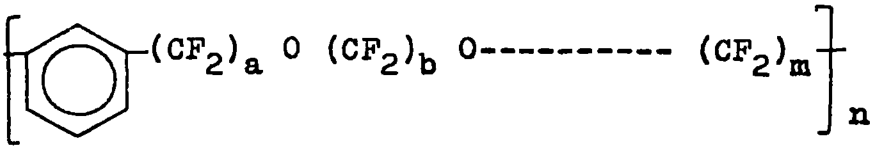
Table 1.4

Some useful points may be observed among the figures given. The perfluoro alkylene chain possesses a usefully higher thermal stability than the corresponding hydrocarbon linkage. Insertion of ether linkages actually increases this stability, presumably as a result of a consequent relaxation of steric stress in the polymer backbone, and by impeding the normal 'unzipping' degradation mode in PTFE. The  CF_2 bond apparently has a similar influence. The ester linkage between aromatic rings displays an outstanding stability, while ester links between aliphatic, and aliphatic and aromatic groups change stability in a rather complex manner on fluorination, but an increase in stability can be obtained by suitable choice of fluorination pattern.

Having examined briefly the available basis for predicting the service temperature range of a hypothetical polymer structure, it remains to derive from theory an idea of the structures which might be incorporated into a polymer to provide technologically useful materials.

Model Polymer Structures and Their Synthesis

In the last section, the enhancement of thermal stability of a polymer by fluorine substitution was emphasised, and it remains broadly true at present that it is in the field of fluorinated polymers that the main hope for advances in thermally stable solvent resistant elastomers resides. The application of the ATP approach to T_g prediction in this field has therefore been carried forward, and has already been referred to briefly. Certain conclusions emerge strikingly from this and earlier studies.[23,33] The effect of fluorine as a side-chain substituent is to cause a significant reduction in T_g, while in the main chain, fluorine substitution causes a progressive increase in the transition temperature, presumably due to steric interaction increasing chain rigidity. This effect may be offset by the incorporation of flexible groups into the chain with $—CF_2-O-CF_2—$ and  $-CF_2$ - linkages being very useful in this role. Although the ether group contributes to a lower T_g than a corresponding concentration of phenylene rings, a practical polymer might usefully incorporate a certain number of these hydrocarbon moieties as potential cross-linking sites, and because of their bulk they may be expected to have a disordering effect on the chain and therefore inhibit crystallisation. A meta-substitution pattern on the ring is to be preferred, both for minimising the tendency to crystallisation, and for obtaining the lowest T_g in the final polymer. A tentative model structure therefore emerges for a polymer which might be expected to satisfy the requirements which have been set out, and formula I below represents such an idealised structure:



I

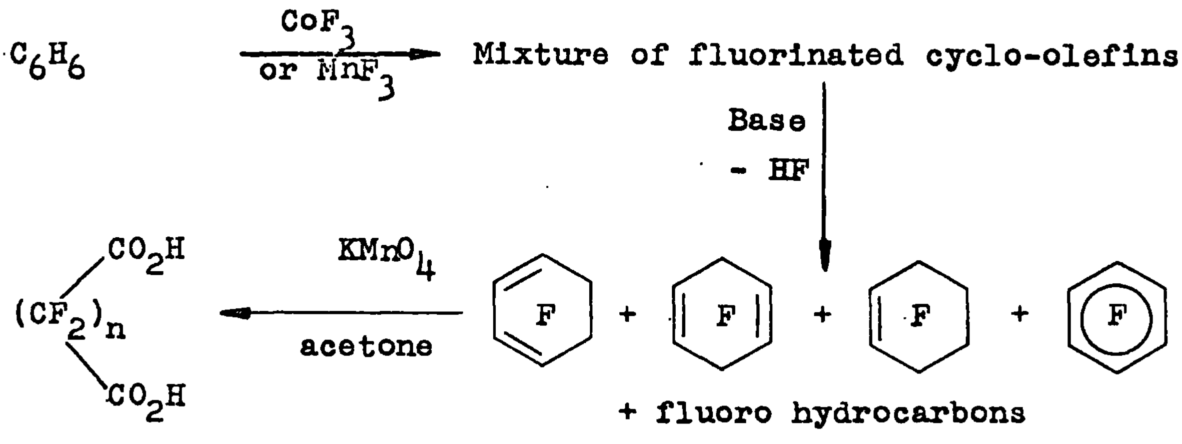
Unfortunately, the ideas of the model builders have outpaced the skill of synthetic organic chemists, and a successful synthesis of a high molecular weight polymer of structure I has yet to be devised. The next section will therefore be devoted to an examination of established reactions which might be of use in a synthetic approach to a structure similar to I.

Synthetic Routes to Perfluoroalkylene Oxide Polymers

The established reactions of highly fluorinated organic compounds allow a number of different approaches to be taken to the synthesis of polymer precursors containing fluorinated ether units. In the following section, the reactions are divided into three categories according to the nature of reactants and products.

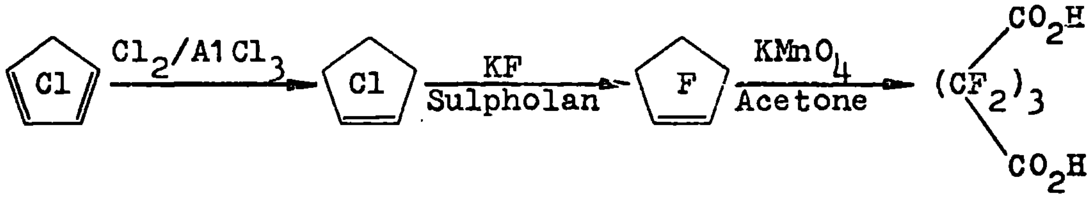
1. Synthesis of Bifunctional Fluorinated Compounds

The long established route to functional fluorocarbon derivates via fluorination of benzene remains a valuable synthetic method for preparation of difunctional C_3 - C_6 compounds, and this route is outlined in the flow chart below:

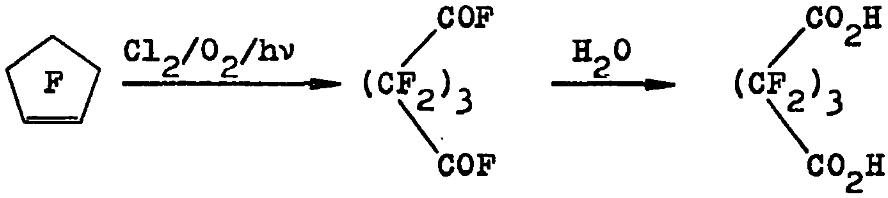


n = 1, 2, 4.

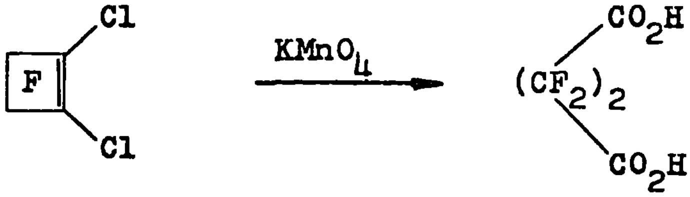
The remaining member of this series, hexafluoroglutaric acid, can be prepared from a commercially available chlorocarbon,[36] by the route summarised below:



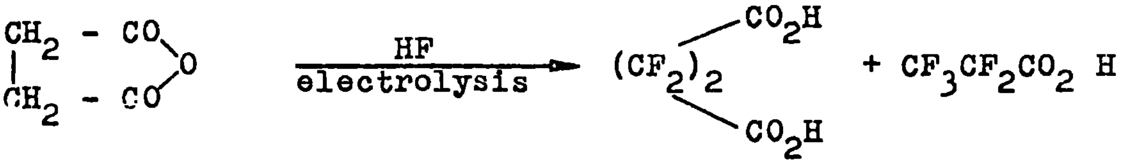
The final stage of this synthesis can also be performed by a photochemical oxidation[37] in the presence of chlorine as a photosensitiser:



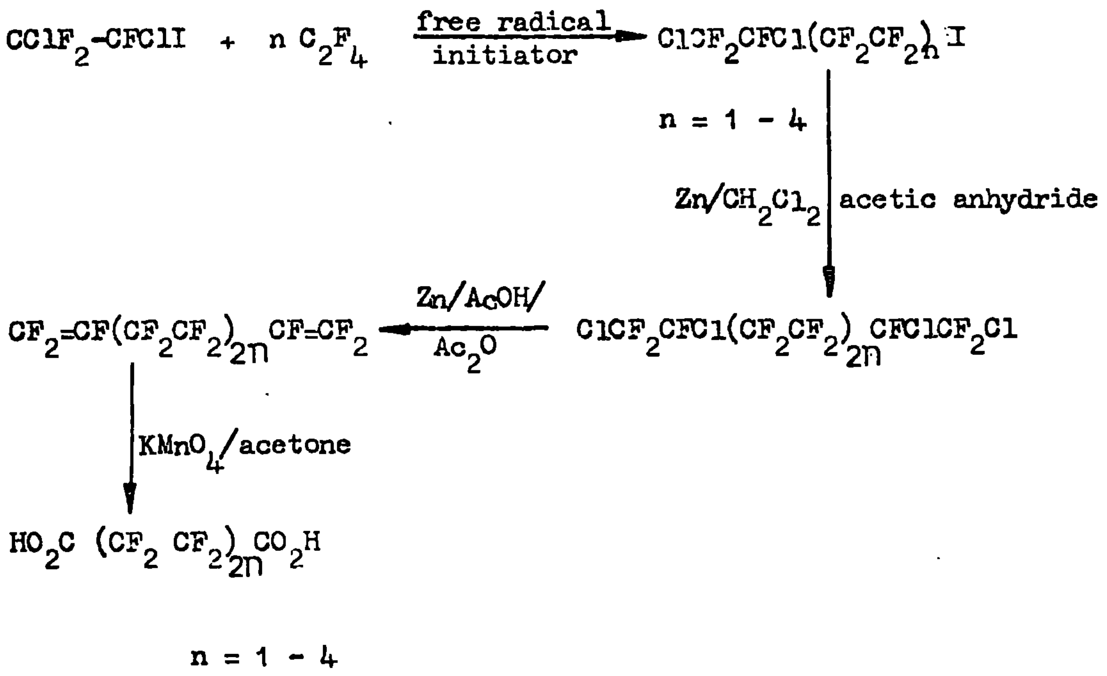
On a laboratory scale the permanganate oxidation reaction appears preferable, because of the wide variety of photochemical reactions into which fluorinated olefins may enter. It is usually claimed to be a general route to the fluorinated difunctional carboxylic acids, and may, for example, be applied to the synthesis of perfluoro succinic acid as shown below:



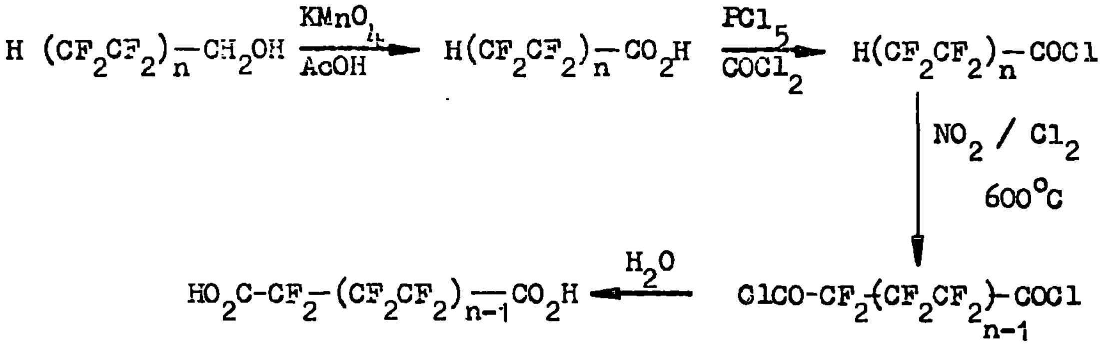
The fluorinated dicarboxylic acids may also be prepared by electrochemical fluorination,[38] for example:



An alternative synthesis beginning with the telomerisation of tetrafluoroethylene[39] is summarized below:

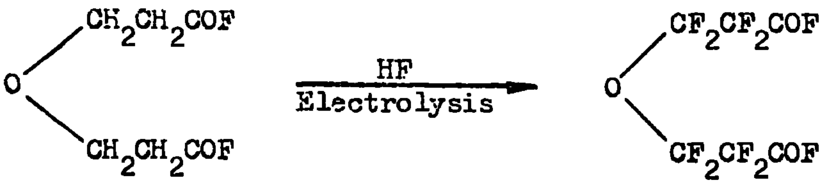


This sequence provides a route to bifunctional acids having an even number of carbon atoms only. A synthesis of the odd numbered members of the series begins with the commercially available telomer alcohols:[40]

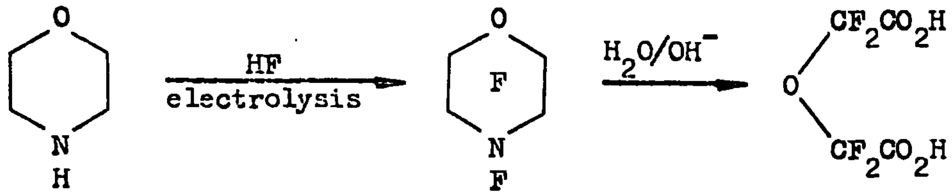


A few fluorinated dicarboxylic acids which contain ether groups have been synthesised:

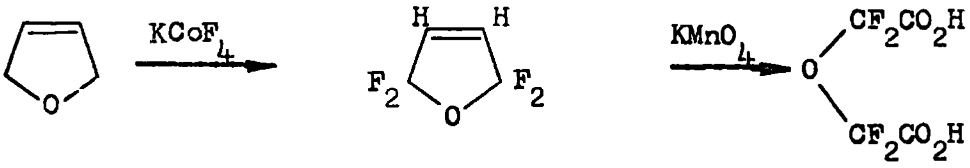
Ref.



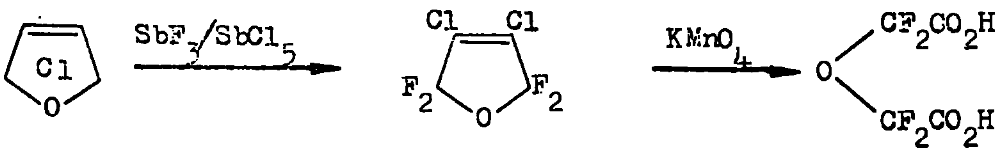
41



42



43



44,45

All the foregoing reactions have been shown leading to

Some Transformations of Fluorinated Carboxylic Acids

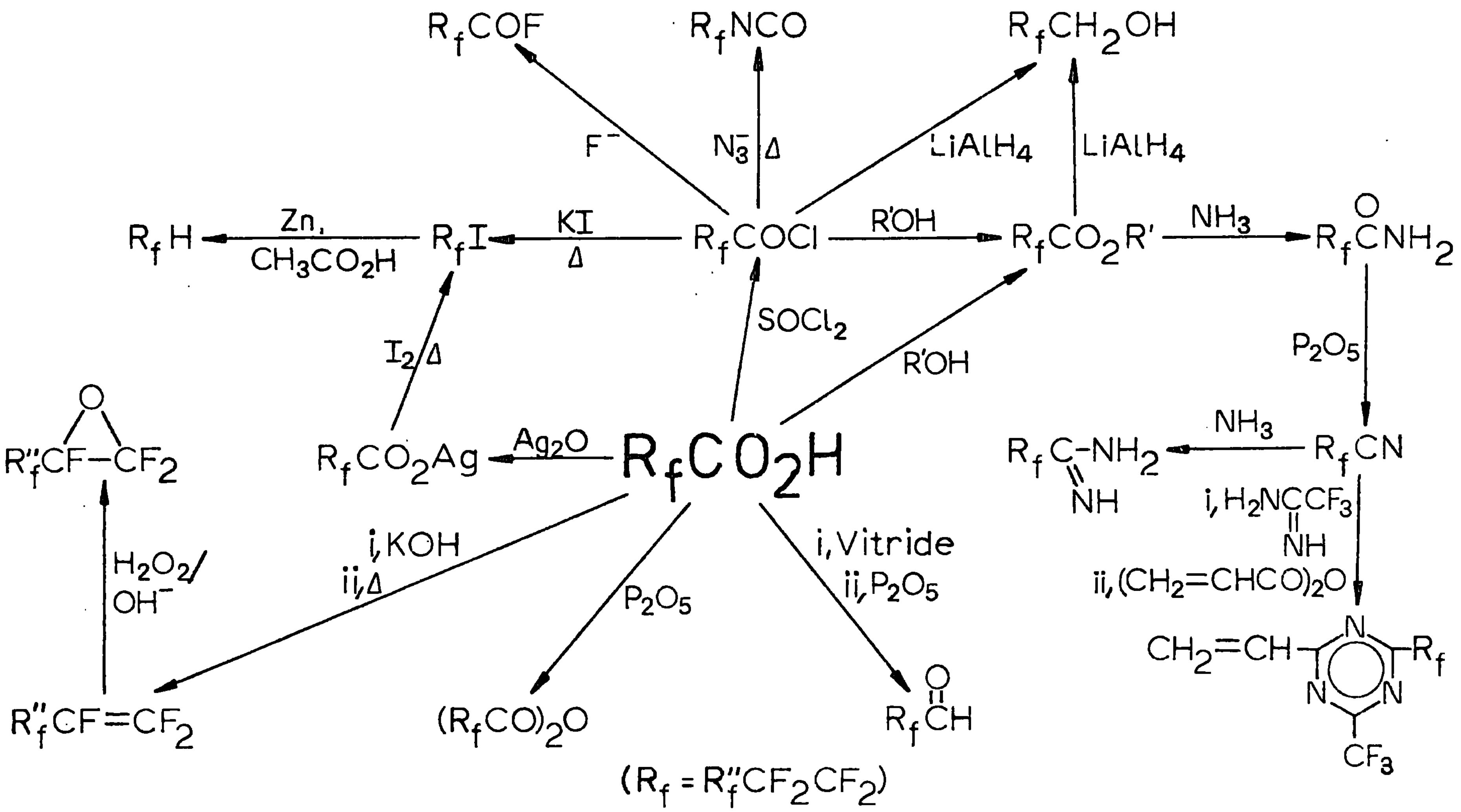


Figure 1.10

carboxylic acids although the intermediates encountered in the syntheses may be useful in certain cases. The emphasis on routes to the carboxylic acids is justified by the great variety of compounds which are readily derived from them; some of these transformations are shown diagrammatically in Figure 1.10.

It will be realised from the reactions shown above that a wide variety of derivatives can be prepared from reasonably accessible starting materials. The scheme above is not comprehensive, and in particular many groups containing hydrogen substituents are not included. It will be noticed that no reaction shown above allows incorporation of a perfluoro ether group, this group of reactions being dealt with in the next section on chain extension reactions.

2. Chain Extension Reactions

This section deals with reactions which increase the length of a fluorocarbon chain, but which have not at present been developed to the point where they can yield high molecular weight polymers. The coupling of perfluoroalkyl chains is commonly carried out by Henne's method:[46]

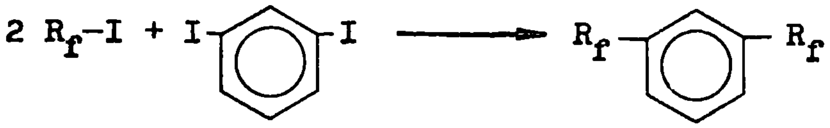
$$R_f\text{-}I \xrightarrow[CH_2Cl_2]{Zn/(CH_3CO)_2O} R_f\text{-}R_f$$

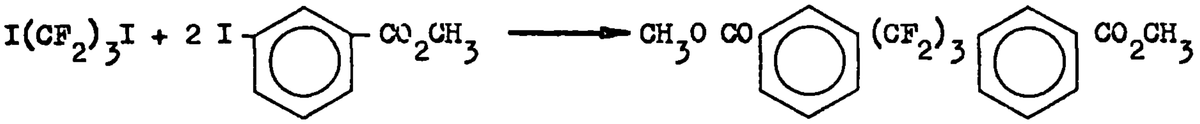
This reaction proceeds in high yield, the chief competing process being the reductive replacement of I by H, a chain terminating process in attempts to prepare polymers by coupling di-iodides.

A reaction involving the in situ generation of a perfluoroalkyl copper compound allows coupling of a fluorinated chain with an aryl iodide.[47]

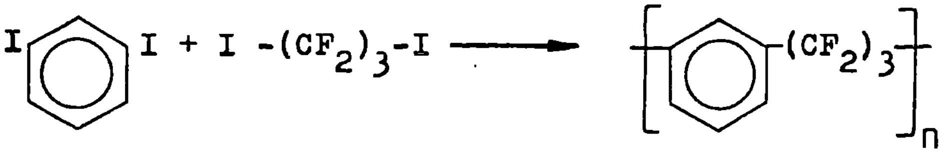
$$R_f\ I + I - Ar \xrightarrow[\text{Polar Aprotic Solvent}]{\text{Cu}} R_f - Ar$$

A wide variety of substituents can be tolerated on the aromatic group, and bifunctional compounds may also be used:





Compounds such as the last shown, referred to as 'dumbbell' compounds, have been explored as precursors to condensation polymers,[48,45] as they are reasonably easily prepared and show an obvious similarity to structure I. The coupling occurs in high yield in favourable cases, and an attempt has been made to prepare polymers by use of bifunctional fluoralkylene iodides and phenylene iodides,[49]



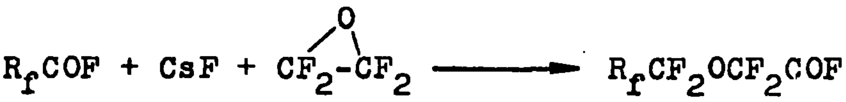
unfortunately the product was of only moderate molecular weight, due apparently, to reductive replacement of I by H.

The incorporation of ether groups into a fluorinated chain may be accomplished by a modified halohydrin reaction:[50]

$$R_fCOF + CsF + C_2F_4 + I_2 \longrightarrow R_fCF_2OCF_2CF_2I$$

Alkenes other than tetrafluoroethylene may be used to prepare a variety of functional fluorinated ethers, and modification of the products by means of a Grignard reaction to yield a terminal $-OCF_2CF_2CO_2H$ group has been described.[51]

A somewhat similar reaction may be carried out with a fluorinated epoxide taking the place of the alkene/ halogen combination.[52]

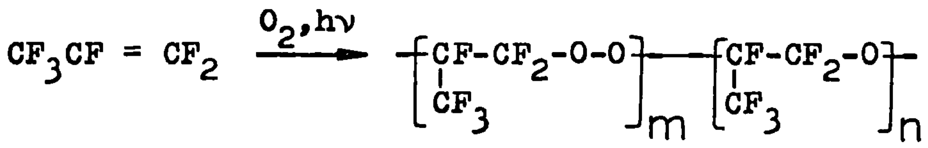


$$R_fCOF + CsF + \overset{O}{CF_2\text{-}CF_2} \longrightarrow R_fCF_2OCF_2COF$$

Again, a variety of epoxides may be used. It will be noted that the product of this reaction has the same functionality as one of the reactants, and in principal a polymer might be obtained by multiple addition of epoxide. In practise, a product of very high molecular weight cannot be obtained but several ether groups can be readily incorporated in one step, and cleanly bifunctional polymers of moderately high molecular weight can be obtained[53] by careful control of reaction conditions. These compounds show considerable promise as prepolymers for use in some of the polymer forming reactions mentioned in the next section.

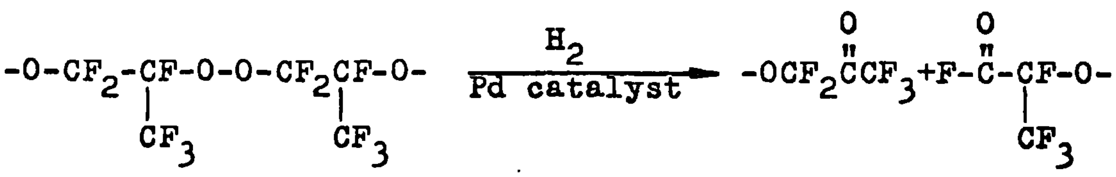
The last three reactions mentioned above are discussed in more detail later in this thesis.

The oxidation of fluorinated alkenes can under appropriate conditions be used for the synthesis of functional polyethers.[54] Oxidation in the liquid state in the presence of an inert diluent and under u.v. irradiation leads to a high molecular weight polyether containing a variable proportion of peroxide groups:



$$CF_3CF = CF_2 \xrightarrow{O_2,h\nu} -\left[\underset{CF_3}{CF}-CF_2-O-O\right]_m-\left[\underset{CF_3}{CF}-CF_2-O\right]_n-$$

By very careful regulation of conditions, the peroxide content of the product can be kept low, and these groups can be reductively split to yield bifunctional polyethers:



$$-O-CF_2-\underset{CF_3}{CF}-O-O-CF_2\underset{CF_3}{CF}-O- \xrightarrow[\text{Pd catalyst}]{H_2} -OCF_2\overset{O}{\overset{\|}{C}}CF_3+F-\overset{O}{\overset{\|}{C}}-\underset{CF_3}{CF}-O-$$

As the addition of alkenes proceeds chiefly in a head to tail manner, the ultimate product after reduction and hydrolysis is a mixture of oligomeric keto-acids. Similar results may be obtained from oxidation of alkenes other than hexafluoropropene. This reaction appears to have the potential of yielding a number of useful products. Its disadvantages lie in the sensitivity of the product composition to reaction conditions, and the hazard inherent in the handling of the dangerously explosive perfluoro peroxidic compounds.

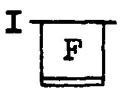
3. Polymer Forming Reactions of Functional Fluorocarbons

The coupling of bifunctional polyfluoro compounds to give high molecular weight polymers may be accomplished by at least three methods. Fluoroalkyl iodides may be coupled by irradiation with U.V. light in the presence of mercury:[31,55]

$$R_fI + IR_f' \xrightarrow{Hg,h\nu} R_f\text{-}R_f'$$

The radicals R_f and R_f' may be similar or different, and use of difunctional iodides allows polymer production.

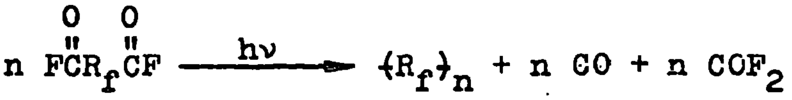
$$n\ ICF_2CF_2OCF_2CF_2I \xrightarrow{Hg,h\nu} \left[(CF_2)_4O\right]_n$$



$$+ I(CF_2)_2O(CF_2)_5O(CF_2)_2I \xrightarrow{Hg,h\nu}$$

$$-\left[(CF_2)_2-O-(CF_2)_5-O-(CF_2)_2\right]\left[\boxed{F}\right]_m\Big]_n-$$

The chief disadvantage of this polymerisation method is the use of high power U.V. lamps; the product is a reasonably linear polymer and incorporation of structures such as the last shown offers the promise of crosslinking to form a highly stable polymer. A somewhat similar reaction occurs on irradiation of acyl fluorides.[56,57]

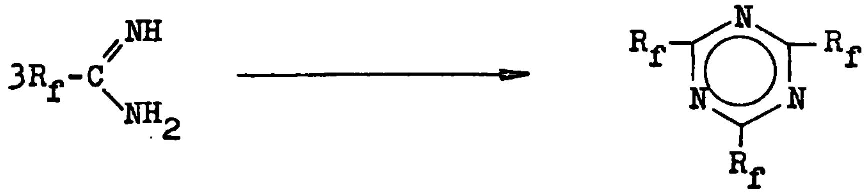

$$n\ F\overset{\overset{O}{\|}}{C}R_f\overset{\overset{O}{\|}}{C}F \xrightarrow{h\nu} \{R_f\}_n + n\ CO + n\ COF_2$$

The polymer in this case is crosslinked as a result of radical addition reactions at some of the carbonyl groups, and consequently insoluble. This reaction has also been used to couple low molecular weight compounds to a limited degree.[58] The liquid reactants are refluxed from a lower vessel, and the vapour passes into an irradiation space, where coupling occurs, before being condensed and returned. As the coupled products have a much lower volatility than the reactants, they are effectively retained in the lower flask, and polymer production is avoided. In this way, good yields of functional dimers may be obtained from fluorinated acyl fluorides. A crosslinked polymer may also be obtained by pyrolysis of the mercury salts of dicarboxylic acids:[59]

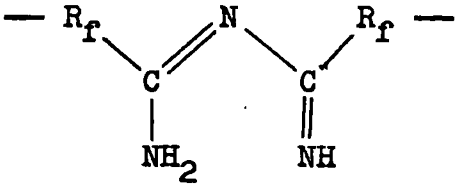
$$^{-}O_2C-R_f-CO_2{}^{-}Hg^{2+} \xrightarrow{400^\circ C} (R_f)_n + CO_2 + Hg$$

The perfluoroalkylene group may contain ether linkages, when the product is a tough elastomer. The products of the last three reactions show exceptional thermal stability and resistance to most reagents. The polymer from pyrolysis of the mercury salts is freed of metal by digestion with boiling concentrated nitric acid, and is unchanged after this treatment. Unfortunately, the product is insoluble and infusible.

The thermolysis of fluoroalkyl amidines yields a crosslinked polymer consisting of a network of triazine groups.[60]



This reaction has been the subject of considerable development work, and other routes to the triazine group have also been explored. By condensation of a bis nitrile with a bis amidine, a soluble polymer can be obtained, containing the structural units:



This polymer can be fabricated, then cured by reaction with a fluorocarbon nitrile to form the triazine structure.[61] Polymers of this type containing ether links in the fluoroalkylene chain ($-R_f-$, above) form rubbers of low T_g, providing encouraging parallels with polymers of structure I. However, doubts have been cast as to the hydrolytic stability of the triazine ring; and, in particular, structural weaknesses resulting from incomplete reaction have as yet prevented large scale exploitation of these initially promising materials.

A wide range of condensation reactions occur with functional fluorocarbons. In most cases, these parallel the reactions of the corresponding hydrocarbons. Methods have been published for the preparation of fluorinated polyesters, polyamides, polycarbonates, polyphosphates, polysulphones etc., and much of this work is covered in reviews, to which the reader is referred.[62,63] For the purposes of the present work, the polyesterification reaction was considered to show the most favourable characteristics of the various polymer-forming reactions. As has been seen, fluorinated polyesters of suitable structure have good thermal stability, and this condensation reaction is particularly well understood. The synthetic chemistry described in this thesis therefore has as its primary aim the preparation of ether containing, and highly fluorinated difunctional compounds, for use in polyesterification reactions. The various approaches taken to this problem are described in subsequent chapters.

CHAPTER 2

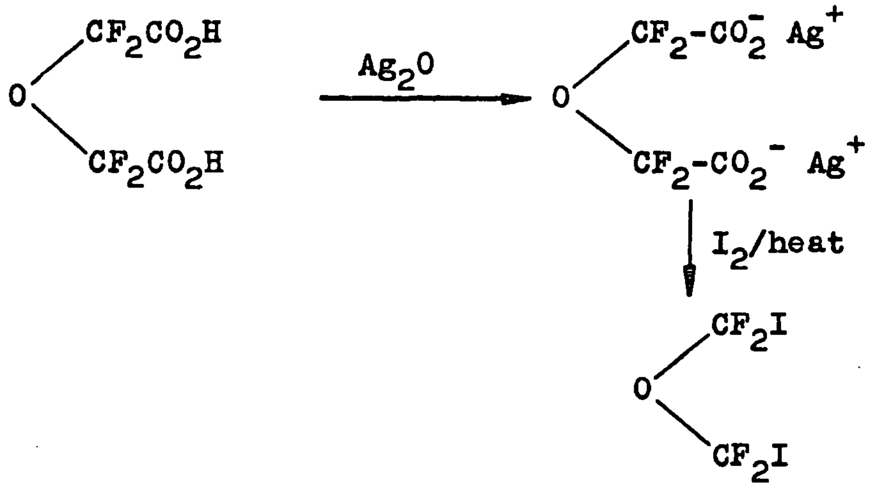
The Synthesis of Some m-Phenyleneperfluorooxyalkylene Type Monomers

Introduction

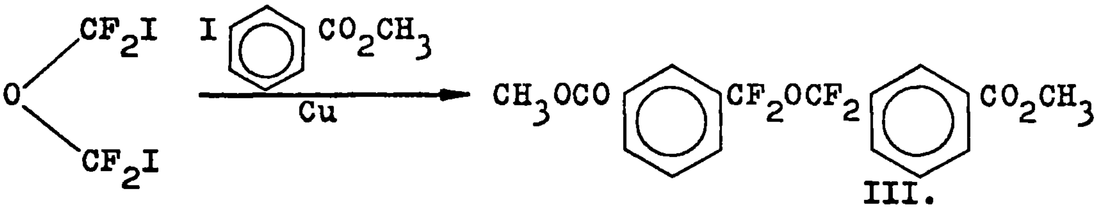
Approaches to Polymers of the m-Phenyleneperfluorooxyalkylene Type

In order to set in context the work described in this thesis, this section will be devoted to a brief review of synthetic approaches to polymers of structure I, which have been explored by previous researchers on this project. This review will also provide much of the background necessary for discussion of the work described later in this chapter.

According to the principles described in Chapter 1, whereby the T_g of a novel polymer may be related to its chemical structure, an early priority of workers on this project was the preparation of fluorinated difunctional ethers. The route initially chosen[45] from the known compound perfluorooxydiacetic acid is outlined below:-

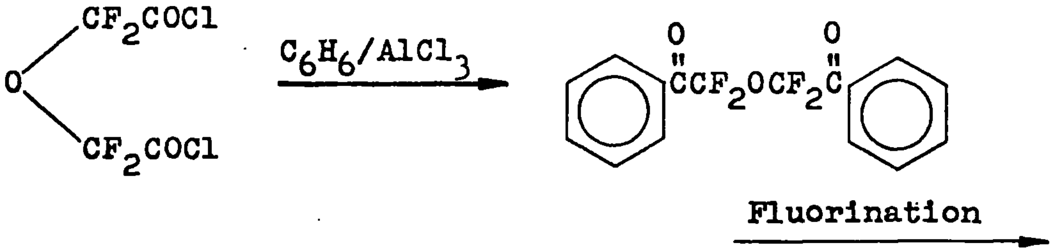


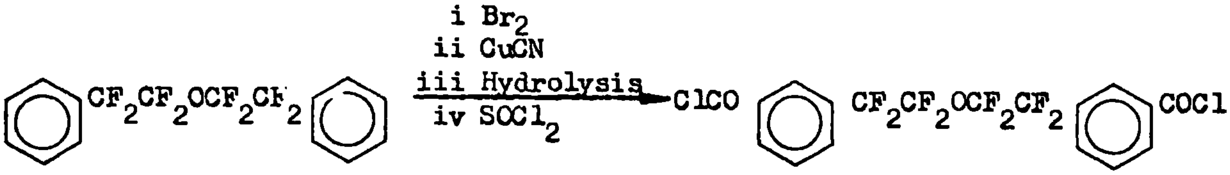
II.


III.

Unfortunately, the envisaged decarboxylation of silver perfluorooxydiacetate did not proceed smoothly, the only products isolated being formed by fragmentation of the molecule. The reaction of perfluorooxydiacetyl chloride with potassium iodide was also explored as a potential route to the di-iodide II, but a similar fragmentation reaction occurred, and none of the desired product could be isolated. In view of the fact that the bis-piperidinium salt of perfluorooxydiacetic acid did decarboxylate on heating to yield sym-tetrafluorodimethyl ether, HCF_2OCF_2H, it would appear that the failure to prepare II is a consequence of the detailed nature of the transition state of the decarboxylation reaction, rather than any inherent instability of the CF_2 - 0 bond.

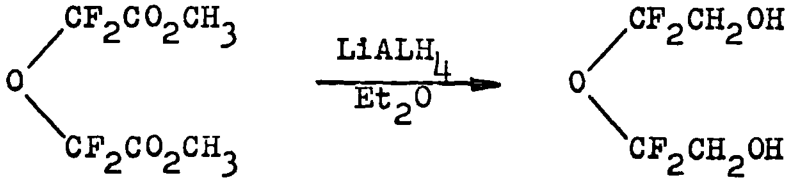
An alternative route to a useful polymer precursor was envisaged through a Friedel-Crafts reaction of perfluorooxydiacetyl chloride.



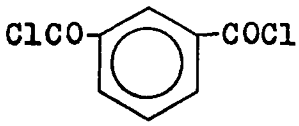


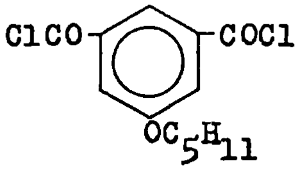
In practise, it was found that the first step of this sequence, the Friedel-Crafts acylation, resulted in extensive decomposition, and isolation of the desired product could not be achieved. It is perhaps significant that although the analogous reaction using perfluoroglutaryl chloride is known,[64] its success is highly dependent on the regulation of the reaction temperature within a very narrow range (<u>ca</u>.2°).

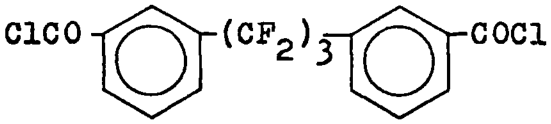
The disappointing results obtained from the reactions described above, each of which has been performed successfully on the analogous system perfluoroglutaric acid, led to the conclusion that the ether link in perfluorooxydiacetic acid derivatives leads to a significant change in the energetics of reaction transition states. However, the reduction of the methyl ester of this acid led to the production of 2,2,4,4,-tetrafluoro-3-oxapentane-1,5-diol in good yield.



and this diol was successfully incorporated into polymers[27] by reaction with the m-phenylene based dicarboxylic acid chlorides shown below:

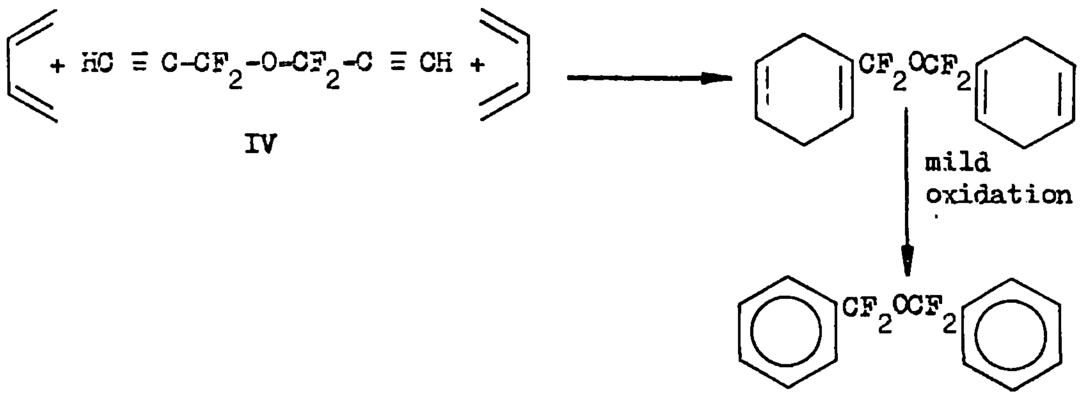




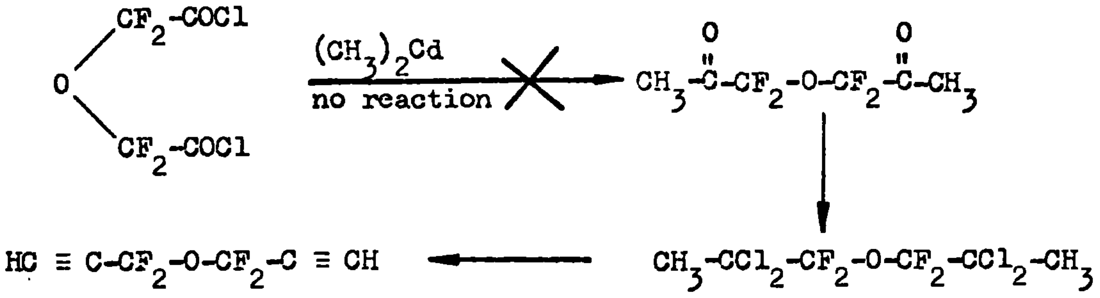


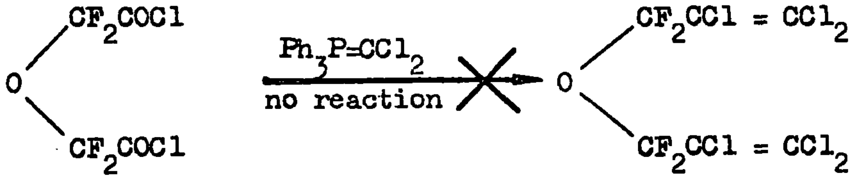
These polymers were compared with those derived from 2,2,3,3,4,4-hexafluoropentanediol, and showed in each case a slightly higher T_g and lower thermal stability than polymers lacking the fluorinated ether link. Although these results did not bear out the anticipated effects of incorporation of an oxygen atom into a fluorinated alkylene chain, it was felt that they were a reflection of the detailed environment of the functional group and did not negate the general principles discussed in Chapter 1.

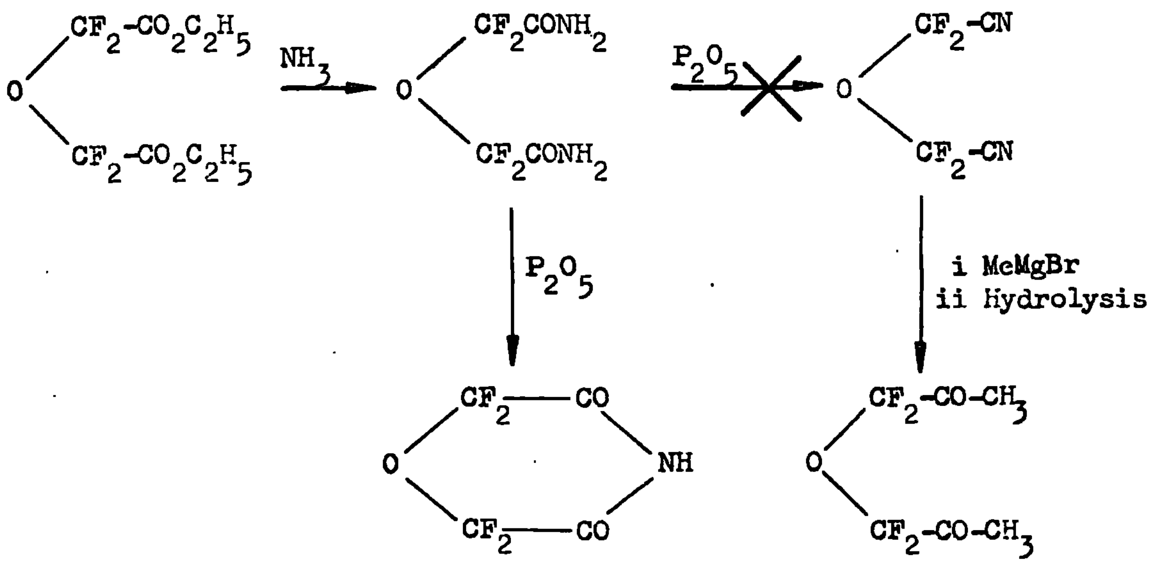
It remains, for completeness, to mention in conjunction with this work, a further attempt to prepare compound III, the chemistry of which is not so directly related to the work described in this thesis. The key reaction in this attempt was a Diels-Alder addition of a partially fluorinated di-yne:


IV

Several attempts were made to synthesise the di-acetylene IV, and these are summarised in the reaction schemes below:

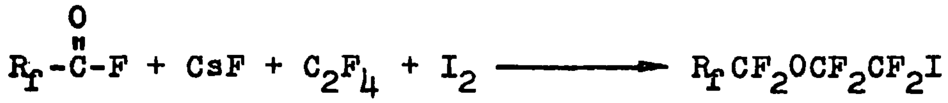






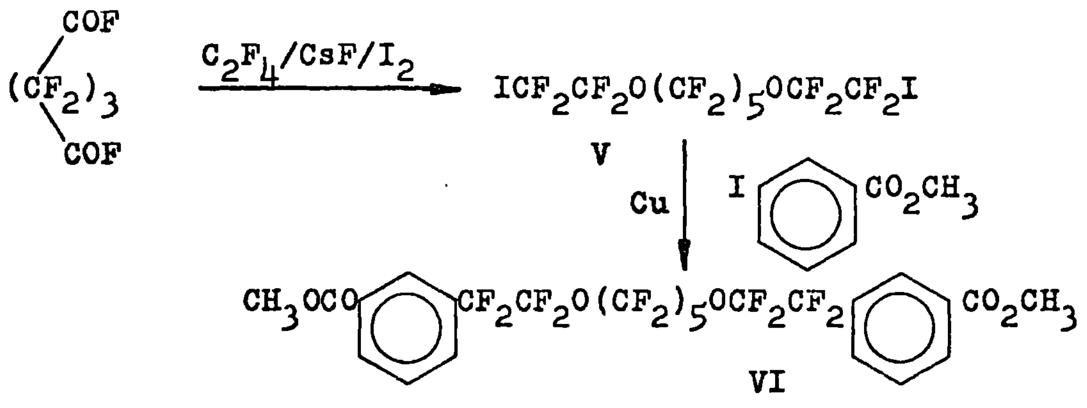
These sequences each failed at the point shown, and compound IV could not be prepared. It had become clear at this point that the reactions of these fluorocarbon derivatives do not, in general, correspond to those of simpler model systems, and in particular that the manipulation of functional groups adjacent to a $-OCF_2-$ linkage leads to peculiar difficulties with regard to the stability of reactive intermediates. At the same time, it was considered that the basic ideas regarding ideal polymer structures still held, and that research should continue to be directed to synthetic approaches to polymers resembling structure I as closely as possible.

The reaction of a perfluoroacyl fluoride with a halogen and tetrafluoroethylene has already been referred to in Chapter 1:



$$R_f-\overset{\overset{O}{\|}}{C}-F + CsF + C_2F_4 + I_2 \longrightarrow R_fCF_2OCF_2CF_2I$$

As the product of this reaction is a functional ether in which two fluorinated methylene groups separate the oxygen link from the reactive site, it seemed reasonable to hope that the reactions of such compounds should be free from the degradations and side reactions which had prevented the success of the earlier work. Accordingly, it was decided to investigate this reaction, as applied to a bifunctional carboxylic acid fluoride. The product should be an ether-containing di-iodide which could be used in the copper coupling reaction mentioned previously. The envisaged reaction scheme therefore became:



V

VI

It was found[65] that the first of these reactions yielded the required di-iodide as a minor product, the principal product after work-up being the acid-iodide:

$$\mathrm{ICF_2CF_2O(CF_2)_4CO_2H}$$

VII

this being the product of reaction at only one acyl fluoride group of the starting material. This material, after esterification with diazomethane, was utilised in the following reaction scheme:

$$\mathrm{CH_3OCO(CF_2)_4OCF_2CF_2I} \xrightarrow{\mathrm{Zn/Ac_2O/CH_2Cl_2}} \mathrm{CH_3OCO(CF_2)_4O(CF_2)_4O(CF_2)_4CO_2CH_3}$$

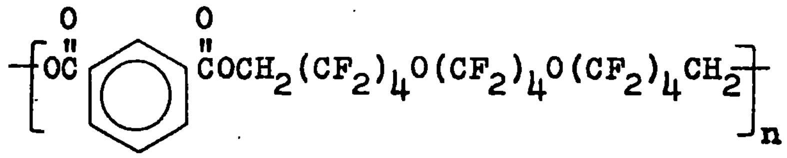
$$\xrightarrow{\mathrm{LiAlH_4}} \mathrm{HOCH_2(CF_2)_4O(CF_2)_4O(CF_2)_4CH_2OH}$$

VIII

A similar reaction sequence has been investigated more recently by American workers.[66]

The ether di-iodide (V) could be obtained in fair yield by use of an excess of caesium fluoride and iodine, and enough material was accumulated to allow investigation of the copper coupling reaction with m-iodomethyl benzoate. This reaction proceeded in poor yield, and insufficient time and materials were available to optimise this reaction, or to prepare sufficient of the product to allow investigation of the incorporation of such compounds into a polymer.

The diol (VIII) was incorporated into a polymer by means of a polycondensation reaction with isophthaloyl chloride to yield the polyester



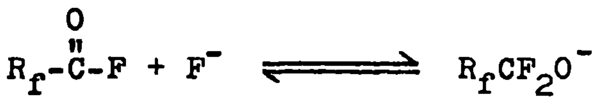
This polymer, as initially obtained, was a tough elastomer displaying an encouragingly low T_g of 259 K, and a good resistance to swelling by hydrocarbon solvents. However, probably as a consequence of the structural regularity of the incorporated diol unit, this polymer crystallised slowly at room temperature to give an opaque, leathery material. It was felt on this basis that the conceived relationships between polymer structure and physical properties, which were discussed in Chapter 1, had been given some support, and that polymers of this type, having less structural regularity than (~~IIX~~ VIII), merited further investigation. In view of the established synthetic route to (VI), it was decided to develop the reactions involved in this sequence, and to attempt the incorporation of this compound as a structural unit in a condensation polymer. The work involved in this attempt is described in the second section of this chapter.

Discussion

The Preparation of Octadecafluoro-1,11-diiodo-3,9-dioxaundecane (V)

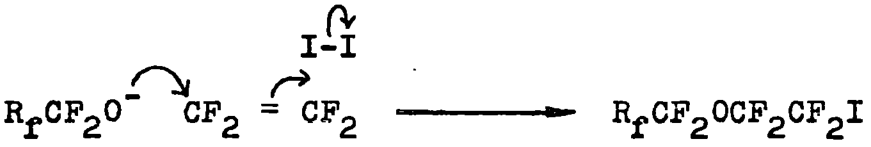
The reaction of perfluoroglutaryl fluoride with tetrafluoroethylene (TFE) and iodine in the presence of caesium fluoride had been investigated in earlier work on this project, as previously mentioned, and it had been shown to be a practical route to V, although the yield was uniformly low over a series of preparations. Published accounts of this reaction are confined to a mention of the product in the patent literature,[67,68] and to a contract research report[56] which came to hand while this work was in progress. However, in the corresponding reaction of monofunctional acyl fluorides, yields are reported to be good, but with low conversions to the desired products.[50]

It has been proposed that this reaction proceeds via the initial formation of a caesium perfluoroalkoxide, species which are known to exist in acyl fluoride/caesium fluoride solutions.[69,70]



$$R_f\text{-}\overset{\overset{O}{\|}}{C}\text{-}F + F^- \rightleftharpoons R_fCF_2O^-$$

This perfluoroalkoxide is too weak a nucleophile to attack a fluorinated alkene, and earlier workers have suggested that tetrafluoroethylene forms a complex with iodine which is more susceptible to attack. This proposed mechanism can be summarised as follows:-



$$R_fCF_2O^-\ CF_2 = CF_2 \quad \overset{I-I}{} \longrightarrow R_fCF_2OCF_2CF_2I$$

A possible alternative is the initial formation of a perfluoralkyl hypoiodite, and its subsequent addition to TFE:-

$$R_fCF_2O^- + I_2 \rightleftharpoons R_fCF_2OI + I^-$$

$$R_fCF_2OI + CF_2{=}CF_2 \longrightarrow R_fCF_2OCF_2CF_2I$$

However, such species have neither been isolated nor detected spectroscopically and may be expected to be rather unstable. Because of the intermediacy of perfluoroalkoxide species in either of these mechanisms, it is essential to carry out the reaction in a medium which favours formation of these ionic compounds, and a polar aprotic solvent is therefore chosen. Earlier work had indicated that diglyme was particularly favourable in this respect. Accordingly, a reaction was initially run in this solvent as a repeat of the earlier work. Similar results were obtained, the product consisting of a mixture of V and VII.

The principal features of this reaction scheme as described in the literature consisted of initially mixing the acyl fluoride, caesium fluoride and solvent, then adding the iodine and tetrafluoroethylene when alkoxide formation was complete. The practical procedure by which this was accomplished was cumbersome however, due to the necessity of adding a solid to the alkoxide solution without admitting moisture. Accordingly, the effect of mixing the iodine with the other reagents at the beginning of the reaction was investigated, and it was found that no deterioration of yield accompanied this change. At this stage in the work a report[56] of research on this reaction by an American group became available. These workers claimed a substantial increase in yield from the reaction following a change in procedure similar to that described above, and they also used a variety of solvent systems. In an attempt to gain the benefit of these reported improvements in the manipulation of this reaction, an experiment using acetonitrile as solvent was carried out. The result was disappointing, the yield being even lower than that obtained previously when diglyme was used. It should be noted that there are several differences between our procedure and that of the American workers.

Thus, not only was the solvent system varied in the American work, but tetrafluoroethylene was added under pressure, and both iodine and iodine monochloride were used as iodine sources. It was not possible to imitate all the modifications introduced by these workers, partly because of the hazard inherent in handling monomers above atmospheric pressure and lack of suitable equipment, and partly because of the competitive addition of iodine monochloride to tetrafluoroethylene. In subsequent reactions, therefore, a return to diglyme solvent was made and every precaution was taken to prevent moisture entering the system. This was found to give some increase in the yield of the iodo-acid (VII) while the yield of di-iodide (V) was unaffected. A competing reaction in this synthesis is the removal of halogen from the system by formation of polyiodide ions. This may be expected to have a significant effect on the reaction if the complex into which the halogen is initially combined is rather weakly bound. An excess of iodine is therefore desirable in these reactions. In view of the claim made in the original paper on the reaction, that formation of the product occurs in high yield but low conversion, an attempt was made to recover unreacted perfluoroglutaryl fluoride, but none could be obtained by distillation or vacuum transfer of volatile materials. Any of this compound retained in the reaction mixture would be hydrolysed and lost in the work up.

Preparative Reactions of Di-Iodide (V) and Iodo-Acid (VII)

	Reagents Used				Yield		Total Product Recovery
Reaction	CsF	HFGF	Solvent[a]	I_2	Di-iodide (V)	Iodo-Acid (VII)	
1[b]	18 gm	14 gm	40 ml	30 gm	6.3 gm 14.9%	4.9 gm 17.5%	32.4%
2	18 gm	14 gm	40 ml	30 gm	12.7 gm 30.1%	3.9 gm 13.9%	44.0%
3	35 gm	27 gm	80 ml	65 gm	18.2 gm 22.3%	20.6 gm 38.1%	60.4%
4	75 gm	56 gm	160 ml	150 gm	32.0 gm 18.9%	27.2 gm 24.3%	43.2%
5	56 gm	48 gm	160 ml	150 gm	19.0 gm 13.1%	17.2 gm 17.9%	31.0%
6	80 gm	56 gm	150 ml	170 gm	36.0 gm 21.3%	43.1 gm 38.5%	59.8%

Notes

a. The solvent in each reaction was diglyme, except in reaction 5, where acetonitrile was used.

b. Practical procedure I was used in reaction I; thereafter method II was used.

Table 2.1

The work carried out on this reaction had led to a modest increase in yield, and a considerable simplification of the practical procedure but no obvious approach to a further improvement of the reaction presented itself. Since the principal object of the work was the accumulation of material for later use, a further preparative reaction was carried out making use of the improvements which had been made. The results of all these reactions are summarised in Table 2.1.

The Preparation of Octadecafluoro-3,9-dioxa-1,11-bis-(3-methoxycarbonylphenyl) undecane (VI)

The work described in the last section had led to the accumulation of *ca.*120g of the di-iodide (V), and attention was therefore turned to its use as an intermediate in the synthesis of the diester (VI). The reaction to be used for this transformation was the copper coupling route[47] referred to in Chapter 1, which proceeds via a perfluoroalkyl copper intermediate.

$$R_fI \xrightarrow{Cu} R_f{-}Cu \xrightarrow{ArI} R_f - Ar$$

The reaction is carried out in a polar solvent, and in the absence of oxygen; although the perfluoroalkyl copper compounds are remarkably hydrolytically stable, optimum yields are normally obtained in dry aprotic solvents. The scope of this reaction is confined to highly fluorinated alkyl halides, and the iodides give considerably better yields than the corresponding bromides or chlorides. Similarly, an aryl iodide is superior to other aryl halides. The reaction may be applied to bifunctional fluoroalkyl or aryl iodides to give good yields of bis-coupled products in favourable cases, although the reaction fails when applied to 1,2-diiodotetrafluoroethane when tetrafluoroethylene is the major product. The reaction similarly fails with dibromodifluoromethane.

A wide variety of functional groups can be tolerated on either halide without adversely affecting the yield, and this is true even of substituents containing active protons. Yields are generally of the order of 60%, but several systems have been observed to give anomolously high or low yields, without immediately obvious explanations. The preferred solvent for the reaction is dimethylsulphoxide (DMSO), although many polar aprotic solvents have been used successfully. Reaction times of several hours at a temperature of 100^{o} - 150^{o}C are employed. Above this temperature thermolysis of the fluoroalkyl copper intermediate becomes more significant, and side reactions involving proton abstraction from the solvent or from the aryl iodide are observed. A further refinement in this reaction, developed while seeking a direct route to polymers of the m-phenyleneperfluoroalkylene type, consists in adding a chelating agent to the system. This apparently stabilises the copper species in solution, and in some cases has permitted quantitative yields to be obtained from the reaction.

Prior to the present work, an attempt to carry out the copper coupling reaction between the di-iodide V and m-iodo methyl benzoate had resulted in a very poor yield of product (10 - 20%) and both starting materials had been destroyed in the reaction. Reduction of the aryl iodide to methyl benzoate was a significant competitive reaction, but no by-product of the fluorinated iodide was identified. The product was purified by column chromatography, but only a small quantity could be obtained in the time available.

Initial experience with the reaction in this particular system confirmed these results; the product consisted of a bright green sticky oil containing some fine suspended solid. Column chromatography on this material yielded a small quantity of yellow oil, as well as forefractions containing methyl benzoate and m-iodo methyl benzoate. The yield from the reaction was evidently small, and considerable reduction was taking place. A reaction was therefore carried out, making use of improvements developed by workers at R.A.E. Farnborough, who had shown that the use of an inert co-solvent and $2,2^1$-bipyridyl[71] as a chelating agent led to a very efficient reaction. Accordingly, benzotrifluoride and bipyridyl were added to a reaction, which was otherwise carried out and worked up as before. The product washed from the column, however, now consisted of a very small quantity of brown sticky material, the mass spectrum of which was inconsistent with the desired product, although the infra-red spectrum was similar to that of an authentic sample. Insufficient material was available for further characterisation. The only other substance obtained from the column was m-iodo methyl benzoate.

It was apparent at this point that the copper coupling reaction was not taking its usual straightforward course. A series of small scale reactions were therefore run to try to optimise conditions for the synthesis. The course of each reaction was monitored by analytical gas chromatography. It was found that the di-iodide starting material was consumed steadily under all conditions examined, and very rapidly at high temperatures. Ullman coupling of the aryl iodide was significant at high temperatures, and reductive dehalogenation occurred. A large number of products were formed in low yield, but the chief high-boiling product was different, according to whether or not $2,2^1$-bipyridyl was added. When pyridine was used as solvent, an obvious exotherm was observed which caused the solvent to boil, but the products formed were similar to those obtained when other solvents were used. No di-iodide remained at the end of any reaction. The series of reactions showed that there was no likelihood of an improved yield being obtained by changing temperature, solvent, the relative proportion of reactants, or their rate or order of addition. The general procedure employed in the reaction, and the suitability of solvents and reagents were tested by the preparation of methyl 3-perfluoroheptylbenzoate from methyl 3-iodobenzoate and perfluoroheptyl iodide under the same reaction conditions. Although the product was obtained in only moderate yield (55%), unreacted fluorocarbon iodide was identified in the reaction mixture, and the yield based on consumed starting material was virtually quantitative.

Despite the results described above, it was decided to commit the remaining di-iodide (V) to attempts to produce the di-ester (VI), albeit in low yield, rather than any further investigation of the reaction. Two further reactions were therefore performed, using 20g and 50g of di-iodide respectively, and the products combined. The green oil which was isolated from the reaction mixture was degassed, and purified by molecular distillation at 200°C/10^{-3} torr. Some material was carried over by splashing, but the distillation was repeated to yield a total of 11·3g of yellow oil, identified by NMR, IR, and mass spectroscopy as the di-ester VI. A summary of reactions carried out is presented in Table 2.2

The reason for the anomalously low yield of coupling product obtained in this reaction must lie in

Copper Coupling Reactions

No.	Method	Solvent	Di-iodide (V)	Iodo-acid (VII)	Copper	Temp.
1	a	20 ml. D.M.S.O.	5 gm.	10 gm.	4 gm.	80°C
2	a	15 ml. Benzotrifluoride. 3 ml. D.M.S.O.	5 gm.	7 gm.	3·6 gm.	Reflux
3	b	4 ml. D.M.S.O.	·73 gm.	·61 gm.	·3 gm.	85°C
4	b	2 ml. D.M.S.O.	·46 gm.	·3 gm.	·2 gm.	130°C
5	b	5 ml. D.M.S.O.	·7 gm.	2 gm.	1 gm.	70°C
6	b	4 ml. D.M.S.O.	·7 gm.	0	·3 gm.	85°C
7	b	4 ml. D.M.S.O.	0	·6 gm.	·3 gm.	85°C
8	b	2 ml. D.M.S.O.	·4 gm.	·3 gm.	·2 gm.	100°C
9	b	2 ml. D.M.F.	·4 gm.	·3 gm.	·2 gm.	100°C
10	b	2 ml. pyridine	·4 gm.	·3 gm.	·2 gm.	Reflux
11	b	2 ml. pyridine	·4 gm.	·3 gm.	·2 gm.	70°C
12	c	100 ml. D.M.S.O.	20 gm.	45 gm.	15 gm.	80°C
13	c	30 ml. D.M.S.O.	10 gm. $C_7F_{15}I$	7 gm.	4 gm.	90°C
14	c	140 ml. D.M.S.O.	50 gm.	100 gm.	35 gm.	70-110°C

Reactions 2, 3 and 5 contained 100, 60 and 60 mg. of 2,2'-bipyridyl respectively. In reaction 4, the di-iodide was added slowly to the other reactants, which were already at reaction temperature. In reaction 11, a similar procedure was adopted with the copper bronze.

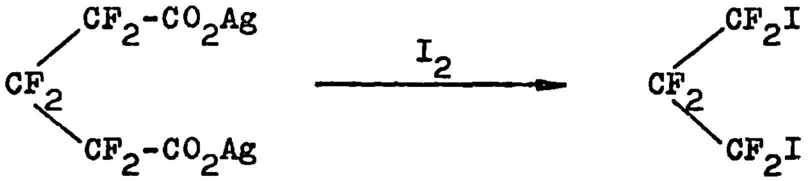
Table 2.2

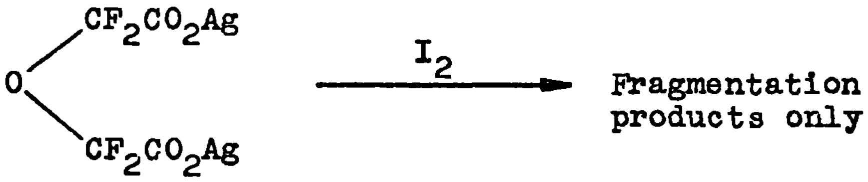
the effect of the oxygen link situated β to the reactive centre. Although the analogy may be drawn between this compound and the 1,2-dihalotetrafluoroethanes, which also fail to afford good yields, the effect must be different, since the latter class of compounds evolve tetrafluoroethylene under the reaction conditions used. In the 50g scale reaction, some evidence of gas evolution was seen, but the amount was exceedingly small, and the rate of evolution very low; an attempt to trap this gas gave a trace of condensate, but a satisfactory analysis was not possible. However, the 1,2-elimination reaction does appear to be significant, since American workers using the same di-iodide in an analogous copper coupling reaction have identified the alkene

$$CF_2 = CF\text{-}O(CF_2)_5OCF_2CF_2H$$

as a major product.[72] It appears that the ether group has changed the charge density on the adjacent carbon atom sufficiently to make elimination energetically favourable. The fluoride elimination is presumably favoured because of the relative instability of perfluoro alkoxides, even of alkali metals.

The difficulty encountered in this reaction emphasises the uncertainty inherent in extrapolating results even from apparently closely related systems in this field of chemistry. The introduction of ether links into an α,ω-diiodoperfluoroalkane could not be anticipated to cause problems in this reaction, bearing in mind the chemical stability of the bonds involved. A parallel may be seen, however, with the attempted decarboxylation of perfluorooxydiacetic acid already referred to:

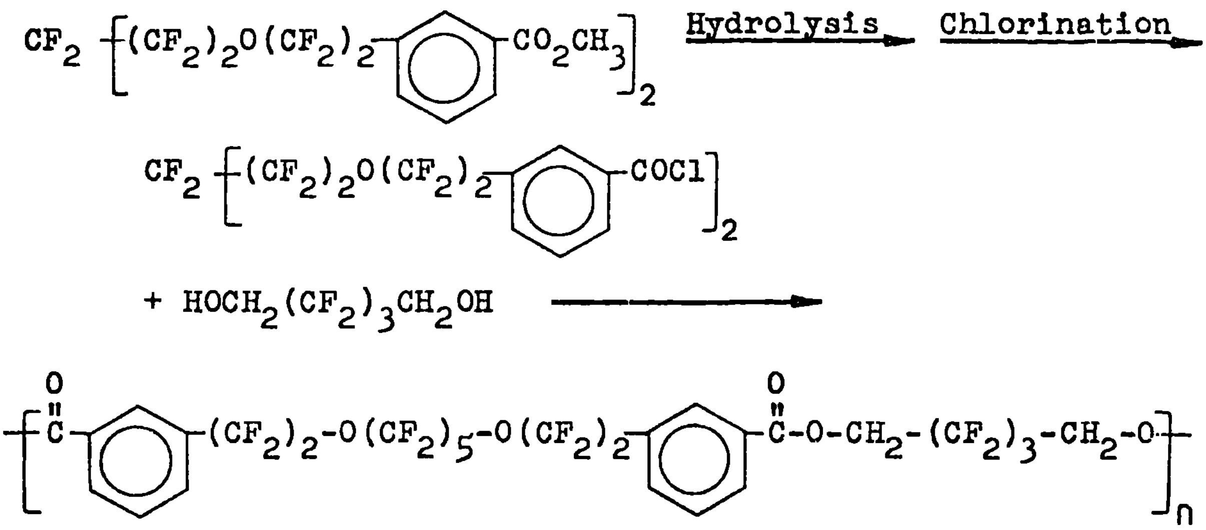




In this case, however, the substitution lies α-to a reacting centre, and the route to the major products, carbonyl fluoride and difluorocarbene, may be more readily envisaged.

Attempted Preparation and Polymerisation of Octadecafluoro-3,9-dioxa-1,11-bis (3-chlorocarbonyl phenyl) undecane

The work described up to this point had led to the production of some 11g of the diester VI. The projected use of this compound was to be as follows:



The final stage of this reaction sequence comprises a condensation polymerisation of a bifunctional acid chloride with a diol, and a discussion of the requirements of this type of reaction will be given later in this thesis. However, a prime condition for the success of such a reaction is a high standard of purity for each monomer. The diester obtained from the work described was a highly viscous yellow oil, which showed no tendency to crystallise on cooling. Although the material could be distilled, the extremely low pressure necessary made fractionation out of the question. However, repeated distillation of the material under these conditions was used to ensure removal of impurities of markedly different volatility. Chromatographic purification of the material was considered, but preparative scale g.l.c. was ruled out by the involatile nature of the material. Attempted purification by column chromatography of material from early preparative runs had yielded an incompletely refined product. The problem of final purification was therefore unresolved, and it was reluctantly decided to commit the ester to further reaction while it still showed traces (2 - 3%) of contamination on analytical GLC.

The hydrolysis of VI was hampered by failure to find a suitable medium in which the ester was reasonably soluble. An attempt was initially made using aqueous ethanolic potassium hydroxide solution, but after refluxing 24 hours in this medium, the material appeared unchanged, and no acidic component separated on neutralisation of a portion of the ethanolic layer with hydrochloric acid. The ester was therefore recovered by ether extraction, and an aqueous ethanolic solution of hydrochloric acid substituted as the hydrolytic reagent. Refluxing overnight led to some apparent reaction, and the hydrolysis was continued for a further 24 hours. After this time, ether extraction and evaporation of the solvent yielded an extremely viscous, dark-coloured, and sticky material, which after removal of volatiles was used in a chlorination reaction without attempting purification. Chlorination was attempted using thionyl chloride in large excess, and the mixture was refluxed until evolution of gas ceased. Excess thionyl chloride was distilled from the reaction mixture, the last traces being removed by pumping under vacuum (10^{-3} torr). The dark-coloured involatile residue was refined by molecular distillation, ($190^{o}/10^{-3}$ torr), a process which was repeated to yield a light yellow viscous oil.

The technique of conducting condensation polymerisations between bifunctional acid chlorides and diols is reserved for discussion in Chapter 4 of this thesis, and will therefore not be presented here. As a result of the work described, a quantity of 2.4g of yellow oil, tentatively identified as the desired di-acid chloride, was available for polymer synthesis. It was decided to react this with hexafluoropentane diol. Accordingly, a polymerisation reaction was performed on carefully measured equimolar quantities of these two compounds. The expected evolution of gas was observed, but when the temperature of the reaction was raised, a white solid, presumably hexafluoropentane diol, was observed subliming from the mixture. The sublimate was returned to the reaction by melting and scraping, but no further reaction was evident, and solid again volatilised from the mixture. When the reaction was discontinued, after it had become clear that no further action was taking place, volatiles were pumped out of the dark brown product, which on cooling was revealed as an extremely viscous liquid, but plainly not a high polymer. This product was examined by I.R. spectroscopy and by NMR, which allowed an estimation of the relative concentrations of $-(CF_2)_3-$ and $(CF_2)_2O(CF_2)_5O(CF_2)_2$ groups, and revealed that only 1 diol molecule had reacted with every 2 acid chloride molecules, i.e., the acid chloride had behaved as a monofunctional compound, possibly due to incomplete reaction at the hydrolysis stage. It was decided at this point that further research on these lines would not be effective in terms of time and results, so this approach was abandoned.

Although this work had met with severely limited success regarding the synthesis of polymer intermediates, several valuable lessons had been learned. It firstly appeared that the presence of oxygen links at least β to a reaction site can drastically effect the course of reactions in fluorocarbons. On the other hand, it may be conjectured that a chain of three fluorinated methylene groups between the reactive site and the ether link will result in the disappearance of abnormalities in the reaction, since this situation is analogous to the 1,3-dihalohexafluoropropanes which react normally in copper coupling reactions, or to hexafluoroglutaric acid which undergoes the Hunsdiecker reaction and other decarboxylations smoothly. The greatest care should therefore be exercised in the planning of synthetic routes involving intermediates with ether groups linked by one or two fluorinated methylene groups to a reacting site.

Perhaps the most significant barrier to the success of this route to fluorinated alkylene oxide type polymers however, is the great difficulty in handling the intermediates. The high molecular weight monomers show characteristics of low crystallisability, solubility and volatility, as well as a very high viscosity which makes even transfer from one vessel to another a non-trivial operation. Coupled with the inaccessibility of these materials, which renders a thorough optimisation of their reactions impossible, these factors make the synthesis and refinement of the monomers to the necessary 99+% purity an extremely difficult task. It is therefore desirable to plan the synthesis of polymers in such a way as to avoid very high molecular weight intermediates, particularly those containing hydrocarbon and fluorocarbon groups together. The synthesis of acid chlorides, involving hydrolysis and subsequent use of thionyl chloride or similar reagents is also a less suitable reaction scheme than the reduction of an ester to an alcohol group, since side reactions and tar formation are usually significant in the preparation of an acid chloride. The consequences of these observations regarding the preparation of polymer intermediates will be considered in the next chapter.

Experimental

Preparation and Purification of Starting Materials, Solvents and Reagents

Diglyme was dried by refluxing over sodium, and purified by distillation, all operations were conducted in a dry nitrogen atmosphere. Acetonitrile was refluxed over phosphorus pentoxide and fractionally distilled

(79° - 81°) under an atmosphere of dry nitrogen; the process was repeated using fresh phosphorus pentoxide until the solvent no longer developed an orange colour when refluxed with the dessicant. Caesium fluoride was powdered and heated under reduced pressure (10^{-3} torr) the temperature was progressively increased to 250°C; the material was periodically transferred to a nitrogen purged glove box and ground to a fine powder. The heating and grinding process was continued until a white free flowing powder was produced, which did not lump together on further heating. Iodine was sublimed in vacuum, and powdered in the glove box. Tetrafluoroethylene had been prepared by depolymerisation of P.T.F.E. in vacuum by a previous worker, and was used without further purification. Hexafluoroglutaryl fluoride was prepared from octachlorocyclopentadiene by the route outlined in Chapter 1. Dimethyl sulphoxide and dimethyl formamide were dried by refluxing over calcium hydride, and then distilled in an atmosphere of dry nitrogen. Copper bronze was activated by washing with 2% iodine solution in acetone, then rinsed with acetone. Meta-iodo methyl benzoate was prepared by esterification of m-iodo benzoic acid using methanol and conc. sulphuric acid, and purified by vacuum distillation (72 - 74°C, 10^{-3} torr line pressure).

The Preparation of Octadecafluoro-1,11-diiodo-3,9-dioxaundecane (V)

Method 1

A 3-necked round bottomed flask (100ml) was charged in a nitrogen purged glove box with caesium fluoride (18g), and a magnetic stirrer follower was added. The flask was purged with dry nitrogen while a dropping funnel and reflux condenser were assembled round it. The condenser was topped by an adaptor carrying a gas inlet, and a solids flask charged with iodine (30g). A syringe was used to add diglyme (40mls) and hexafluoroglutaryl fluoride (14g) to the reaction flask, against a counter current of nitrogen. The flask was frozen in liquid nitrogen, and the whole apparatus evacuated (10^{-3} torr). After warming slightly, (ca.-50°C), the apparatus was filled with tetrafluoroethylene gas at atmospheric pressure, held in a series of rubber bladders. The apparatus was then tilted and shaken so that the iodine dropped down the condenser into the reaction flask. The temperature of the flask and contents was raised to 80°C, and the mixture was stirred for 7 hours, until no further gas was absorbed, as judged by observation of the bladders. The dark purple reaction mixture was then poured into saturated sodium bisulphite solution (300mls). A heavy yellow oil separated, which was removed, and saturated sodium bicarbonate solution (75mls) was added. The residual clear oil was washed with water, and dried under vacuum (10^{-3} Torr) to leave octadecafluoro-1,11-diiodo-3,9-dioxaundecane (V) (6.3g). The sodium bicarbonate solution was acidified with hydrochloric acid, and the oil which precipitated was collected, washed, and dried to yield dodecafluoro-8-iodo-6-oxaoctanoic acid VIII (4.9g). The aqueous residues were ether extracted and the extracts were examined for organic material, the presence of diglyme and a fluorinated carboxylic acid was established by I.R. spectroscopy.

Method 2

A two-necked flask (100mls) was charged in the glove box with caesium fluoride (18g) and iodine (30g). A magnetic stirrer follower was added, and the flask sealed, then purged with dry nitrogen while a dropping funnel and reflux condenser were assembled onto it. Diglyme (40mls) and hexafluoroglutaryl fluoride (14g) were transferred in by syringe, then the flask was frozen in liquid nitrogen and evacuated (10^{-3} Torr). Tetrafluoroethylene was introduced at atmospheric pressure, and the reaction and work-up continued as for Method 1, to yield V (12.7g) and VII (3.9g).

Copper Coupling Reactions

a) Small Scale Investigative Reactions

A round bottom flask (10mls) was charged with a miniature teflon-coated magnetic stirrer follower, freshly distilled D.M.S.O. (2mls), methyl 3-iodobenzoate (0.3g), and freshly activated copper bronze (0.2g). A reflux condenser was fitted, and a Pasteur pipette inserted down it, which was used to purge the apparatus with dry nitrogen. This purge was maintained, while the flask was immersed in an oil bath at 130°C. After the mixture had been allowed to attain the temperature of the oil bath, di-iodide (0.46g) was added down the condenser, dropwise over 30 minutes. The reaction was studied by withdrawing samples (0.2mls) which were quenched in water (2mls). The organic material was extracted into dichloromethane (1ml), which was examined by G.L.C. The results were discussed earlier.

b) Small Scale Preparative Reactions

A test tube equipped with a closed side arm was charged with DMSO (20mls), di-iodide V (5g), and methyl 3-iodobenzoate (10g). A miniature teflon-coated magnetic stirrer follower was added, and activated copper bronze (4g) placed in the side arm. The test tube was closed with a cone-tap adaptor, through which the apparatus was evacuated to the limit of a rotary pump (ca.10^{-3} Torr). The top was sealed, and the apparatus placed in an oil bath at 80°C before the copper was added by tilting the tube. The mixture was allowed to react overnight, then quenched in water (100mls). The product was extracted into ether, and evaporation of the solvent yielded a small quantity of viscous sticky green oil (ca.1g), which was identified as containing the required product by comparison of I.R., nmr and mass spectra with those of an authentic sample.

c) Large Scale Preparative Reactions

A round bottomed two neck flask (500mls) was charged with DMSO (140mls) di-iodide (50gm) methyl-3 iodobenzoate (100g), and copper bronze (35g) in a glove box. The apparatus was purged with dry nitrogen while a reflux condenser was connected, and the flask placed in an oil bath at 70°C. The purge was maintained while the reaction proceeded overnight, during which time the bath temperature rose to 110°C. The product was worked up as for method 2, and the green oil combined with that from other reactions for purification. The oil was transferred to a home-made molecular still, and initially outgassed at 10^{-3} Torr. The pot temperature was raised to 80°C, when a damp sublimate (methyl benzoate and methyl 3-iodobenzoate) appeared on the condenser. This was removed mechanically, and when no more appeared, the bath temperature was raised to 250°C, when a yellow oil passed over. This was contaminated with green material by splashing of the crude product, so the distillation was repeated twice, to yield a clear yellow viscous oil, identical in nmr, IR and mass spectra with an authentic sample. A black, exceedingly viscous residue, was left in the distillation pot. The total yield was 12.75g (16.6%) after purification.

Attempted Preparation of Octadecafluoro-3,9-dioxa-1,11-bis(3-chlorocarbonylphenyl)undecane

The di-ester (VI) was added to ethanol (500mls) and water (50mls). Solution was imperfect in this medium. Potassium hydroxide was added to give a 10% solution. The solution was refluxed overnight, after which the appearance of the mixture was unchanged, excepting slight discolouration of the fluorocarbon. The alkali concentration was doubled, and refluxing continued a further five hours. A portion of the ethanolic solution was removed after this time, and adjusted to pH 1 with hydrochloric acid. No material precipitated. The whole solution was therefore cooled, and acidified. The fluorocarbon was extracted into trichlorotrifluoroethane, and the solvent distilled off. The residue was added to a further portion of ethanol (500mls), and conc. HCl (100mls) added. The solution was again refluxed overnight, and a portion of the undissolved fluorocarbon examined by IR spectroscopy, which showed peaks indicative of a carboxylic acid. Extraction of the liquid as before yielded a dark coloured sticky material. This was treated with thionyl chloride (20mls) and refluxed overnight. Excess reagent was distilled off, and the residue transferred to the molecular still used in purification of the ester. Distillation at 10^{-3} Torr and 230°C, yielded a light yellow viscous oil (2.3g), and a dark residue.

Polymerisation of the oil was attempted according to the first procedure described in Chapter 4 of this thesis.

CHAPTER 3

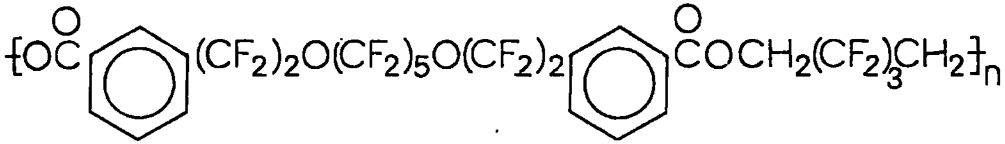
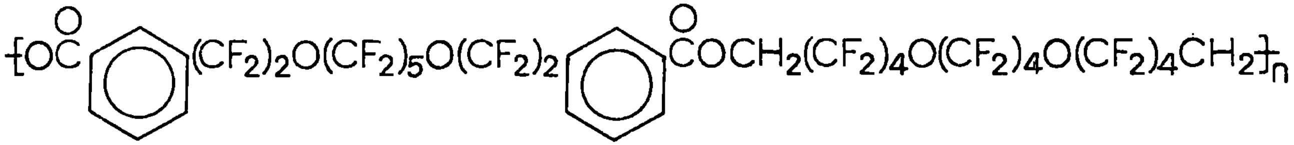
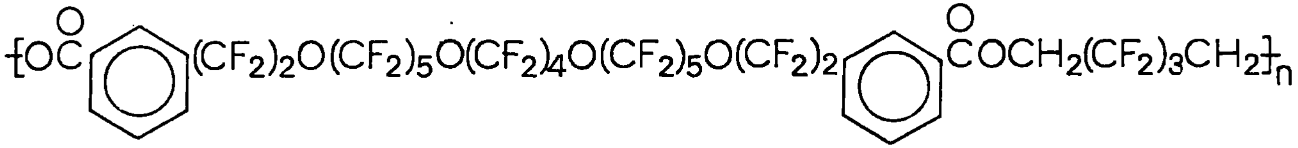
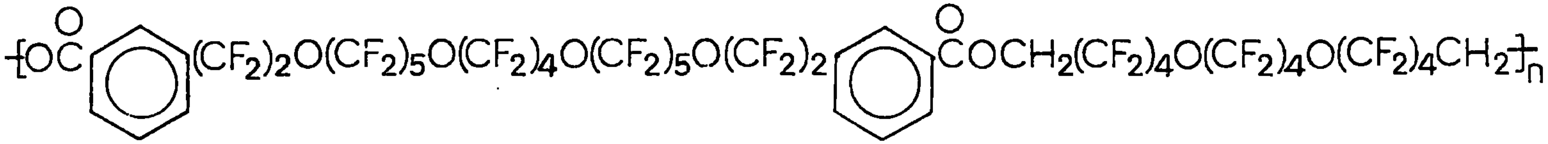
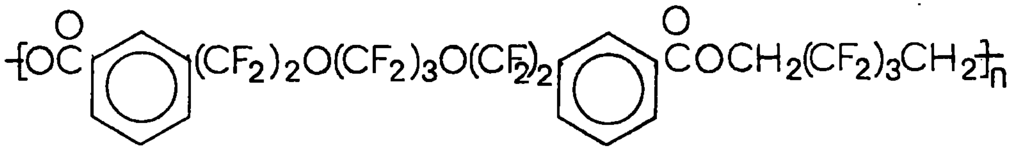
Preparation of Difluoromalonyl Chloride and Some Fluorinated Diols

Introduction

Following the failure to realise a polymer synthesis by the methods described in Chapter 2, a critical review of the projected course of work was undertaken. In addition to the practical experience gained in the earlier work, consideration was taken of theoretical predictions of T_g, made by the additive temperature parameter method. A table of these predictions was produced by scientists from R.A.E. Farnborough, and is reproduced in Table 3.1. An examination of these predicted T_g values lends support to the ideas put forward in Chapter 1. The longer perfluoroalkylene oxide chains, and increasing proportions of ether links within these chains, favour a low glass transition temperature.

In the above table, polymers 1 - 6 are derived from α,ω-bis-phenyleneperfluoroalkylene oxide type carboxylic acids, the synthesis of which would necessarily follow the general lines of the earlier work already described. Furthermore, the particular intermediates required share the common feature of an ether link β to the reacting centre, and it may be confidently expected that the synthesis of these compounds would be attended by identical difficulties to those experienced in the earlier work. Polymers 7 - 10 in the table however, are derived from the readily available isophthaloyl chloride, and a fluorinated α,ω-diol. These compounds are obtained in good yield by the reduction of the esters of fluorinated carboxylic acids, and the synthesis of two such materials,[27,65]

Predicted Glass Transition Temperatures of Some Fluorinated Polyesters

	Polymer Structure	Predicted T_g (°
1		271
2		252
3		259
4		247
5		265

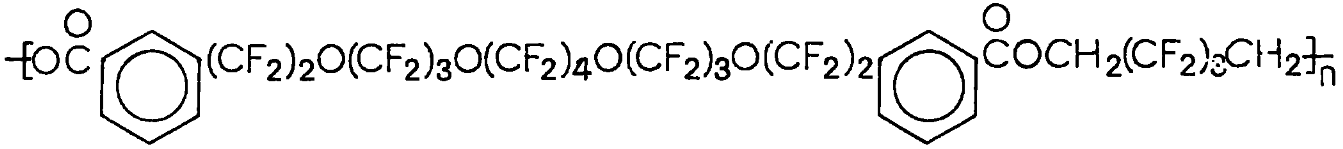
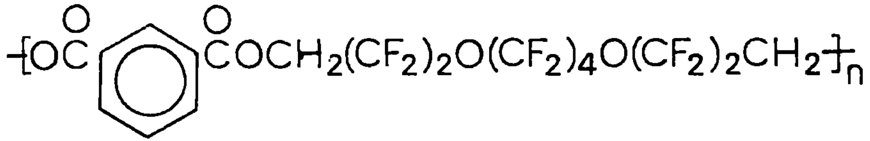
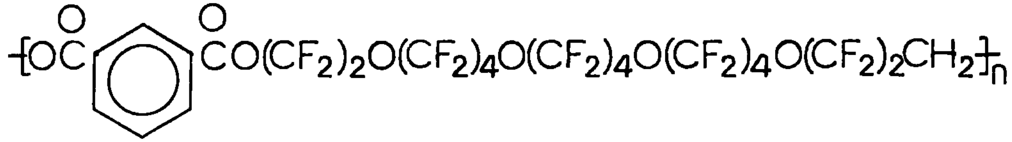
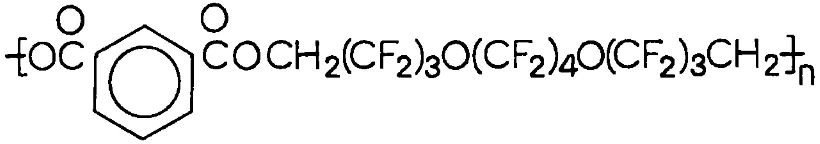
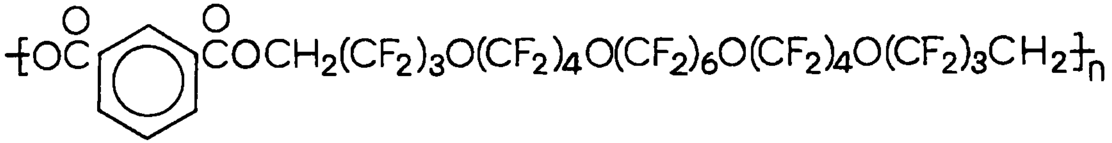
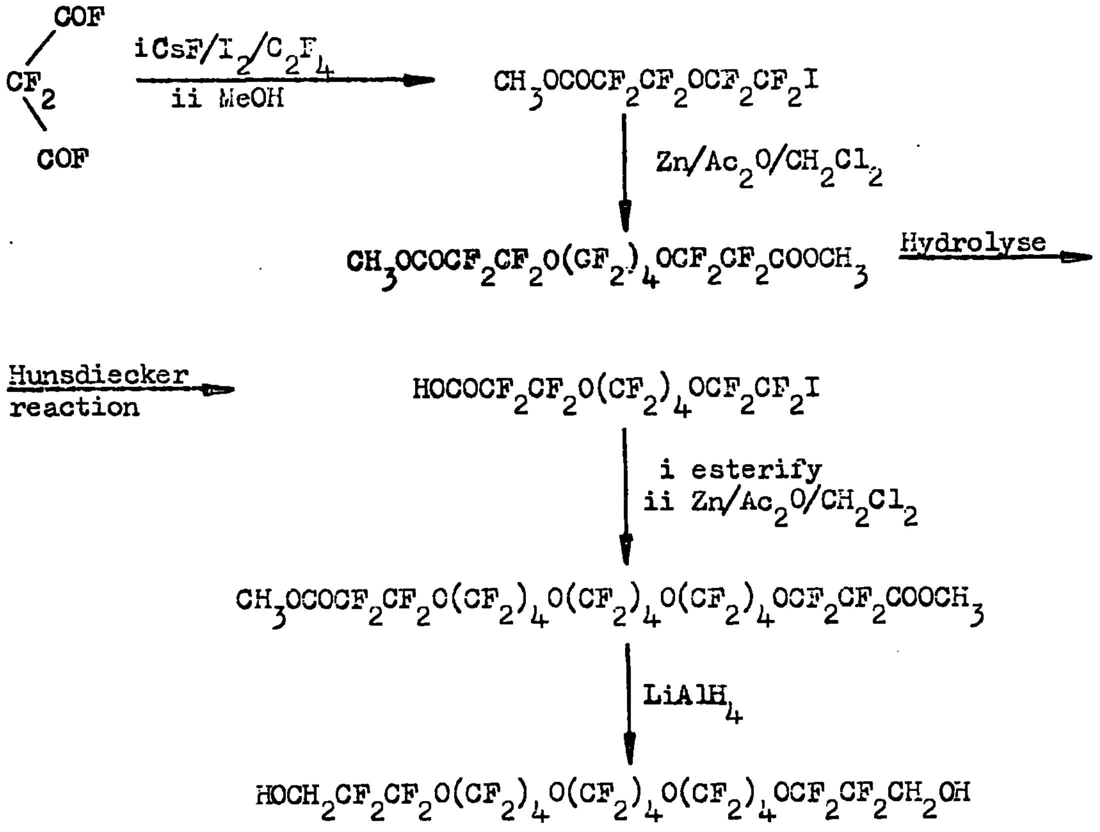
6		249
7		254
8		239
9		250
10		246

Table 3.1

and their polyesterification with isophthaloyl chloride, have already been mentioned in the introduction to Chapter 2. The generally lower molecular weight of these intermediates results in a greater volatility, with correspondingly easier purification. The polymer of this type having the lowest predicted T_g, No.8 in the above table, is obtained from a diol whose projected synthesis is outlined in the scheme below:



Although the mono-Hunsdiecker reaction which constitutes the key reaction of this sequence may well be expected to proceed in poor yield, it does not appear to have been investigated in the past. Even if this step cannot be accomplished, however, the intermediates containing a higher proportion of ether links than those previously synthesised could yield polymers of some interest, and the decision was therefore taken to investigate this sequence.[73]

The starting material in the scheme described above is the di-acid fluoride of difluoromalonic acid, which had been previously obtained only as a minor product,[74,75] or as a product of electrochemical fluorination.[76] In the absence of the equipment necessary for this latter process, an alternative synthesis was sought, and this work is described in the first part of this chapter. The remainder of the chapter is devoted to the synthesis of some simple fluorinated diols, which were prepared with a view to extending the available data on non-ether containing fluorinated polyesters.

Discussion

Attempted Synthesis of Difluoromalonyl Fluoride

The synthesis of difluoromalonyl fluoride was envisaged as proceeding via difluoromalonic acid. This compound should be obtained by oxidation of perfluorocyclohexa-1,4-diene, which is available as a by-product of the synthesis of other fluorinated cyclic olefins and dienes.

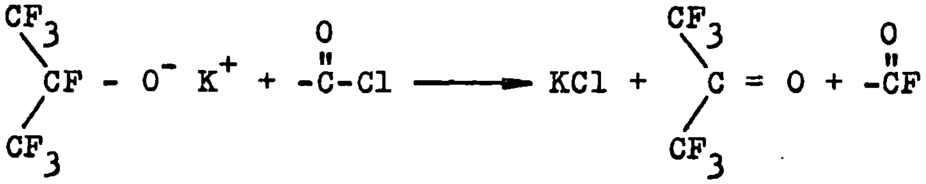
Initially, attempts to oxidise this compound were based on the procedure used for the analogous oxidation of perfluorocyclopentene to hexafluoroglutaric acid. The conditions used in this synthesis are an excess of potassium permanganate in neutral acetone, the reagents being mixed at low temperature and slowly allowed to warm to the ambient then finally refluxed for several hours to complete oxidation. The work-up involved addition of water, and sufficient sulphur dioxide was bubbled through the mixture to dissolve manganese dioxide which had precipitated. The volume of the solution was reduced by distillation, and the residual liquid made strongly acid, then ether extracted. The extracts were distilled, and the product was left as a residue which was purified by vacuum distillation.

Application of this method to perfluorocyclohexa-1,4-diene yielded only a dark tarry oil, which was water soluble, but from which no crystalline matter could be obtained. Attempted chlorination of this oil with thionyl chloride gave no identifiable product. In the light of this result, the reaction conditions were varied by adding potassium carbonate or hydroxide at the commencement of the reaction, but this had no effect on the course of the oxidation. The most likely route by which the anticipated product might be lost, is via a decarboxylation reaction. Although difluoroacetic acid might be expected as a major product of such a degradation, the mechanisms by which such reactions proceed are complex, and might cause a more drastic fragmentation of the molecule. In order to try to minimise such reactions, an attempt was made to carry out the oxidation in emulsion in aqueous acid. Small scale experiments proved that this method yielded a crystalline acidic product, but that this product was destroyed by any work-up procedure in which water was distilled from the mixture. Finally, therefore, a method was evolved whereby sulphuric acid and potassium permanganate were added simultaneously to a vigorously stirred mixture of the diene and water. A rather large quantity of oxidising agent could then be used in a small volume of solution, whereas other procedures resulted in decomposition of the permanganate in strong acid, or alkaline or neutral oxidation taking place, which resulted in degradation of the product. Alternatively, the theoretical quantities of acid and permanganate could be dissolved in sufficient water to keep the acid concentration low ($\lesssim 1$ N) and the diene added with vigorous stirring, but this results in a rather dilute solution of difluoromalonic acid. In either case, the solution was decolourised with sulphur dioxide and ether extracted overnight. The ether extract, on removal of solvent, yielded a semi-solid mixture of difluoromalonic acid and water, which could be worked up either by removal of water under vacuum, or by azeotropic distillation with benzene. The azeotropic distillation permits crystallisation of the product as the residual benzene solution cools, but some material is lost by tar formation. The product is a highly hygroscopic crystalline solid.

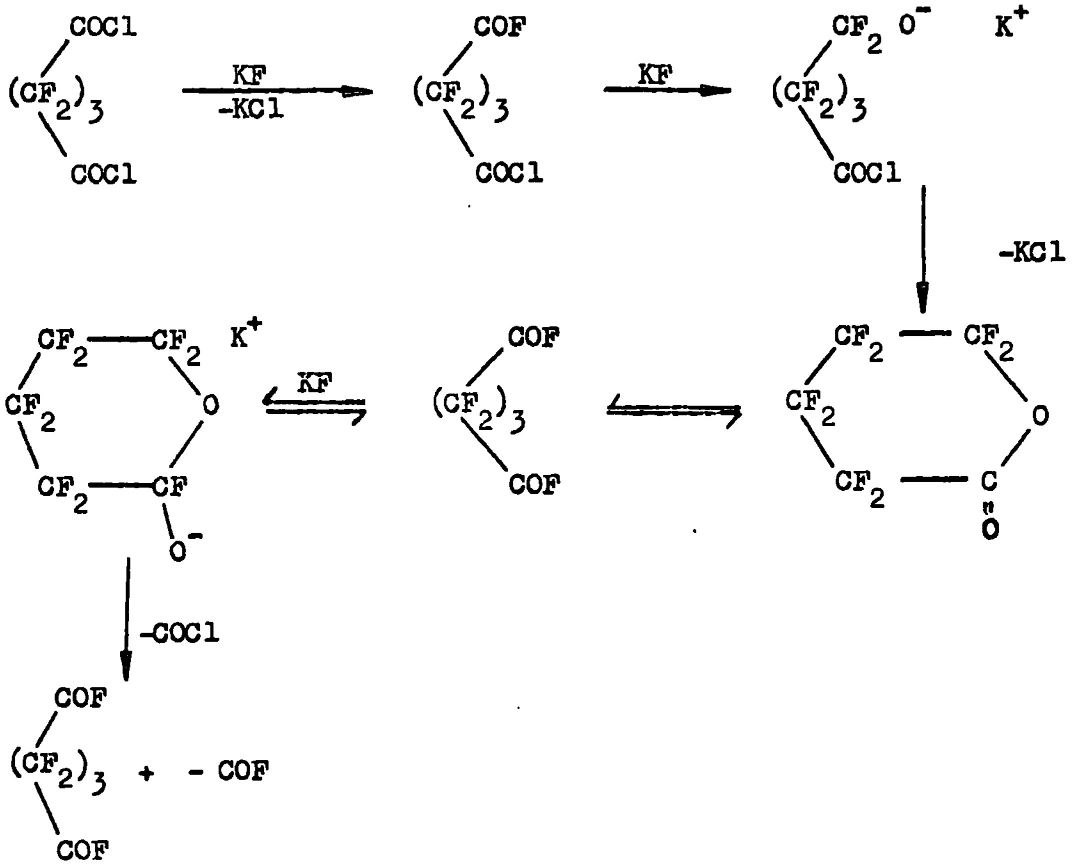
Conversion of difluoromalonic acid to the acyl chloride was readily accomplished by use of thionyl chloride containing ca.2% dimethyl formamide as a catalyst.[77] The reaction with this reagent proceeded at a satisfactory rate at room temperature, and an efficient condenser was used to minimise the carry-over of the volatile product with evolved gas. After the reaction had continued overnight, distillation of the mixture gave a fraction bp 67 - 70°C (lit 67.8°C)[78] identified as difluoromalonyl chloride by conversion to the methyl ester and analysis. Difluoromalonyl chloride is an extremely irritating compound, inhalation of a small concentration of the vapour causing uncontrollable coughing. The greatest care is necessary in its handling and use.

Attempts to synthesise difluoromalonyl fluoride by the same method as has been used for hexafluoroglutaryl fluoride, namely, adding the acid chloride to a stirred suspension of potassium fluoride in acetonitrile proved unsuccessful; the use of caesium fluoride and of diglyme in place of potassium fluoride and acetonitrile likewise resulted in no detectable reactions. Although the KF/acetonitrile reaction proceeds rapidly at room temperature and atmospheric pressure in the case of hexafluoroglutaryl fluoride, the more general technique which has been used by other workers requires use of an excess of the metal fluoride at temperatures above 100°C,[79,80] and under correspondingly high pressure; this technique can be used to prepare the acyl fluorides of other fluorinated carboxylic acids, although reaction times of several hours are necessary. In order to avoid the use of these conditions on a scale of at least several hundred grams of material, an alternative fluorinating agent was sought which would permit the reaction to be performed under atmospheric pressure.

The adduct of potassium fluoride to hexafluoroacetone has been described as a useful reagent for the replacement of a chlorine atom with fluorine.[80] A solution of this compound was therefore prepared by passing hexafluoroacetone into a stirred suspension of potassium fluoride in acetonitrile until the solid had dissolved. Stirring was then continued as an equivalent quantity of difluoromalonyl chloride was added. A solid precipitated, and a vapour was evolved which was condensed on a cold finger cooled with acetone/solid CO_2. These observations were in accord with the anticipated reaction

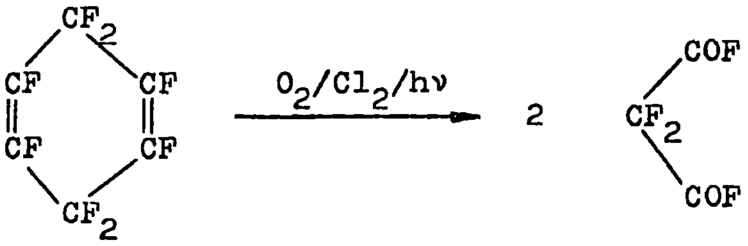


in which case the volatile material evolved should be a mixture of hexafluoroacetone and difluoromalonyl fluoride, and an infra-red spectrum of the product mixture indicated the presence of an acyl fluoride (absorption at 1885cm^{-1}) as well as hexafluoroacetone. Unfortunately, the volatilities of the compounds were too similar to permit any separation of the mixture by trap to trap distillation, and no means of chemical separation could be devised. It was conjectured, however, that the same mechanism which led to the efficacy of the KF/hexafluoroacetone adduct as a fluorinating agent could be exploited in a different way. As has been stated, the facile fluorination of hexafluoroglutaryl chloride with KF in acetonitrile appears to be a reaction specific to this and closely analogous systems. An autocatalytic reaction scheme was postulated:



If this scheme were operative, a slow uncatalysed reaction would initiate a rapid catalytic fluorination, and the overall effect would be of a fast reaction. It therefore seemed possible that hexafluoroglutaryl fluoride might exhibit a catalytic influence on the fluorination of difluoromalonyl chloride, and an experiment was carried out along these lines. Potassium fluoride was stirred into a slurry with acetonitrile and difluoromalonyl chloride, then a catalytic amount of hexafluoroglutaryl fluoride was added. No action was apparent, however, and no novel product could be detected in the reaction mixture.

A reaction is described in the patent literature,[37] whereby a fluorinated cyclic olefin is oxidised directly to a diacid fluoride or chloride. The conditions required are an oxygen atmosphere and U.V. irradiation, with chlorine present as a photosensitisor. The same conditions may be used to oxidise acyclic halogenated olefins to monoacid fluorides or chlorides, and the preparation of a variety of compounds, including hexafluoroglutaryl fluoride and octafluoroadipoyl chloride is described. Application of this method to the synthesis of tetrafluorooxydiactetyl fluoride has been described separately.[81] Although the application of the reaction to a cyclic diene is not described in the literature, it appears to offer a convenient one-step route to difluoromalonyl fluoride:



In the design of the experiment, potential photochemical side reactions were considered. Coupling of perfluoroacyl fluorides is known to occur under U.V. irradiation with the splitting off of carbon monoxide and carbonyl fluoride.[58] In addition, fluorinated olefins react with oxygen under irradiation and in the presence of certain photosensitisors to yield epoxides[52] and peroxy polymers.[82] The competitive addition of chlorine to olefinic bonds should be minimised by keeping the temperature and chlorine concentration low. Since chlorine is excited by relatively long wavelength radiation, the reaction was carried out in a pyrex flask, which served to remove much of the short wavelength U.V. responsible for the coupling of acyl fluoride groups. Difluoromalonyl fluoride may be expected to be a gas at room temperature, and it was intended to condense the product on a cold finger cooled with acetone/solid CO_2. An ice/water cooled cold finger was used to return any unreacted vapour to the reaction flask. The apparatus was assembled as in figure 3.1. The flow rates of oxygen and chlorine were regulated by needle valves and gauged by observation of the flow through oil filled wash

Apparatus for Photolytic Oxidation of Fluorinated Olefins

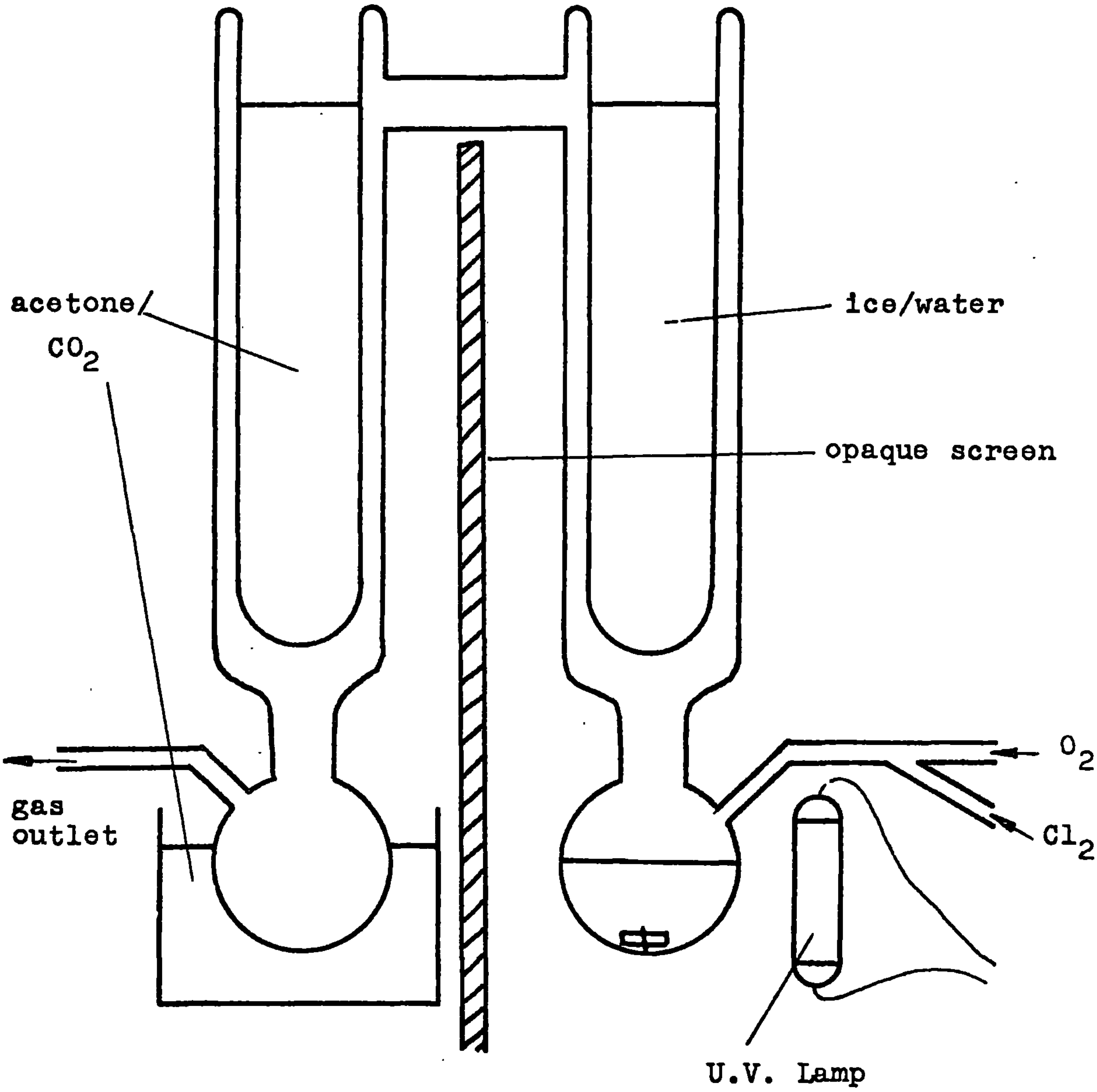


Figure 3.1

bottles. Initially, difficulty was experienced due to condensation of liquid chlorine in the product flask, but careful regulation of gas flow rates allowed the apparatus to be run without further problems. Oxidation of perfluorocyclohexa-1,4-diene in the apparatus over a period of 6 hours resulted in ca.50% of the starting material mass being transferred to the product flask. The product did not contain an appreciable quantity of material boiling below room temperature, and the material in both product and oxidation flasks consisted of clear fuming liquids. These were examined by glc/mass spectroscopy, and found to be essentially identical mixtures of ca.14 compounds, all of which had molecular weights consistent with fluorinated C_5-C_6 compounds. All showed a strong peak corresponding to the $C_5F_5^+$ ion. Infra-red spectroscopy indicated the presence of acyl fluorides in the mixture (band at 1887 cm^{-1}), but no fluorinated ketones were detected. It seems likely from these observations that whereas some oxidation is taking place, side reactions involving double bond migration and skeletal rearrangements are dominant. In this connection, it is known that fluorinated cyclic olefins can undergo molecular rearrangements under U.V. irradiation.[83] Because of these side reactions, however, the prospect of synthesising difluoromalonyl fluoride by means of this reaction seems to be small, and due to the failure to find any facile synthesis of this compound the approach was abandoned.

Preparation of Fluorinated α,ω-diols

Although the polymer of hexafluoropentane diol with isophthaloyl chloride has been described in the literature,[26,84] the analogous polymers with fluorinated diols containing more or less than five carbon atoms do not appear to have been previously synthesised. As these polymers should provide a relatively easy test of the predictive value of programmes based on the ATP treatment of glass transition temperatures, it was decided to synthesise the propane, butane and hexane diols and the polymers therefrom. The polymer from the commercially available hexafluoropentane diol was also made, to ensure comparability of results between this and the earlier work. The routes to these diols were envisaged from fluorinated olefins to the respective acids, conversion to the methyl esters and reduction to the diols with lithium aluminium hydride.

The preparation of octafluoroadipic acid was accomplished by the neutral oxidation of decafluorocyclohexene in acetone, using a procedure similar to the method established for the preparation of hexafluoroglutaric acid. The work-up involved solution of precipitated manganese dioxide with sulphur dioxide, reduction of the volume of the mixture by distillation, then ether extraction. Distillation of the ether extract, followed by drying of the residue by heating in vacuum, yielded crude octafluoroadipic acid, which was used without further purification. The acid was esterified using an excess (10 volumes) of methanol and sulphuric acid as catalyst. The dimethyl octafluoroadipate was isolated by addition of water, and ether extraction of the resulting emulsion. The extract being washed, dried, and the solvent removed, the residue was distilled under vacuum up a short Vigreux column, (bp 98° - 105°/15 torr, lit 126°/25 torr[85]). The diol was prepared by reduction of the ester with excess lithium aluminium hydride in diethyl ether at room temperature. The remaining reducing agent was destroyed by the careful addition of water, and hydrochloric acid was added to dissolve inorganic matter. The resulting solution was ether extracted, and distillation of the solvent yielded octafluorohexane-1,6-diol which was purified by vacuum sublimation at 60°C/0.1 torr.

A similar reaction sequence was applied to 1,2-dichlorotetrafluorocyclobutene to yield in turn tetrafluorosuccinic acid, dimethyl tetrafluorosuccinate (bp 174°/atmospheric pressure, lit 115°/100 torr[85]) and tetrafluorobutane-1,4-diol, purified by sublimation at 75°/0.1 torr.

It is stated in the literature, that reduction of the dimethyl ester of difluoromalonic acid does not yield difluoropropane-1,3-diol, but that this product is obtained on reduction of difluoromalonyl chloride.[78] Accordingly, an attempt was made to carry out this reduction with lithium aluminium hydride in ether. It was found that the reaction was extremely uncontrolled, and proceeded violently both during the addition of the acyl chloride, and subsequently when the mixture was being worked up by addition of water or ethyl acetate. On completion of the work up, only a tarry oil was obtained in small yield. It is believed that the sample of difluoromalonyl chloride used may have been contaminated with thionyl chloride.

An account of the polymerisation of these diols with isophthal oyl chloride is reserved for Chapter 4 of this thesis.

Experimental

Preparation of Difluoromalonic Acid

A mixture of perfluorocyclohexa-1,4-diene (50g) and water (400mls) was vigorously stirred in a round-bottomed flask (1L) equipped with a thermometer, dropping funnel, and reflux condenser. The dropping funnel was used to add sulphuric acid (15mls) in water (150mls), while potassium permanganate (70g) was added in small portions down the condenser. The addition of these two reagents was made in proportion, so far as possible, and the rate of addition was such as to maintain the temperature of the mixture below 50°C. The flask was cooled with water as necessary. After all the reagents had been added, the mixture was allowed to stir at room temperature overnight, then the apparatus was dismantled, and sulphur dioxide was bubbled through the liquid until all dark solid matter had dissolved. The solution was continuously extracted with ether, and the solvent was distilled off to yield a slurry of difluoromalonic acid in water. Removal of water by heating under vacuum (120°C/0.001 torr) yielded crude difluoromalonic acid (40g, 64%).

Preparation of Difluoromalonyl Chloride

Difluoromalonic acid (57g) was placed in a round bottomed flask (500ml) fitted with a double surface reflux condenser vented through a sulphuric acid wash bottle. A teflon covered magnetic stirrer follower was added, and thionyl chloride (250ml) and dimethyl formamide (2ml) were added to the flask. The mixture was stirred for 24 hours, then a Vigreux column and still head were fitted, and the product distilled, the fraction bp 67 - 70°C (lit 67.8°C) being collected, yield 51g (71%).

Attempted Fluorination of Difluoromalonyl Chloride

a. Dry powdered potassium fluoride (10g) and dry acetonitrile (50ml) were charged into a two necked round bottomed flask (100ml) attached by one neck to a nitrogen/vacuum manifold. Nitrogen was passed through the flask while difluoromalonyl chloride (10g) was introduced by syringe through a tap on the second neck of the flask. No action was apparent on stirring the mixture, and no vapour condensed in a trap connected to the apparatus.

b. A two necked round bottomed flask (500ml) containing dry acetonitrile (150ml) and dry potassium fluoride (9.5g) was fitted with a gas lead-in drawn out to a fine tube dipping below the liquid surface, and a solid CO_2/acetone cooled reflux condenser. Stirring was maintained by a teflon coated magnetic stirrer bar, while hexafluoroacetone was slowly passed in, at such a rate that it was absorbed by the mixture. As the addition proceeded, the solids slowly dissolved, until a cloudy liquid remained. Difluoromalonyl chloride (25g) in acetonitrile (100ml) was stirred in a round bottomed flask (500ml) and the KF/hexafluoroacetone solution was slowly added from a pressure compensated dropping funnel. A solid precipitated as the addition was made, and vapour began to be evolved, which was collected in a trap cooled in liquid air. When the addition was complete, the reaction mixture was warmed in a water bath to 80°C to drive over remaining volatiles. Attempts to separate the volatile materials in the product mixture by fractional vacuum transfer failed.

Attempted Oxidation of Octafluorocyclohexa-1,4-diene

The apparatus shown in figure 3.1 was charged with 50g of diene, the flow rates of oxygen and chlorine adjusted to give a steady stream of oxygen, and very slow stream of chlorine and irradiation carried out for 6 hours under a Hanovia 400W medium pressure mercury vapour lamp. At the end of this period, ca. half the mass of the organic matter had transferred to the product flask. The liquids in the reaction and product flasks were sampled by GLC/mass spectroscopy; each had a similar composition, and consisted of a complex mixture of ca.14 components, none of which had a mass spectrum consistent with the required product.

Preparation of Tetrafluorosuccinic Acid

A suspension of potassium permanganate (112gm) in acetone (600ml) was cooled in a round bottomed flask (2L) to the temperature of an acetone/solid CO_2 bath. The suspension was stirred mechanically while 1,2-dichloro-tetrafluorocyclobutene (158g) was added dropwise. The mixture was allowed to warm slowly to room temperature, then the bath was replaced by a heating mantle, and the solution was refluxed for three hours. Chlorine was evolved throughout the oxidation, and a precipitate formed. Water (600mls) was added to the reaction mixture, then sulphur dioxide was passed in until the solids had dissolved. Acetone and water (800mls) were distilled out, and the residue was made strongly acid by addition of sulphuric acid. Ether extraction of the resulting solution and removal of the solvent yielded a slurry from which tetrafluorosuccinic acid (53.5g, 35%) was obtained by removal of water under vacuum.

Preparation of Octafluoroadipic Acid

A procedure similar to that described for the preparation of tetrafluorosuccinic acid was used to oxidise decafluorocyclohexene (50g) with potassium permanganate (300g) in acetone (1L). The yield of octafluoroadipic acid was 48g (87%).

Preparation of 2,2,3,3-tetrafluorobutane-1,4-diol

Tetrafluorosuccinic acid (30g) was esterified by refluxing in methanol (300mls) in the presence of concentrated sulphuric acid (10mls) for 2½ hours. At the end of this time, the bulk of the excess methanol was distilled off, and saturated sodium carbonate solution added until gas evolution ceased. The organic layer was separated off, and the aqueous layer washed with ether (2 x 50ml), which extracts were combined with the organic product, and the ether distilled off to yield methyl tetrafluorosuccinate, which was purified by distillation up a Vigreux column (bp 174°C, lit 115°C/100 torr). Dimethyl tetrafluorosuccinate (13.7g) in ether (100mls) was added dropwise to a rapidly stirred suspension of lithium aluminium hydride (10g) in ether (200mls) at room temperature. When the addition was complete, the mixture was stirred for one hour at room temperature, then water (25mls) was added followed by sufficient dilute HCl to dissolve the inorganic solid which precipitated. The ether layer was separated, the aqueous layer washed with ether (2 x 50mls) and the ethereal solutions combined. Distillation of the solvent yielded

2,2,3,3-tetrafluorobutane-1,4-diol as a white hygroscopic solid purified by vacuum sublimation (75°/0.1 torr). The yield was 9.3g (92%) of product m.p. 80.5 - 81°C (lit 81°C).[85]

Preparation of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol

A similar procedure was used to that described for the preparation of tetrafluorobutane diol. Dimethyl octafluoroadipate (20g) bp 98 - 105°C/15 torr was reduced with lithium aluminium hydride (10g) to yield octafluorohexane-1,6-diol (15.5g, 94%) purified by vacuum sublimation to m.p. 70 - 70.5°C (lit 69°C).[85]

Attempted Preparation of 2,2-difluoropropane-1,3-diol

Diethyl ether (400mls) was added to lithium aluminium hydride (20g) in a three necked round bottomed flask (1L), which was equipped with a dropping funnel, reflux condenser vented through a bubbler, and mechanical stirrer. Dropwise addition of a solution of difluoromalonyl chloride (40g) in diethyl ether (200mls) resulted in violent reaction, often preceeded by an induction period after addition of each drop. The addition was completed over a period of ca. 2 hours, and the mixture was stirred for 1 hour at room temperature. Attempted destruction of excess reducing agent by dropwise addition of water led to a very violent reaction, accompanied by orange flashes within the flask. Substitution of ethyl acetate for the water still gave a violent reaction. The mixture was ultimately worked up by pouring cautiously on to ice (*ca*.1 Kg), but separation of the etherial layer and removal of solvent yielded only a dark tarry material, from which no crystalline product could be obtained. The foul sulphurous smell of this material led to the belief that the original malonyl chloride may have been contaminated with thionyl chloride.

CHAPTER 4

The Preparation of Some Epoxide Derived Diol Monomers and Polymer Production

Introduction

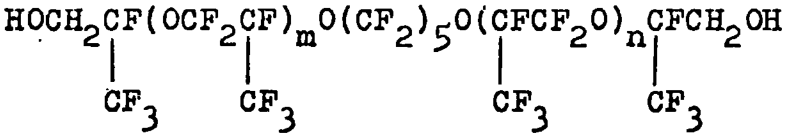
An attractive alternative to the stepwise synthetic routes to fluorinated ether containing bifunctional monomers described previously is the reaction of a fluorinated epoxide with the intermediates derived from the reaction of an alkali metal fluoride with a fluorinated diacid fluoride. The products of such reactions are bifunctional compounds, and by controlling the conditions of reaction, the number of epoxide groups adding on to each acid fluoride group may be regulated. In practical terms, therefore, the addition reaction of fluorinated epoxides with fluorinated diacyl fluorides provides a route to a mixture of bifunctional fluorinated ethers, which may be used as monomers in polycondensation reactions. Although the primary product of the reaction is a diacyl fluoride, the endgroups of such compounds may be modified by standard reactions to provide a very great number of terminal functions, a patent claim[86] lists 57; however, the most useful are probably nitrile, amidine and alcohol. In view of the obvious synthetic possibilities of this reaction, a great deal of research effort has been devoted to its investigation, and the reaction has been developed to the point where high molecular weight pre-polymers may be synthesised in good yield.[53] Further research has yielded a variety of curing reactions which may be utilised to prepare polymers,[56,87,92] some of which are elastomeric, from suitably chemically modified monomers.

It is a consequence of the nature of this addition reaction, that the product consists of a mixture of adducts of different molecular weights, and further that each molecular weight fraction is formed as a mixture of isomers, according to which end of the molecule each new epoxide unit adds. The preparation of a well characterised polymer requires a pure monomer of unequivocal structure to be used, and at the commencement of this work no fluoro-epoxide based high molecular weight polymer samples of completely known structure had been described. In order to assess the effect of the introduction of epoxide derived perfluoroalkylene ether groups into the main chain of a polymer, on the physical properties, and especially the T_g of the product, just such well characterised polymer samples are required for examination. The sponsors of this research were particularly interested in the examination of the effect on polymer T_g of the hexafluoropropene oxide derived group by the A.T.P. method, and this chapter describes experiments in the oligomerisation of hexafluoropropene epoxide with hexafluoroglutaryl fluoride, the separation and purification of the products, and their incorporation into condensation copolymers. Chapter 5 will deal with the characterisation of the polymers synthesised.

Discussion

The Oligomerisation of Hexafluoropropene Epoxide

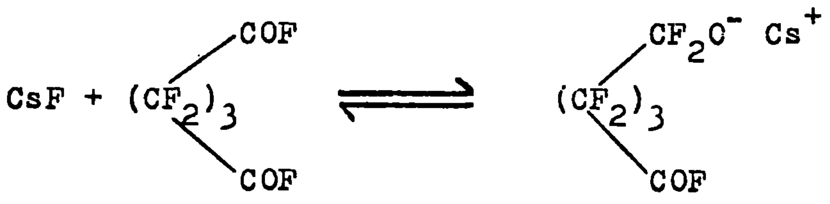
In order to evaluate the effect of the hexafluoropropene epoxide derived group in lowering the T_g of condensation polymers, compounds of the following structure were required:



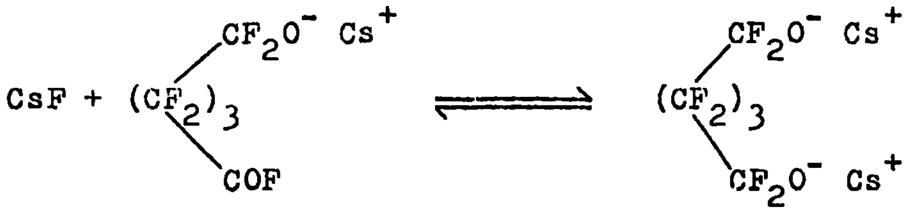
$$HOCH_2\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})_mO(CF_2)_5O(\underset{CF_3}{CF}CF_2O)_n\underset{CF_3}{CF}CH_2OH$$

Figure 4.1

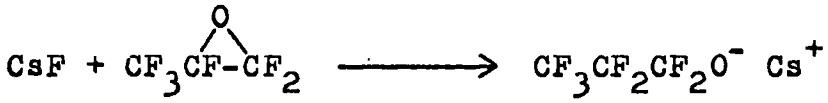
having known values of m and n. Such compounds result from the reaction of hexafluoropropene epoxide (HFPO) with hexafluoroglutaryl fluoride, and a review of the literature revealed that this reaction has been thoroughly investigated in the past.[52,53,76,81,93-114] A kinetic study of the reaction has been carried out, which allowed high molecular weight bifunctional products to be obtained by careful control of conditions.[53] The mechanism for the various stages of the oligomerisation was described by the set of reactions shown below:



4.1

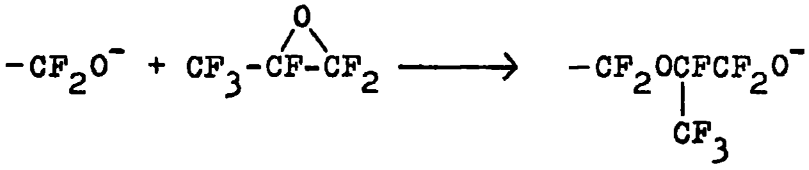


4.2

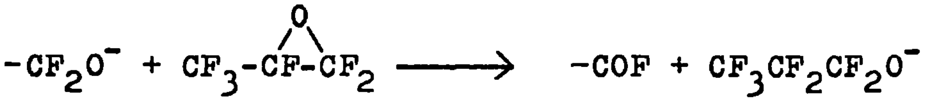


4.3

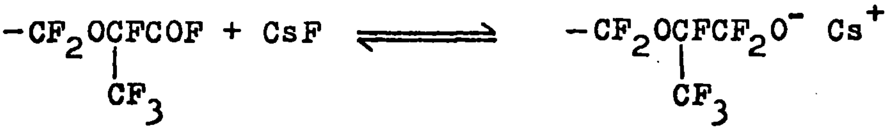
$$CsF + CF_3CF_2\text{-}COF \rightleftharpoons CF_3CF_2CF_2O^- \; Cs^+ \qquad 4.4$$



4.5



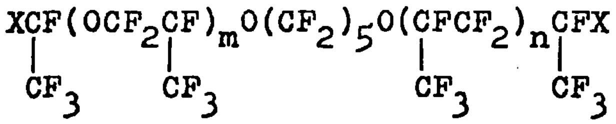
4.6



$$-CF_2O\underset{\displaystyle CF_3}{\underset{|}{C}}FCOF + CsF \rightleftharpoons -CF_2O\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O^- \; Cs^+ \qquad 4.7$$

Reactions 4.1 and 4.2 result in the generation of the nucleophilic alkoxide initiating species; the equilibria are well to the right-hand side, and the alkoxide species are sufficiently stable to be isolable. However, fluorine exchange is rapid in solution at ambient temperatures, and a narrow n.m.r. signal indicating a a very slow or negligible fluoride exchange rate can only be obtained for the fluoroalkoxide group on cooling to temperatures in the region of -70°C. Reaction 4.3 represents direct attack of a fluoride ion on the fluorinated epoxide, the product again being an alkoxide. An equilibrium exists (4-4) between this alkoxide and caesium fluoride and perfluoropropionyl fluoride. Insofar as these reactions result in a species which acts as a monofunctional initiator of the epoxide oligomerisation, their occurance is wasteful of material, and under certain circumstances may lead to a product mixture from which separation of pure bifunctional compounds is difficult. It is therefore desirable to minimise the amount of free fluoride ion in the solution of reacting species. It is claimed that the presence of hexafluoropropene in the reaction mixture acts as a trap for fluoride ions, resulting in the production of dimers and trimers of the propene without incorporation of oxygen containing species. Equation 4.5 represents the required oligomerisation reaction, while equation 4.6 represents a chain transfer reaction. This process too results in a monofunctional product, and also results in cessation of reaction of a bifunctional molecule. Fortunately, the rate of chain transfer was found to be strongly temperature dependent, and can effectively be prevented by carrying out the reaction at <u>ca</u>.-40°C. Equilibrium 4-7, like 4-1, 4-2 and 4-4, lies well over to

Compounds Derived from the Addition of HFPO to Hexafluoroglutaryl Fluoride



$$X\underset{CF_3}{\underset{|}{C}}F(OCF_2\underset{CF_3}{\underset{|}{C}}F)_mO(CF_2)_5O(\underset{CF_3}{\underset{|}{C}}FCF_2)_n\underset{CF_3}{\underset{|}{C}}FX$$

			Compound
$m = 0$	$n = 0$	$X = COF$	IX
$m = 0$	$n = 1$	$X = COF$	X
$m = 0$	$n = 2$	$X = COF$	XI
$m = 1$	$n = 1$	$X = COF$	XII
$m = 0$	$n = 0$	$X = COOCH_3$	XIII
$m = 0$	$n = 1$	$X = COOCH_3$	XIV
$m = 0$	$n = 2$	$X = COOCH_3$	XV
$m = 1$	$n = 1$	$X = COOCH_3$	XVI
$m = 0$	$n = 0$	$X = CH_2OH$	XVII
$m = 0$	$n = 1$	$X = CH_2OH$	XVIII
$m = 0$	$n = 2$	$X = CH_2OH$	XIX
$m = 1$	$n = 1$	$X = CH_2OH$	XX

Figure 4.2

the RHS; consequently the chain terminating loss of fluoride ion from fluoroalkoxide need not prevent the attainment of relatively high DP's.

The target of this work was primarily the preparation of adducts in which the ratios of HFPO to hexafluoroglutaryl fluoride were 2:1, 3:1, and 4:1, compounds IX — XII in figure 4.2. The influence of the various factors discussed above on the product distribution of the oligomerisation reaction were taken into account in designing the detailed procedures adopted for these syntheses. Thus, in order to minimise fluoride ion initiated monofunctional oligomerisation of the epoxide, it was decided to preform the adduct of caesium fluoride and hexafluoroglutaryl fluoride, rather than merely mixing the components in situ. The rate of the chain transfer reaction is apparently strongly temperature dependent, and can be effectively eliminated by carrying out the reaction at -40°C. Although previous workers had bled hexafluoropropene epoxide slowly into the reaction as a gas, this procedure necessitates maintaining a gas pressure considerably below atmospheric within the system, to avoid condensation of the epoxide as a liquid. The attendant danger of leakage of air and water vapour into the system led to an alternative experimental method being adopted, wherein the epoxide was condensed into a flask cooled in liquid air and containing the caesium alkoxide. The mixture was warmed to -40°C, and stirred for the duration of the reaction time. Hexafluoropropene epoxide prepared by the alkaline peroxide oxidation of hexafluoropropene contains a variable proportion of unchanged olefin, and this mixture was used in the reaction without any attempt being made to remove the impurity. The proportion of epoxide in the gas was estimated from the relative intensities of characteristic bands in the I.R. spectrum[115] and the total weight of gas used was adjusted so as to give the required molar quantity of epoxide in the oligomerisation reaction.

Consideration was next given to the purification of the adducts of HFPO with glutaryl fluoride. The necessary criterion of isomeric purity was expected to be the major difficulty in preparing polymer precursors, as isomer separation in reasonable yield had been attempted unsuccessfully by previous workers by means of distillation[110] and preparative g.l.c.[109] However, it has been shown that some crystalline derivatives of these compounds display significant solubility differences between isomers,[81] so it was planned to separate adducts of different molecular weight first by distillation, and subsequently to prepare derivatives for testing of fractional crystallisation techniques. The distillation equipment available for the first stage of this process utilized a glass concentric tube fractionating column, so it was decided to convert the adducts to their methyl esters, rather than distilling the acid fluorides which form the primary product of the oligomerisation reaction.

A preliminary reaction carried out according to the plan outlined above showed the practicality of the methods adopted. Glutaryl fluoride, mixed with dry diglyme was stirred with excess caesium fluoride at room temperature overnight before being filtered through a fine glass frit into the reaction flask which already contained a magnetic stirrer follower. These operations were carried out in sealed apparatus in a dry nitrogen purged glove box, to avoid hydrolysis of the acyl fluoride. The reaction flask was sealed, removed from the glove box, and connected to a gas/vacuum handling line which was used to purge the flask with dry nitrogen while a CO_2/acetone cooled condenser and thermometer were connected to it. The flask was frozen in a liquid nitrogen bath, and evacuated on the vacuum line (0.1 torr) then the pump was isolated from the line and a mixture of hexafluoropropene and hexafluoropropene epoxide was bled in and allowed to condense in the reaction flask. When transfer of volatiles was complete, the system was brought back to atmospheric pressure with dry nitrogen, the condenser was charged with acetone/solid CO_2, and the liquid nitrogen bath was replaced by an acetone bath, whose temperature was maintained at ca.-50°C by addition of small lumps of solid CO_2. When the reaction flask had equilibrated with this bath, the flask temperature was ca.-40°C. As soon as the viscosity of the reaction mixture permitted, stirring was commenced; and the reaction was allowed to procede at -40°C for ca.5 hours. At the end of this period, the addition of solid CO_2 to the cooling bath was stopped, and the mixture was allowed to warm slowly to room temperature. When the flask contents reached a temperature of ca.-20°C, an exothermic reaction occurred, with refluxing of a liquid on the condenser, and the reaction temperature rose to -5°C. The exotherm then subsided; no further reflux was observed, and the cooling bath was removed. The reaction mixture at this stage consisted of a clear colourless liquid with a white lumpy precipitate. The apparatus was dismantled, and the reaction mixture was poured slowly and with stirring into a large volume of methanol. An exothermic reaction was observed, and the mixture was left to stir overnight. Addition of water to the methanolic solution led to the separation of an organic liquid layer which was denser than water. This was separated from the aqueous methanolic solution which was then extracted with ether. The ether extract and organic layer were combined, washed with water and the solvent removed to yield a crude fluorocarbon product.

A series of similar reactions gave comparable results to the above; it was found that the exotherm varied in degree according to the time allowed for reaction prior to the temperature being allowed to rise, Hexafluoroglutaryl Fluoride/Hexafluoropropene Epoxide Addition Reactions

HFPO (g)	CsF (g)	Glut F (g)	Diglyme (ml)	Product (g)	Volatiles (g)
29	17.7	14.2		17.2	25.7
32	20.0	16.0		42	
35	40	19.3	70	48	
85		40.0		85	
100	75	49		118	

Table 4.1

but that the product distribution as indicated by g.l.c. was virtually identical from different reactions. Scaling up of the oligomerisation presented no particular difficulty, and the reactions carried out are listed in Table 4.1. Gas chromatographic analysis of the product from the first of these reactions indicated a complex mixture of some 24 components; many of these were, however, present in only small quantity. The ^{19}F nmr spectrum of the mixture was too complex to allow meaningful conclusions to be drawn, so a crude vacuum distillation of the mixture was carried out, and low boiling material was removed under vacuum (40°C/0.1 torr), then a broad boiling range fraction was distilled (40°-100°C/0.01 torr) and re-examined. The work of earlier researchers indicated that this higher boiling product should contain the bifunctional oligomers of hexafluoropropene epoxide, while the most volatile components of the mixture should be monofunctional compounds.

Analysis of the high boiling fraction of the product mixture by g.l.c. indicated a mixture consisting predominantly of four major components; this observation encouraged the running of a ^{19}F n.m.r. spectrum, and comparison of the spectrum obtained with the results reported by previous workers[53,81] indicated that the desired difunctional compounds were indeed present. Similar results being obtained with subsequent small scale reactions, the products were combined after removal of low boiling material as above, to facilitate further purification, and vacuum distillation up a short vacuum jacketed column packed with nickel gauze rings allowed fractions to be taken which were examined by g.l.c. and n.m.r. The g.l.c. examination was hindered by the fact that two of the components of the mixture had identical retention times on a column of silicone gum rubber, while one of these components had a retention time identical to that of a third component, when the analysis was carried out on an alternative high temperature column packed with 2-cyanoethyl methyl silicone. Because the distillation apparatus employed was relatively inefficient at low pressure, fractions containing several components were obtained; however, fractions in which the major components constitute about 90% of the mixture were obtained in this way and they were sufficiently pure to allow meaningful n.m.r. analysis.

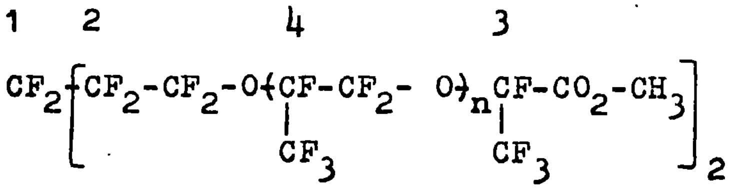
The ^{19}F n.m.r. spectrum of three components of the product mixture (b.r. 40°-100°C/0.01 torr) had important peaks in common, which are set out in Table 4.2

Peaks Observed in the ^{19}F n.m.r. Spectrum of Hexafluoroglutaryl Fluoride/HFPO Derived Esters

Peak		1	2	3	4	
Peak Position		123.6	126.8	133.2	146.6	
	Fraction					Assignment
Integrated	A	1	2	1	0	XIII
Intensities	B	2	4	2	1	XIV
	C	1	2	1	1	XV &/or XVI

Table 4.2

The assignment of these peaks, both from the observations made in the course of this work, and with regard to the earlier literature on this reaction, is shown in Figure 4.3. The structures of the possible acyl fluoride terminated adducts, together with the reaction pathways leading to them are illustrated in Figure 4.4.



$$\overset{1}{CF_2}\left[\overset{2}{CF_2}-CF_2-O\left(\overset{4}{\underset{CF_3}{CF}}-CF_2-O\right)_n\overset{3}{\underset{CF_3}{CF}}-CO_2-CH_3\right]_2$$

Figure 4.3

Routes to Product Formation in the Hexafluoroglutaryl Fluoride/HFPO Addition Reaction

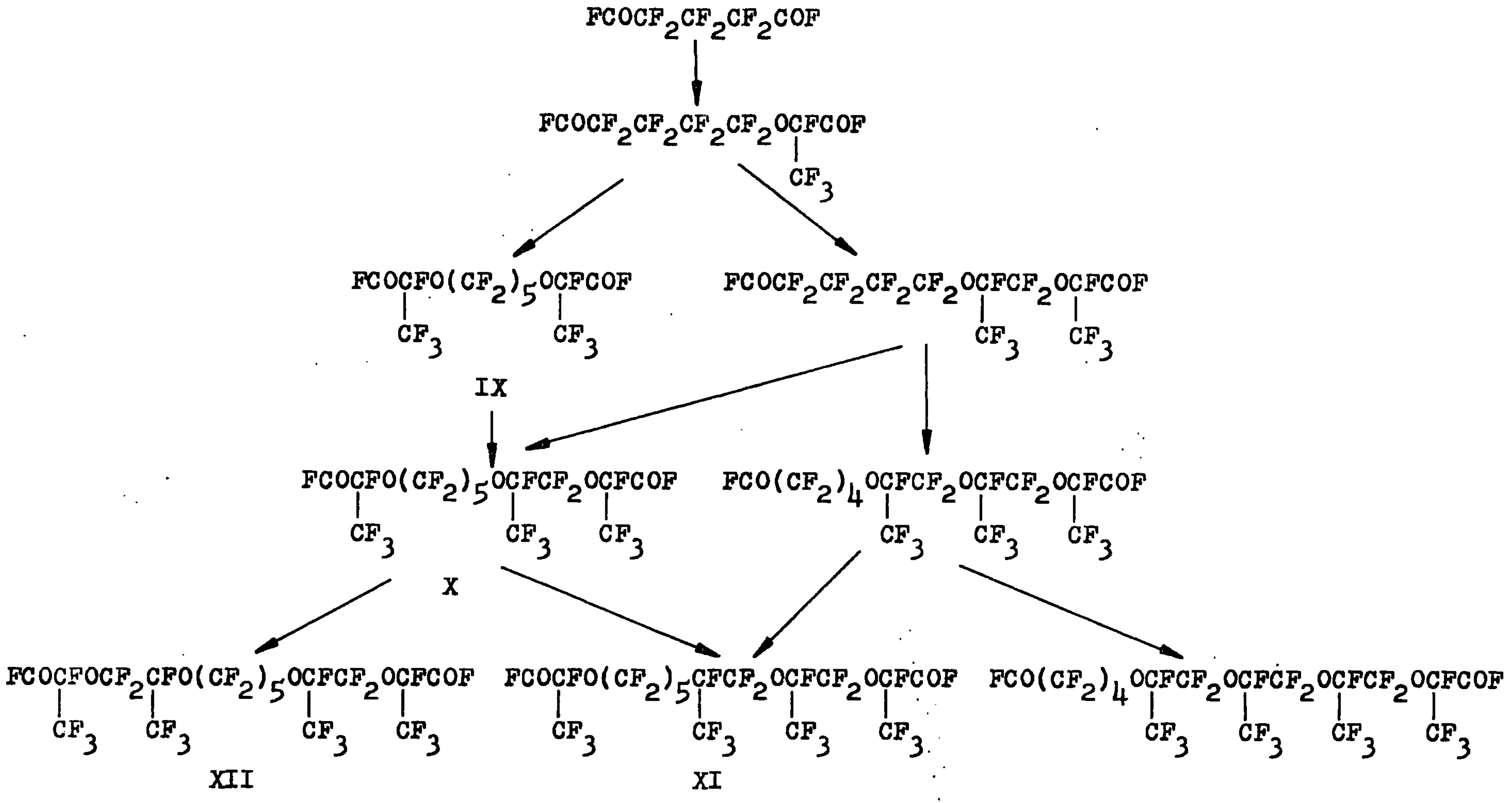


Figure 4.4

This assignment accounts for the observed progression in the relative intensity of peak 4, as well as the fixed intensity ratios of the other peaks, while the difluoromethylene groups adjacent to ether links, and the trifluoromethyl groups produce overlapping resonances in the region of 80 ppm from $CFCl_3$. Fraction A may therefore be identified as the diester XIII derived from the 2:1 adduct of HFPO with hexafluoroglutaryl fluoride IX, B as the diester XIV derived from the 3:1 adduct X, and C as the diesters XV and/or XVI derived from adducts XI and/or XII. Comparison of these spectra with that of IV lends support to these assignments, since a correspondence may be found between peaks 1 and 2 in Table 4.1, and peaks in the same intensity ratio at 115.2 and 118.5 ppm assigned to the central peaks of the perfluoropentamethylene group in compound V; although the observed shifts are different the separation between the peaks is essentially the same. These peaks derive from the most symmetric isomers of the adducts, that is, isomers resulting from addition of HFPO to both ends of the hexafluoroglutaryl fluoride residue. The least symmetric isomers will each contain the group

$$CH_3OCOCF_2CF_2CF_2CF_2O-$$

(resulting from addition of HFPO at only one end of the HFGF residue) and may be expected to display a series of peaks in the n.m.r. spectrum corresponding to the identical group present in VII i.e. a pattern of three peaks of equal intensity with chemical shifts of ca.120.3, 124.5 and 126.8 ppm, the difluoromethylene group adjacent to the ether link producing a peak close to 80 ppm which could be easily confused with the other resonances in that part of the spectrum. However, a search for such a pattern of peaks proved fruitless, and furthermore, the ^{19}F n.m.r. spectrum of the volatile matter removed from the product mixture at the first stage of the examination of the material, similarly displayed no such signal pattern. In view of the fact that this volatile fraction contained a large proportion of dimethyl hexafluoroglutarate, and that the less volatile fraction contained the diester XIII derived from the 2:1 adduct IX, the implication is, that no 1:1 adduct (i.e. $FCO(CF_2)_4OCF(CF_3)COF$) was present in the reaction product mixture, since this compound has only one isomer, which contains the above group. Further study of more highly purified fractions of diesters derived from the HFPO oligomerisation made it clear that none of the 1:1 adduct was present in the product, that the 2:1 adduct consisted of only the symmetric isomer, and that the 3:1 and 4:1 adducts contained none of the least symmetric isomers where all epoxides had added to one end of the HFGF residue. Structural assignments were made on the basis of n.m.r. spectra, but the identity of the 2:1

isomer was confirmed by reference to the work of earlier researchers, who had prepared fairly pure samples of the two isomers of this compound by preparative g.l.c. of the mixture obtained from their reaction.[109] The infra-red spectrum of the unsymmetric isomer displays a strong absorption peak at a wavelength of 983 cm^{-1}, the intensity of which is comparable with a neighbouring peak of wavelength 1040 cm^{-1}. The symmetric isomer, by contrast, displays only the latter absorption in its infra-red spectrum, and the peak at 983 cm^{-1} is either weak or absent. More subtle differences in the spectra of the two isomers are apparent in a range of peaks of moderate intensity in the 700-850 cm^{-1} region. Comparison of the spectra of the two isomers with that of the ester derived from the 2:1 adduct showed an extremely close correspondance between the product previously assigned as the symmetric isomer, and the product obtained in this work. The spectra of the 3:1 and 4:1 adducts, as well as those of higher boiling fractions of the product mixture, show a band at 983 cm^{-1} whose intensity rises relative to that of the 1040 cm^{-1} band, as the molecular weight rises. It seems likely, therefore, that the 1040 cm^{-1} and 983 cm^{-1} absorptions are characteristic of the ether groups linking an HFPO unit with a terminal ester group, and with a second HFPO unit or fluorinated methylene chain respectively. The assignment is supported by the observation that the peak at 1040 cm^{-1} is absent in the

Previously Reported Product Distributions from Fluorinated Epoxide Oligomerisation Reactions

Reaction No.	Acyl Fluoride	Epoxide	F^- Source	Solvent	Temperature	Products[b)]	Sym/assym.[c)] Ratio	Ref.
1	Glutaryl	HFPO	CsF ($\frac{1}{2}$ mole)	Diglyme	-25° - $+25^\circ$C	7:1 average	No analysis	102
2	"	"	" "	"	-13° - $+10^\circ$C	6:1 - 9:1	"	105
3	"	"	" catalytic amount	"	30° - 40°C	4:1 - 9:1 $(HFPO)_3$ - $(HFPO)_6$	"	104
4	"	"	" "	"	0° - 35°C	1:1, 2:1 $(HFPO)_2$ $(HFPO)_3$	"	81
5	"	"	" "	Probably as reaction 13	Probably as reaction 13	2:1	2:1	110
6	"	"	" "	Diglyme	30° - 40°C	1:1 2:1	4:1	109
7	"	"	" "	"	0°C	1:1 2:1 3:1	1:1 4:1	81

Reaction No.	Acyl Fluoride	Epoxide	F$^-$ Source	Solvent	Temperature	Products[b]	Sym/assym.[c] Ratio	Ref.
8	Glutaryl	HFPO	CsF	Diglyme	0°C	2:1	Claim symmetric	100
9	Glutaryl, Malonyl, Oxalyl	"	"	"	0°C	2:1	Claim symmetric	94
10	Malonyl, adipoyl	"	" $\frac{1}{5}$ mole	"	-25°C		Mostly symmetric	76
11	Oxalyl	"	" excess	"	-10° - 0°C	2:1, 3:1 $(HFPO)_2$ - $(HFPO)_4$	No analysis	81
12	Oxydipropionyl	"	" 1 mole	"	-20°C	5:1	"	108
13	$CH_3OCO(CF_2)_3COF$	"	"	"	0°C	2:1	Assymmetric	110
14	Glutaryl	TFEO[a]	$(C_2F_5)_4N^+F^-$	$HCF_2CF_2CH_2Cl$	-35°C	2:1 - 4:1	Mixture	93
15	Malonyl, adipoyl	"	CsF $\frac{1}{5}$ mole	Diglyme	-25°C		Mostly assymmetric	76
16	Glutaryl	"	"	Tetraglyme	-5° - +5°C		All glutaryl fluoride reacts, then assymmetric addition	114

Reaction No.	Acyl Fluoride	Epoxide	F^- Source	Solvent	Temperature	Products[b)]	Sym/assym.[c)] Ratio.	Ref.
17	Glutaryl	Perfluoro Isobutene/ Epoxide	CsF Catalytic amount	Tetraglyme	10°C	2:1 $(PFIBO)_2$	Mostly symmetric	111

a) Tetrafluoroethylene epoxide

b) Ratio of epoxide units adding to each acyl fluoride molecule.

c) Ratio of more symmetric isomers to least symmetric isomer.

Table 4.3

corresponding diols being replaced by a broad peak at $1090cm^{-1}$, but that at $983cm^{-1}$ displays the same progression of intensity as is observed in the esters.

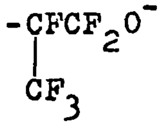
The observation of only those product isomers in the mixture derived from the oligomerisation reaction, which could be derived from the symmetric isomer of the 2:1 adduct, prompted a careful comparison of the experimental procedure used in this work, with the methods used by earlier researchers, none of whom had obtained comparable results. Unfortunately, relatively few of the reports on the use of the epoxide oligomerisation reaction give a useful analysis of the product mixture. A list of those that do, is presented in Table 4.3. It will be seen that few workers even among those who analysed the product distribution went so far as to determine the isomer ratios among the adducts. Reactions 8 and 9 are from the patent literature, and although the symmetric isomers are claimed, no detail of the analysis is given, and it is likely that the symmetric compound is claimed as a convenient shorthand for the isomer mixture. Reactions 5, 6 and 7 quote ratios of isomers obtained for each adduct. The statistical ratios, i.e. the isomer ratios to be expected if each acyl fluoride group were equally reactive, are as below:

Statistical Isomer Ratios in Epoxide/Diacyl fluoride Adducts

Adduct	Sym/Assym Ratio
1:1	-
2:1	1:1
3:1	3:1

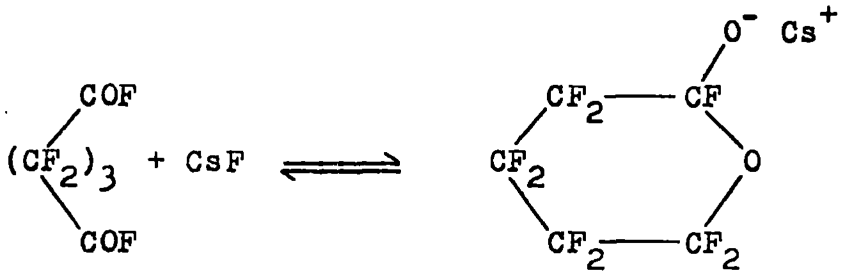
Table 4.4

The routes by which the isomers are formed, are shown for the hexafluoroglutaryl fluoride/HFPO reaction in Figure 4.4.

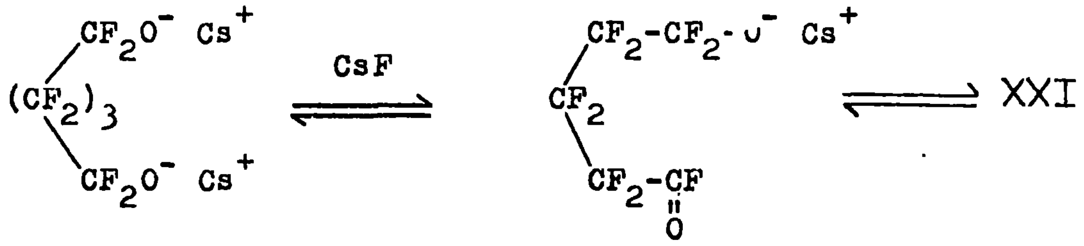
It will be seen that these reactions, particularly at a higher temperature, yield slightly more of the symmetric isomer than might be expected. Reactions 10 and 17 lend limited support to this observation, although the reactants are significantly different. Reactions 10 and 15 were performed by the same workers under comparable conditions, and the difference in isomer distribution was explained by them as arising as a consequence of the greater reactivity of TFEO over HFPO, which results in TFEO adding to the fluoroalkoxide faster than fluoride ion transfer changes the activity of each end of the molecule. This transfer, however, is in turn faster than the addition of HFPO, and the addition of this latter epoxide yields an isomer mixture based on the supposed greater thermodynamic stability of the $-CF_2CF_2O^-$ group over the  $-\underset{CF_3}{\underset{|}{CF}}CF_2O^-$ group. Unfortunately, independant evidence as to the relative stabilities of these groups is hard to find and estimates based on thermal decomposition data at ca.200°C[116] fail to reveal an unequivocal difference. An interesting observation made in the course of reaction 16, is that glutaryl fluoride reacts much faster at one end of the molecule with TFEO than does the resulting perfluoro-2-alkoxy ethoxide group. This species in turn reacts much faster than the other end of the glutaryl fluoride molecule. The reaction was carried out at ca.0°C, and a thermodynamic equilibrium should therefore be rapidly attained between the alkoxide species. In this system, the stabilities of the alkoxides appear to be in the order:

Glutaryl fluoride/CsF adduct > $-OCF_2CF_2O^-Cs^+$ > $-CF_2CF_2CF_2O^-Cs^+$

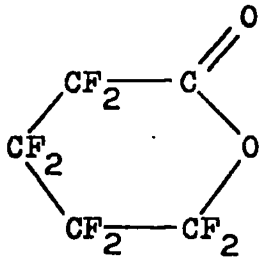
The unexpected difference between the stability of the alkoxide derived from glutaryl fluoride, and from the glutaryl end of the 1:1 adduct molecule, is explained by these workers by invoking a cyclic species:



XXI

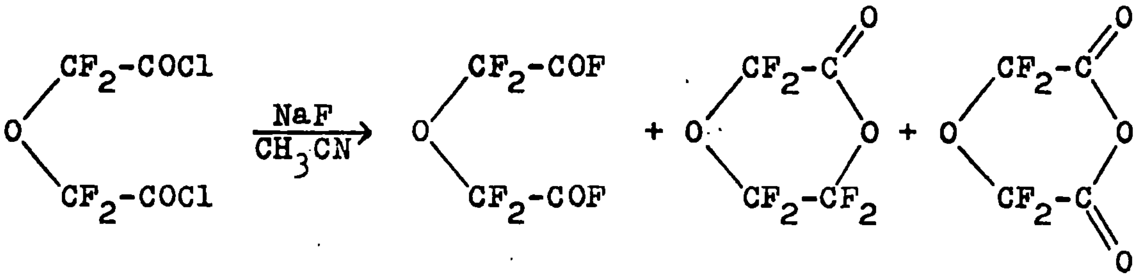


This cyclic species (XXI) is supposed to be the major initiating alkoxide in the oligomerisation reaction. It may be regarded as a derivative of the fully fluorinated lactone



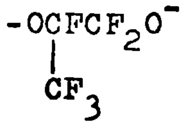
XXII

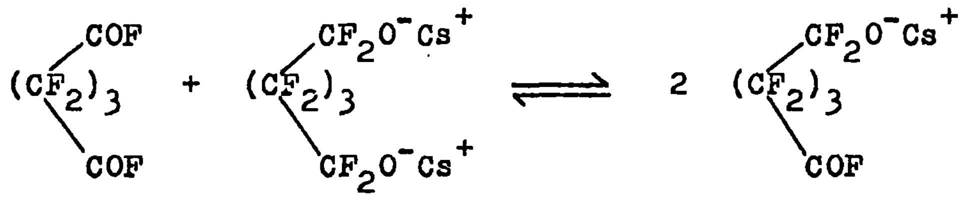
which has been the subject of discussion in the literature but still does not appear to have been isolated. However, the closely related lactone derived from and isomeric with perfluorooxydiacetyl fluoride occurs together with the latter compound in the product of fluorination of perfluorooxydiacetyl chloride.[117,118]



70 : 25 : 5

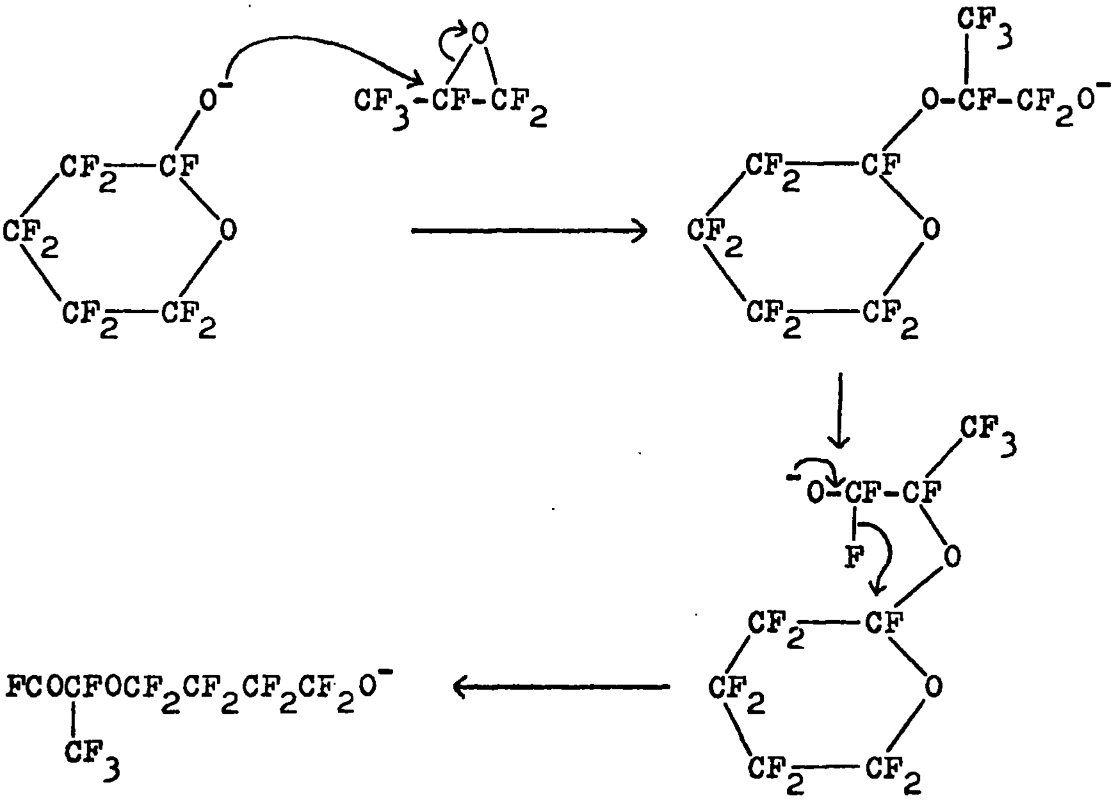
The observed ratio between the acyl fluoride and the lactone is probably the equilibrium ratio at the temperature of distillation (32°C) as fluoride ion catalysed interconversion should be rapid at this temperature. At a higher temperature, the equilibrium is displaced toward the diacyl fluoride, as might be expected.

None of the oligomerisation experiments listed in Table 4.3 were carried out under conditions which are fully comparable with the work described here, although reactions carried out at temperatures down to -25°C are described, it is necessary to invoke moderately rapid intra- and inter-molecular fluoride ion exchange to explain the formation of observed products, and their relative abundance. Hill has demonstrated,[53] however, that at -40°C, the rate of fluoride ion exchange between molecules is very low, and the rate of intramolecular exchange is presumably also slow, at least in the absence of special mechanisms. Now, in the present work the adduct of caesium fluoride and hexafluoroglutaryl fluoride was pre-formed, allowing for the generation of either the mono-, or the dialkoxide. If the dialkoxide were the initiating species in the oligomerisation, there seems no reason why the observed product distribution should deviate greatly from the statistical figures unless the $-CF_2CF_2CF_2O^-$ group is much more active in the initiation than the  $-O\underset{\substack{|\\ CF_3}}{C}FCF_2O^-$ group. If this were the case, the product distribution can be explained, but the observation that the product mixture contains a considerable quantity of dimethyl glutarate (from hexafluoroglutaryl fluoride) requires that the equilibrium



must lie well to the left. This is perhaps an unlikely condition, which must be fulfilled if this explanation of the products obtained in the reaction is to be accepted.

The second alternative, that the mono-alkoxide of hexafluoroglutaryl fluoride is formed, would be expected to yield the 2:1 adduct wholly as the assymmetric isomer, in the absence of fluoride ion exchange between the ends of the molecule. It is difficult to devise a satisfactory mechanism for such a process if the open chain monoalkoxide predominates. If, however, the alkoxide of perfluoro δ-valerolactone (XXI) is the initiating species, a series of reactions leading to specific transfer of activity from one end of the molecule to the other, may be formulated:



XXIII

The key step in this scheme is the intramolecular fluoride ion transfer; the driving force for such a rearrangement could be provided by the relaxation of steric strain when the ring opens. (Evidence for such strain is provided by the relative stabilities of perfluoro δ-valerolactone and of perfluoro β-oxa-δ-valerolactone with respect to their diacyl fluoride forms, the former lactone never having been isolated whereas the latter is well known.) Although intermolecular fluoride ion transfer is very slow under the reaction conditions, the intramolecular shift is not necessarily ruled out, if it is accomplished without the fluoride ion leaving the solvation shell of the charged species. Molecular models of XXIII indicate that the conformation required for this intramolecular fluoride ion shift is not ruled out on steric grounds (cf Figure 4.5).

Conformation of XXIII Permitting Facile Intramolecular Fluoride Ion Transfer

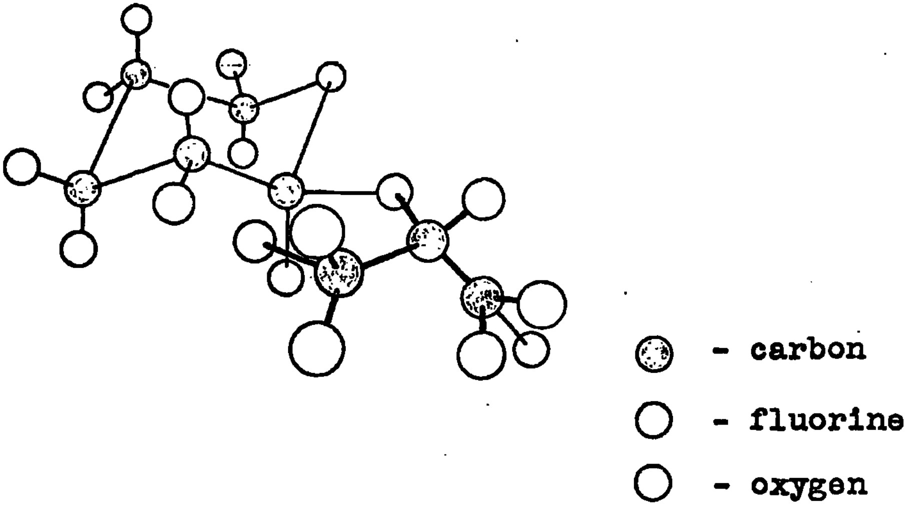
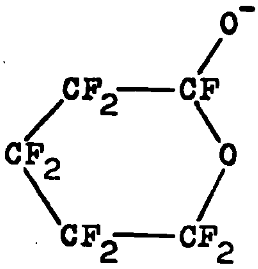


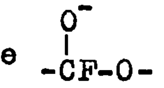
Figure 4.5

An additional condition which is necessary if this mechanism is to explain the observed products of reaction, is that initiation of oligomerisation by the $-CF_2CF_2CF_2O^-$ group must be much faster than initiation by the



group.

Such a condition may be reasonable if this cyclic form of the fluoroalkoxide is sufficiently stabilised to significantly reduce its nucleophilicity. A slow reaction of the alkoxide with the first epoxide molecule then yields a much more active species to react with a second epoxide molecule rapidly, accounting for the failure to observe any 1:1 adduct in the product mixture, as well as the isomer ratio in the products. Any of the cyclic alkoxide which failed to react with any epoxide molecules would be converted to dimethyl glutarate in the work-up.

Clearly, the acceptance of either of the above mechanisms carries a concomitant commitment to accept certain assumptions about the species and equilibria involved which are not necessarily open to facile study by independant methods. It was felt, however, that it might be possible to detect the formation of a lactone-like species in hexafluoroglutaryl fluoride, if this should occur, by means of an n.m.r. study in the presence of caesium fluoride at low temperature. A solution of glutaryl fluoride in diglyme was therefore allowed to stand over caesium fluoride at room temperature overnight, then filtered and sealed in an n.m.r. tube under nitrogen. The ^{19}F n.m.r. spectrum of this solution at room temperature consisted of two peaks at chemical shifts of 119.6 ppm and 126.4 ppm having relative intensities of 2:1 respectively. No signal was observable from the acyl fluoride group, as might be expected if this group were undergoing rapid fluoride ion exchange. On cooling to -40°C, a considerably more complex spectrum was recorded. A pattern of three peaks at 124.2, 119.6 and -26.2 ppm of intensity ratio 1:2:1 was assigned to free hexafluoroglutaryl fluoride, the fluoride ion exchange now being slow compared to the time scale of the recording of the spectrum. The change in the position of the resonance assigned to the central fluorinated methylene group in this compound is unexpected, and the integration of peak intensity rather difficult, but the assignment was made reasonably confidently, on the basis of peak position, and intensity. These peaks were also characteristically narrower than the others in the spectrum. A further series of peaks were recorded, at shift values of 129.9, 128.0, 121.5, 117.5 and 65.5 ppm. Those peaks were all rather broad and roughly in the intensity ratio 2:2:2:2:1. There was no simple whole number ratio between the integrated intensities of the peaks in the two different groups. Clearly, the second set of peaks cannot be explained either by the presence of the dialkoxide of hexafluoroglutaryl fluoride, or by the presence of perfluoro δ-valerolactone (XXII). The alkoxide of this lactone, however, would be expected to display the required five peaks in its ^{19}F n.m.r. spectrum, in the observed intensity ratio. If this explanation is correct the peak at 65.5 ppm must be assigned to the tertiary fluorine on the lactone group itself, but it is difficult to predict the chemical shifts to be expected for the fluorinated methylene groups on each side of the  $-\overset{O^-}{\overset{|}{C}}F-O-$ link in this compound, since there are no sufficiently close analogies. The ^{19}F n.m.r. peak assignments in known fully fluorinated lactones[117,118,119] are shown in the diagram:

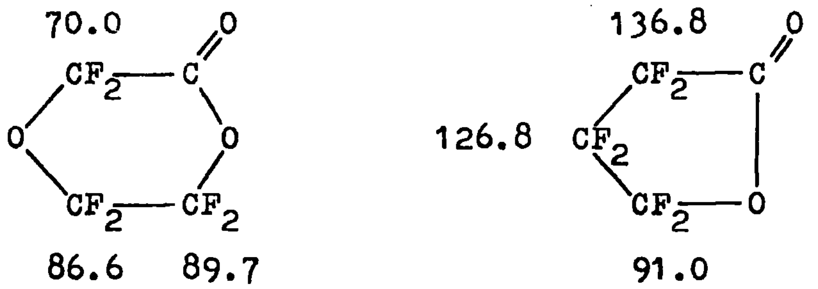


Figure 4.2

If the explanation suggested above is correct, the resonance due to difluoromethylene adjacent to the lactone oxygen (ca.90 ppm) in the neutral molecule shifts upfield to 117.5 ppm in the proposed alkoxide anion, at the same time a downfield shift of at least 8.4 ppm of the difluoromethylene adjacent to the lactone carbonyl must be accepted. It is difficult, a priori, to say whether or not such a set of shifts is consistent with the proposal made above; however, considerably greater problems are posed by an attempt to fit the spectrum to the alternative model. The acyclic monoalkoxide of hexafluoroglutaryl fluoride should display a spectrum of five peaks in the intensity ratio observed, but the chemical shifts anticipated for each end group are quite different from those of any of the observed peaks, as the acyl fluoride group resonates at ca.-15 to -23.6 ppm, and the $-CF_2O^-$ group at ca.-15 to

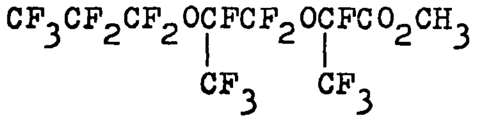
-31 ppm,[116,69] and there are many close analogies to support these assignments.

In summary, therefore, a low temperature n.m.r. study on the CsF/Glutaryl fluoride system provides clear evidence for the formation of a labile species in solution, without sufficient data being available for an unequivocal identification of the compound. As excess glutaryl fluoride appears to exist in the free state, rather than as an alkoxide, the unknown compound is the likely initiator of the epoxide oligomerisation. The author favours the alkoxide form of δ-valerolactone as the best candidate for this species; however, the possibility can also not be ruled out, that more than one species may contribute to the five unassigned peaks in the spectrum.

The Preparation of HFPO Derived Diols

In view of the realisation, as described above, that only the symmetric isomer of the 2:1 adduct, and products derived from it, were present in the high boiling portion of the product mixture, the purification of adducts to the level required for polymer synthesis became much simpler, no isomer separation being necessary. Separation of the adducts was accomplished by vacuum distillation, with appropriate fore-fractions and pot residues being combined and redistilled to avoid wastage of material. Thus, distillation of the crude diester derived from the 2:1 adduct, provided a high boiling residue containing a high proportion of the diester derived from the 3:1 adduct. This was combined with a fore-fraction from the distillation of crude diesters derived from the 4:1 adduct and redistilled. Repetition of this process, using a relatively inefficient vacuum jacketed column packed with nickel gauze rings provided fractions of ca. 95-98% purity. These fractions were finally purified by careful distillation using a concentric tube distillation column having an efficiency of 17 theoretical plates. These laborious and repetitive distillations eventually yielded products of >99.5% purity as judged by g.l.c., and the materials so obtained were considered sufficiently pure for polymer preparation.

In order to complete the examination of products formed in the HFPO oligomerisation, the lowest boiling fraction was examined by ^{19}F n.m.r. spectroscopy. The spectrum obtained showed this material to be a mixture of dimethyl glutarate, and the ester derived from the trimer of hexafluoropropene epoxide



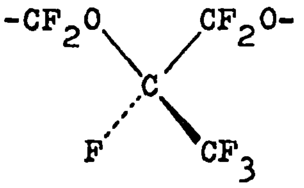
$$CF_3CF_2CF_2O\underset{\underset{CF_3}{|}}{C}FCF_2O\underset{\underset{CF_3}{|}}{C}FCO_2CH_3$$

XXIV

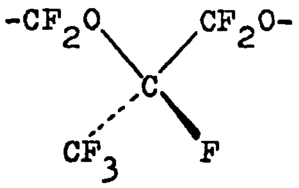
in a mole ratio of ca.7:3. The latter compound may be assumed to be formed as the temperature is allowed to rise toward the end of the oligomerisation reaction, under which condition the rate of fluoride ion transfer becomes significant. The epoxide may be expected to be substantially more reactive towards fluoride ions than an acyl fluoride, accounting for the absence in the product of asymmetric HFPO/glutaryl fluoride adducts which might otherwise be formed at this stage.

Finally, an attempt was made to further characterise the diester derived from the 4:1 adduct of HFPO to hexafluoroglutaryl fluoride. This product derives from the addition of epoxide units to both ends of the acyl fluoride molecule, but two isomers are still permitted by this constraint (XV and XVI). No observable detail in the ^{19}F n.m.r. spectrum allowed an assignment of the product to either of these structures. The mass spectrum of the ester was examined in detail, but no peaks were observed which could not be derived from either XV or XVI, and scrutiny of the I.R. spectra likewise revealed no clues to the final identification of the 4:1 adduct. The question therefore remains unanswered, but for the purposes of the work described in this thesis, the distinction is not of crucial importance, as polymers derived from the two possible isomers should display identical glass transition temperatures within the approximations used in the present ATP approach to T_g prediction.

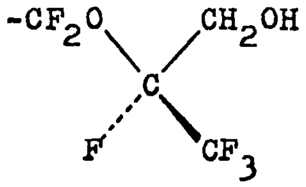
The reduction of the difunctional esters described above to the corresponding diols was accomplished using excess lithium aluminium hydride in diethyl ether. The reduction proceeded smoothly in quantitative yield, and a standard work-up followed by removal of solvent yielded the diols as slightly yellow liquids. These were freed from coloured impurities by molecular distillation, when the diols were obtained as colourless but milky liquids, in agreement with the observations of earlier workers.[106] Over the course of several days, the 2:1 adduct diol crystallised to a waxy solid, m.p. 36-37°C. Previously, this compound has only been reported as a liquid isomer mixture. The 3:1 and 4:1 adduct diols on prolonged standing, partially separated into two liquid layers, the upper layer being present in very small quantity. The milky appearance of the liquids cleared simultaneously. Samples of these upper layers were drawn off, and examined by I.R. and N.M.R. spectroscopy, but these techniques failed to reveal any difference between the upper and lower liquid layers. It therefore appears that both layers consist of similar adducts of HFPO to hexafluoroglutaryl fluoride, with identical functional endgroups. In this connection, it may be noted that the HFPO residues in these compounds can potentially exist in optically isomeric forms:



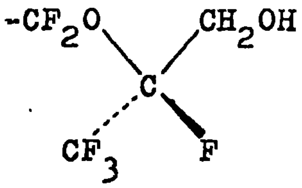
or



and



or



There is therefore a possibility that the 2:1 and higher adducts may exist in diastereomeric forms, although it would perhaps be surprising if these isomers were mutually insoluble.

Condensation Polymer Synthesis

The work described above had resulted in the production of the 2:1, 3:1 and 4:1 adduct diols (XVII, XVIII, XIX and/or XX) in a degree of purity sufficient for polymer production. In addition, the work described in Chapter 3 of this thesis had made available samples of fluorinated butane, pentane and hexane diols. The remainder of this chapter therefore describes the techniques used to prepare polymers from these diols.

The step-growth route to polymer formation imposes important limitations on the reactions and monomers to be used. The progress of polymer formation is described by the degree of polymerisation, $\overline{DP}$, which is the average number of monomer units per polymer molecule. This quantity is related to the degree of reaction, P, i.e., the proportion of functional end groups which have reacted, by the equation

$$\overline{DP} = \frac{1}{1-P}$$

This means, therefore, that for 95% reaction $\overline{DP}$ equals only 20. Such a figure is regarded as a minimum for polymers required for investigational purposes; for polymers which are to be used for fabrication purposes, a $\overline{DP}$ of 50 is normally necessary, and the corresponding P is 0.98. Therefore a figure of at least 95-98% reaction is essential for polymer preparation. The barriers to attainment of such a figure are fourfold; firstly, the presence of monofunctional impurities in either monomer results in a chain terminating reaction. Secondly, in a polycondensation reaction between two different monomers, an exact 1:1 mole ratio of reactants is necessary, or an excess of functional groups of one type will limit chain growth. A third difficulty is side reactions which destroy the reactivity of one functional group toward another, and finally, the reaction is limited by the encounter rate of reactive groups which varies as the square of their concentration and which therefore drops sharply as the reaction nears completion. A further factor which serves to decrease the encounter rate is the increasing viscosity of the reaction mixture as polymerisation proceeds. In practise, these factors conspire to limit the efficiency of polymerisation reactions so that although many reactions are known which will proceed to 90% of completion comparatively few reactions are adaptable to practical polymer synthesis. Some of the best studied of these are polyesterification reactions, and the reaction of a fluorinated diol with a diacyl chloride has been shown to be adaptable to the synthesis of high molecular weight polyesters.[120]

In order to yield polymers whose structures resembled I as closely as possible, it was intended to react the diols described previously, with isophthalloyl chloride. Earlier workers in these laboratories had used a polymerisation apparatus developed by workers at the Royal Aircraft Establishment, Farnborough. This apparatus featured a reaction tube in which the monomers were placed, and equipped with a gas insertion tube leading almost to the bottom of the reaction tube. This was used to bubble nitrogen through the melted reactants, carrying out the hydrogen chloride formed in the reaction and mixing the monomers together in one process. This apparatus was used for the preparation of the first three polyesters, from the non-ether containing diols. The gas outlet tube was protected by a sulphuric acid bubbler, and in the final stages of reaction the nitrogen lead-in was sealed, and the outlet connected to a vacuum line in order to out-gas the product. Although this apparatus has been shown to be capable of use in the preparation of polyesters of acceptably high $\overline{DP}$,[65] it was found that the stream of nitrogen tended to carry volatile monomers out of the reaction mixture in the early stages of a polymerisation. In the later stages of the reaction, however, the melt viscosity increased to the point where an open channel was formed through the polymer which carried the whole gas flow, so that bubbles do not rise through the mixture and the mixing action is lost. Finally, there is the possibility that the rather large volume of gas passed through the mixture may contain sufficient water vapour to hydrolyse a significant number of acyl chloride groups, and oxygen to effect oxidative degradation. An alternative apparatus was therefore devised to alleviate these difficulties. This retained the original reaction tube, which was fitted with a gas lead-out and a mercury sealed stirrer gland. The stirrer was designed to reach to the bottom of the reaction tube, and was spirally shaped to force the melt downwards and maximise circulation of viscous material. When the reaction neared its end, the stirrer was removed, and the tube evacuated to outgas the product as before. In use, this apparatus led to less sublimate appearing on the cool upper section of the reaction tube, and the $\overline{DP}$ of polymers obtained was higher than when the gas circulating technique was employed.

Fluorinated alcohols are significantly more acidic than their hydrocarbon counterparts, but react rather slowly in esterification reactions.[120,121] Polymerisations were therefore carried out over a period of ca. 72 hours each, the reaction temperature being progressively raised over this period from a little above the melting point of the isophthal oyl chloride (ca.70°C) to a limit of 150°-170°C. When no further increase in melt viscosity was observed, and the rate of gas evolution from the mixture had become very slow, the mixture was cooled under vacuum, and removed from the apparatus by freezing in liquid air, and shattering the reaction tube.

The characterisation of the polymeric products obtained, is described in Chapter 5 of this thesis.

Experimental

The Addition of Hexafluoropropene Epoxide to Hexafluoroglutaryl Fluoride

Dry caesium fluoride (75g) was redried by heating in vacuum (250°C/10^{-3} torr) in a two necked round bottom flask (500ml). Into this flask diglyme (ca. 200mls) was freshly distilled from lithium aluminium hydride under an atmosphere of dry nitrogen. The flask was sealed and transferred to a dry nitrogen purged glove box, where hexafluoroglutaryl fluoride (49g) was added, the flask contents mixed, and allowed to stand overnight. Next morning, the solution was filtered from excess caesium fluoride through a sintered glass filter tube into a three neck round bottom flask (1 L) containing a teflon encapsulated magnetic stirrer follower bar. The flask was sealed, removed from the glove box, and connected to a gas/vacuum handling line which was used to purge the apparatus with nitrogen while a thermometer and cold finger condenser were added. The flask and contents were frozen in liquid air, and the apparatus was evacuated (0.1 torr). A can of hexafluoropropene/hexafluoropropene epoxide mixture was attached to the apparatus, which was isolated from the pump and the gas (100g) was allowed to flow and condense into the reaction flask. The relative proportion of hexafluoropropene and hexafluoropropene epoxide in the gas mixture was estimated by comparison of bands at 1790 cm^{-1} (band A, C_3F_6) and 1605 cm^{-1} (band B, C_3F_6O) in the IR spectrum of the mixture.

The proportion of hexafluoropropene in the mixture was estimated as 0.13×(Intensity of band A/Intensity of band B).[113] In this case, the propene was present at a level of only a few percent. When the transfer of volatiles was complete, the apparatus was let down to atmospheric pressure with dry nitrogen, the cold finger was charged with acetone and solid carbon dioxide, and the liquid air bath was replaced with an acetone bath maintained at -50°C by addition of small pieces of solid carbon dioxide. When the flask contents had warmed sufficiently, stirring was started and maintained throughout the reaction. The reaction mixture equilibrated at <u>ca</u>.-40°C, and was stirred for 6 hours at this temperature. After this period, the addition of CO_2 to the cooling bath was stopped, and the flask was allowed to warm slowly to room temperature. When the mixture reached <u>ca</u>.-15°C, a slight exotherm resulted in the temperature rising to <u>ca</u>. 0°C. After this exotherm had subsided, no further action was evident, and the apparatus was dismantled. The liquid product, consisting of two separate layers, was poured into methanol (1L) with stirring; an exothermic reaction was observed, and the methanol solution was left to stir overnight.

In the morning, water (3L) was added, and the heavy oil which separated was removed. The aqueous layer was extracted with ether (1 x 200mls, 3 x 100mls), and the extracts combined with the oil. Distillation of the solvent yielded a crude fluorocarbon product (118g) which was combined with the products from other reactions for separation and purification of the components of the mixture.

Separation and Purification of HFPO Derived Di-esters

The product mixture from a series of HFPO/HFGF reactions performed as above (270g) was progressively separated by a series of nineteen fractional distillations. Where appropriate, intermediate fractions of similar boiling range were combined and redistilled. The principal fractions derived from these distillations, 95-98% pure compounds by g.l.c., were finally purified on a still utilising an efficient glass concentric tube column to yield dimethyl 2,4,4,5,5,6,6,7,7,8,8,10-dodecafluoro-3,9-dioxa-2,10-bis trifluoromethyl undecane-1,11-dicarboxylate, (XIII) 16.1g, b.p. 66°C/0.6 torr (lit 81-82°C/1.5 torr[110]); dimethyl 2,4,4,5,5,6,6,7,7,8,8,10,11,11,13-pentadecafluoro-3,9,12-trioxa-2,10,13-tris trifluoromethyl tetradecane-1,14-dicarboxylate (XIV) 21g, b.p. 87°C/0.6 torr, and dimethyl 2,4,4,5,5,6,6,7,7,8,8,10,11,11,13,14,14,16-octadecafluoro-3,9,12,15-tetraoxa-2,10,13,16 tetrakis trifluoromethyl heptadecane-1,17-dicarboxylate (XV) and/or dimethyl 2,4,4,5,7,7,8,8,9,9,10,10,11,11,13,14,14,16-octadecafluoro-3,6,12,15-tetraoxa-2,5,13,16-tetrakis trifluoromethyl heptadecane-1,17-dicarboxylate (XVI) 28.5g, b.p. 103°C/0.5 torr. These quantities were considered sufficient for polymer production: no attempt was made to recover further quantities of these compounds from intermediate fractions. Also isolated from the mixture was methyl 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-3,6-dioxa-2,5-bis trifluoromethyl nonanoate, 7.4g, b.p. 88°C/16 torr. Dimethyl hexafluoroglutarate and esters derived from higher adducts of HFPO to HFGF were also identified in the mixture.

Preparation of Diols Derived from HFPO

Diester XIV (20g) in diethyl ether (200mls) was added dropwise to a stirred suspension of lithium aluminium hydride (5g) in diethyl ether (50mls). The addition was complete in ca. 30 mins., and the reaction mixture was then allowed to stir for 2 hours at room temperature. Sufficient distilled water was then added to the reaction dropwise, until the grey suspension became white, and the rapid evolution of hydrogen ceased. Hydrochloric acid (10%) was added slowly until the solid had dissolved, then the aqueous layer was removed, extracted with ether (2 x 100mls), and the organic solutions combined. The ether was removed by distillation, and the pale yellow liquid residue was transferred to a molecular still. After outgassing, the product was purified at 105°C/0.001 torr to yield 2,4,4,5,5,6,6,7,7,8,-8,10,11,11,13-pentadecafluoro-3,9,12-trioxa-2,10,13-tris trifluoromethyl tetradecane-1,14-diol (XVIII), 15.8g, 85% after purification.

Diester XIII (11.3g) was likewise reduced with lithium aluminium hydride (5g) to provide 2,4,4,5,5,6,6,7,-

7,8,8,10-dodecafluoro-3,9-dioxa-2,10-bis trifluoromethyl undecane-1,11-diol (XVII) purified by molecular distillation (90°C/0.001 torr) to yield 9.4g (91.7%) of pure product.

Similarly, diester XV and/or XVI (22.7g) was reduced with lithium aluminium hydride (5g) to give 2,4,4,-5,5,6,6,7,7,8,8,10,11,11,13,14,14,16-octadecafluoro-3,9,-12,15-tetraoxa-2,10,13,16-tetrakis trifluoromethyl heptadecane-1,17-diol (XIX) and/or 2,4,4,5,7,7,8,8,9,9,10,10,-11,11,13,14,14,16-octadecafluoro-3,6,12,15-tetraoxa-2,5,-13,16-tetrakis trifluoromethyl heptadecane-1,17-diol (XX), 18.4g (86.2%) after purification by molecular distillation (105°C/0.001 torr).

Polymer Preparation

a) A glass reaction tube was charged with 2,2,3,3-tetrafluorobutane-1,4-diol (7.2648g) and isophthaloyl chloride (9.1000g): the weighings were performed as rapidly as possible to minimise the absorption of atmospheric moisture. The tube was closed with an adaptor carrying a gas inlet tube equipped with a tap, and an outlet. The reactants were melted together by means of a hot air blower, then a slow stream of dry nitrogen was passed down the gas inlet tube and bubbled through the mixture, the outlet tube being guarded by an oil bubbler. Gas was evolved, and after a short period (ca.15 mins.) the mixture became homogenous. The tube was placed in an oil bath at 90°C, and the reaction was allowed to proceed. The oil bath temperature was progressively raised, ultimately to 170°, and the nitrogen flow maintained until the high viscosity of the melt prevented bubbles from forming in the liquid. The nitrogen flow was then stopped, the tap sealed, and the outlet tube connected to a vacuum line, which was used to outgas the polymeric product. When the evolution of gas ceased, the tube was cooled, the vacuum disconnected, and the polymer was recovered by freezing in liquid nitrogen, and shattering the tube.

Polymerisations were likewise carried out between 2,2,3,3,4,4-hexafluoropentane-1,5-diol (10.44g) and isophthaloyl chloride (10.00g), and between 2,2,3,3,4,4,-5,5-octafluorohexane-1,6-diol (5.5629g) and isophthaloyl chloride (4.3090g).

b) A reaction tube was charged with diol XVII (7.2177g) and isophthaloyl chloride (2.6930g). The tube was closed with a stoppered adaptor carrying a gas outlet guarded by an oil bubbler. A hot air blower was used to melt the reagents together, then a glass spiral stirrer carried in a mercury sealed gland was rapidly inserted in place of the stopper. Oil was floated on the mercury surface to prevent splashing, and stirring was maintained at the maximum possible rate while the reaction was continued as in method a). When the reaction neared completion, the stirrer was withdrawn, the stopper replaced, and the polymeric product outgassed and recovered as in method a).

Likewise, polymerisations were carried out between diol XVIII (11.6902g) and isophthal oyl chloride (3.3425g), and between diol XIX and/or XX (13.7827g) and isophthal oyl chloride (3.1936g).

CHAPTER 5

Polymer Characterisation

Introduction

The polymers prepared in the work so far described in this thesis, in common with all polymer samples, consisted of a mixture of molecules of differing molecular weight. In view of the dependance pointed out in Chapter 1 of the physical properties of a polymer on the molecular weight of the sample being examined, $\bar{M}$ is evidently a highly important parameter from the point of view of polymer characterisation. A completely satisfactory specification of a polymeric sample requires a knowledge of the molecular weight distribution, and such a full knowledge of the sample may be gained by the use of gel permeation chromatography combined with one of the techniques of molecular weight measurement described below. Molecular weight distributions for well characterised polymer systems can be routinely obtained from precalibrated gel permeation apparatus, but the procedure can be tedious and difficult for polymers of novel structure where suitable solvents and conditions must be found. It is more usual for an average molecular weight to be obtained, the value of which will depend on the method by which the measurement is made.

The measurement of sedimentation rates in an ultra centrifuge yields the weight average molecular weight, $\bar{M}_w$. The technique relies on the centrifugal force on a polymer particle being balanced by its tendency to diffuse back into the bulk solvent. The same figure, $\bar{M}_w$, may be obtained from measurements of the light scattered from polymer solutions. The scattering arises from local variations in refractive index in the vicinity of polymer particles, and is therefore dependant on the size and weight of the polymer molecules. The apparatus required for carrying out such measurements was not available in these laboratories.

A simple method of molecular weight determination is based on the viscosity of polymer solutions. Measurements of the flow time of a solution, and of the pure solvent in a viscometer allow the calculation of the intrinsic viscosity of the polymer sample

$$[\eta] = \lim_{C \to 0} \frac{t - t_o}{C.t_o}$$

where C is the solution concentration, t is the flow time of the polymer solution and t_o is the flow time of the pure solvent. Then $[\eta]$ is related to the molecular weight of the sample by the equation

$$[\eta] = k \bar{M}^{\alpha}$$

Unfortunately, k and α are empirical constants which cannot be obtained except by viscosity measurements on samples of known $\bar{M}$, though these values may be transferred to other polymers of sufficiently closely related structure. Therefore viscosity studies on novel polymers are in general useful only to establish the order of magnitude of molecular weight. This may, however, be sufficient for purposes of polymer characterisation, if it can be shown that the property in question remains constant for a further increase in molecular weight, i.e., that the plateau value of the property has been reached.

Conventional methods of chemical analysis may be applied to polymer $\bar{M}$ determination in certain cases. The chemical structures at each end of a polymer chain may have different reactivity from the main chain groups, in which case a quantitative test of the end-group concentration in a polymer solution will provide information on the molecular weight of the sample. In samples of high $\bar{M}$, a highly sensitive analytical method is required, since the end-group concentration is low. Typical methods include titration of acid end-groups, or reaction of the polymer chain ends with a suitable reagent to give a spectroscopically detectable derivative. It is possible in some cases to determine end-group concentration directly by spectroscopy. It is obvious that measurements of $\bar{M}$ by such means must be tailored to each individual case, and results must be regarded with care, since chain branching reactions or cyclization can cause large inaccuracies in $\bar{M}$ as observed by end-group analysis.

The most common means of measurements of $\bar{M}$ for all types of samples, is the use of colligative properties. As applied to polymers, these methods yield a number average molecular weight $\bar{M}_n$. Polymer samples usually cause large deviations from ideal thermodynamic behaviour in their solutions, so in all cases, an extrapolation to zero solute concentration is necessary for accurate results to be obtained. Because of the high molecular weight of polymers, only the more sensitive colligative methods are applicable to these systems, and the conventional freezing point depression and boiling point elevation of polymer solutions is immeasurably small. However, osmotic pressure in polymer solutions is appreciable, and provides a useful means of $\overline{M}$ measurement.

Although, as mentioned above, the boiling point elevation of a polymer solution is very small, the changed vapour pressure of such a solution has been used to measure high molecular weights by less direct means, and a commercial instrument is available which works on this principle. A thermostatted chamber is saturated with the vapour of some suitable solvent; supported within the chamber are two thermisters, each of which is fitted with a retaining ring to hold a drop of liquid. A drop of pure solvent is placed on one thermister, and a drop of the solution under test is placed on the other. Solvent vapour then condenses preferentially into the drop of polymer solution, acting against the lowered vapour pressure of this liquid. This phenomenon has been termed vapour pressure osmosis, since a transport of solvent against a solute concentration difference is involved. Because of the condensation of solvent vapour into the polymer solution, compared to the static equilibrium between the pure solvent and its saturated vapour pressure which pertains on the other thermister, the two drops of liquid reach slightly different temperatures, and the

Deviation of Observed from Sample $\bar{M}$ in the Presence of Contaminants

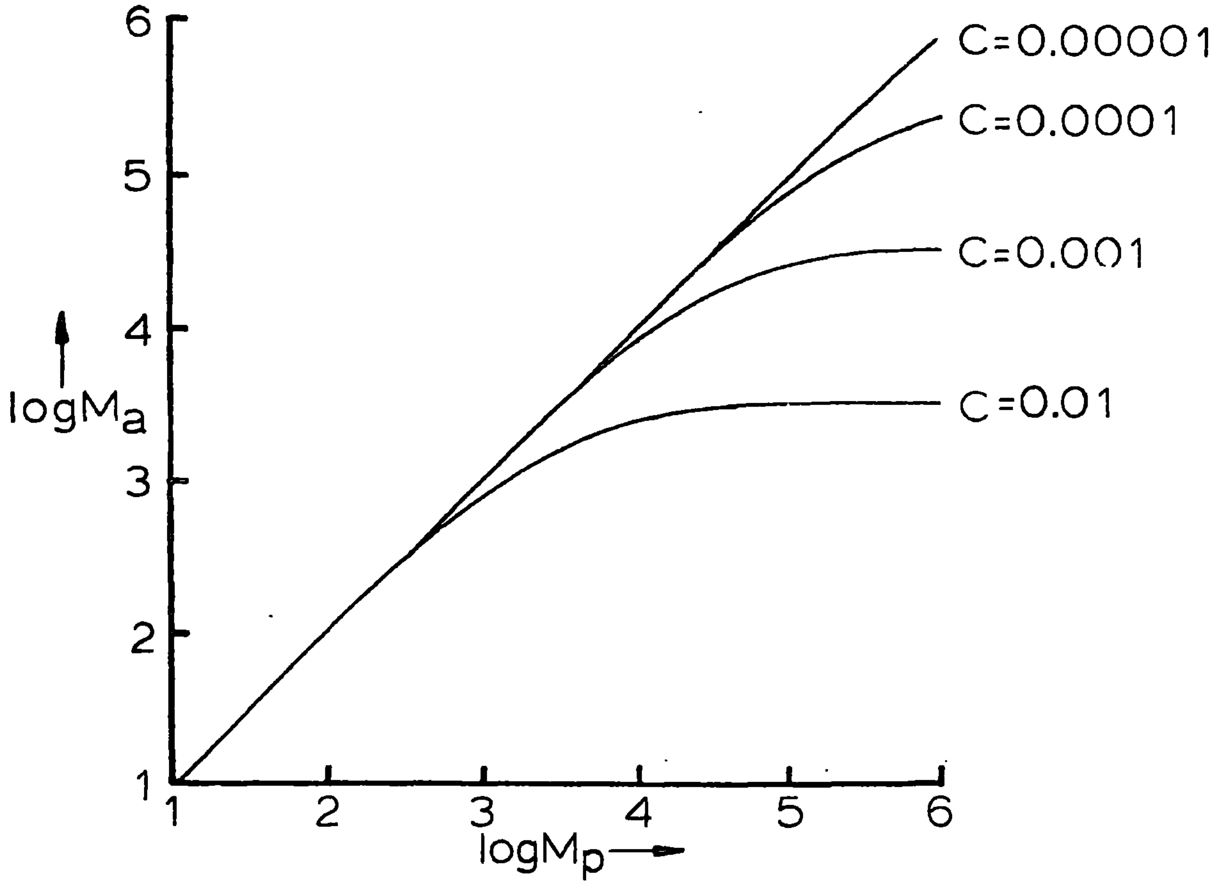


Figure 5.1

difference may be readily measured by including the two thermisters in a bridge circuit. The temperature difference is proportional to the molality of the sample solution, within the approximation of ideal solution behaviour. The actual magnitude of the temperature difference is a characteristic of the particular machine in use, of the solvent in question, and of the detailed conditions of operation, especially the temperature of the chamber.

Use of an instrument of this type allows routine measurement of molecular weights up to ca.40,000, for any sample for which a reasonably volatile solvent can be obtained in pure form. Quite small sample masses are required, and a rapid sample turnover can be achieved. Change-over from one solvent to another is slightly more cumbersome, as rigourous cleaning and drying of the sample chamber is necessary prior to thermal equilibration at a new temperature.

In any molecular weight determination based on colligative properties, the purity of solvent and sample become more critical as the $\bar{M}_n$ of the sample rises. This is because a low molecular weight contaminant can contribute as many particles to solution as a much larger weight of high molecular weight sample. The relationship between the $\bar{M}$ of a sample, and the observed figure in the presence of a low M contaminant is:

$$M_A = \frac{M_p M_c}{M_c + C.M_p} .$$

where M_A is the apparent molecular weight, M_p is the true molecular weight of the polymer sample, M_c is the molecular weight of the contaminant, and C is the proportion of contaminant in the sample by weight. The equation is valid for small C. The consequences of this deviation are graphically illustrated in Figure 5.1 where M_A is plotted against M_p for values of C from 0.01 to 0.00001, with M_c assumed as 32 (i.e. contamination of the sample with from 1% to 0.001% methanol). Qualitatively similar results will be obtained by assuming other fairly low values for M_c. It will be seen that impurity levels as low as 0.1% cause very large inaccuracies in observed M, while the discrepancy is small if the impurity is present at levels below 0.001%. Appropriate precautions to be taken in preparing samples for molecular weight measurement therefore include rigourous degassing of the polymer to remove volatiles, and the careful avoidance of contamination with non-volatile impurities such as vacuum grease. Highly pure solvent is desirable for the measurement of $\overline{M}$, and hygroscopic solvents such as DMF should be kept from contact with the air, as far as possible.

In order to ensure that meaningful results are obtained from the measurement of polymer properties, it is necessary to establish that the property in question has reached its plateau value, i.e., that it is independent of further increase in the molecular weight of the polymer. A set of samples of each polymer is therefore required, of differing $\overline{M}$, and such a set may be obtained from the single polymer sample which results from a polymerisation reaction, by use of a fractionation technique. The most common method is to dissolve the polymer sample in a rather large quantity of solvent, yielding a solution strength of the order of a few percent. A second liquid, which is a non-solvent for the polymer, but which is miscible with the solvent, is then added dropwise with rapid stirring to this solution until a turbidity appears. The solution is allowed to stand and equilibrate, when a second phase separates, which contains the highest molecular weight fraction of the polymer. This fraction is withdrawn by pipette, and the polymer recovered by removal of the solvent and non-solvent under vacuum, after which a further addition of non-solvent precipitates a second fraction, of lower molecular weight. This process may be repeated several times, yielding samples of progressively lower $\bar{M}$, until the final fraction is obtained by distillation of the solvent from the bulk solution. Provided that the physical property under investigation remains constant between the two samples of highest molecular weight, it may be taken that the plateau has been reached.

In the work described in this thesis, the physical properties of primary importance are the thermal stability and glass transition temperature, which together determine the limits of the working temperature range for the polymer. The techniques of thermal analysis used to determine these parameters are therefore of the greatest importance. Polymer decomposition, like any chemical reaction, does not occur sharply at one particular temperature, but proceeds at a rate which rises sharply as the temperature is increased. An apparatus is therefore required which can measure the rate of polymer decomposition as the temperature is varied. Although polymer decomposition can be measured calorimetrically, the most convenient and widely used criterion of polymer decomposition, is that of weight loss. The principle involved in thermal stability measurement is then to suspend the sample from one arm of a balance, so that it hangs in a furnace, whose temperature may be accurately controlled. The temperature of the sample is taken to be the same as a thermocouple which is mounted as physically close to the sample as possible. The temperature may either be held constant at a predetermined figure, or raised at a constant programmed rate. The balance provides an output to a chart recorder, so that the weight loss is automatically obtained in graphical form, if desired. Studies of this type, termed thermogravimetry (TG) have been used in the study of polymers and other systems for many years, and commercial instruments are available.

The various phenomena which occur in the vicinity of the glass transition temperature of a polymer have been discussed in Chapter 1 of this thesis, and several methods of T_g estimation have been used. The use of mechanical methods, and dilatometry are particularly favoured by polymer engineers and physicists, but these methods either require rather large samples, or are time consuming in use. The favoured method of T_g measurement in this work is therefore calorimetric.

The differential scanning calorimeter (DSC) is an instrument consisting of a matched pair of sample pans, each fitted with a temperature sensing element, and an electric heater. The heaters and temperature sensors are linked through control and comparison circuitry, so that the two sample pans are always maintained at the same temperature, and that this temperature can be held constant, or raised or lowered at a controlled rate. The amount of power required to raise the temperature of each sample pan is monitored, and the difference is made available as an output to a chart recorder. If a sample is placed in one pan, therefore, and the temperature raised at a constant rate, an output is produced as a voltage proportional to the specific heat of the sample. A first order thermodynamic transition is displayed by the instrument as a peak on the chart recorder, (Fig. 5.2) while a second order transition, or glass transition produces only a baseline shift (Fig. 5.3).

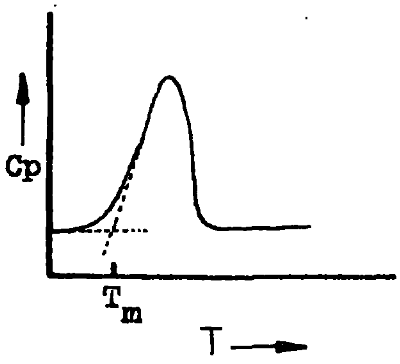


Fig. 5.2
DSC trace of a melting point transition.

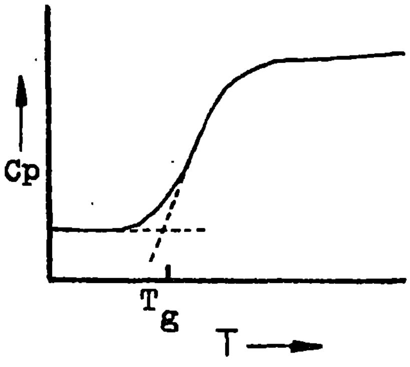


Fig. 5.3
DSC trace of a glass transition.

The calibration of the instrument is checked by reference to samples of known melting point. It is convenient to take T_m as the point of intersection of the extrapolated baseline and the extrapolated straight line portion of the leading edge of the transition peak, as shown in Fig. 5.2. A corresponding extrapolation of the curve in Fig. 5.3 gives the temperature of the glass transition. An alternative procedure is to take T_m as the peak of the melting curve, and T_g is correspondingly taken as the mid-point of the baseline shift, but the former method was employed in this work.

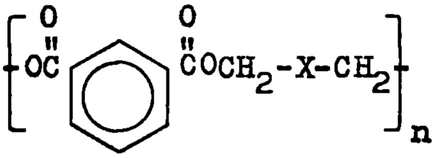
As has been stated earlier in this work, the observed glass transition temperature is dependent on the rate at which the measurement is made, i.e., on the heating rate employed. This factor must therefore be standardised if measurements on different samples are to be comparable. In order to minimise discrepancies due to thermal conductivity it is also desirable to use similar sample sizes, and samples of similar physical form.

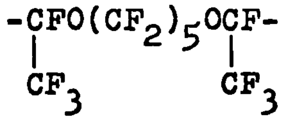
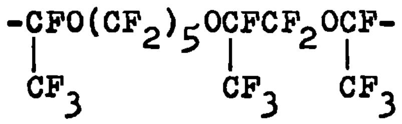
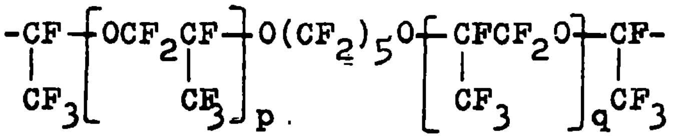
The techniques described above permit the characterisation of a polymer with regard to its working temperature range, while ensuring that the parameters measured are significant in terms of molecular weight. The application of these methods to the polymers prepared in the earlier part of this work, is described in the next section.

Discussion

In the work described in this chapter, eight polymers were examined, all of which were derived from isophthaloyl chloride and fluorinated α,ω-diols. For convenience, these are denoted Polyester 1 — Polyester 8, and the structure corresponding to each number is shown in Figure 5.4

Structures of Polymers Examined



	X
Polyester 1	$-CF_2CF_2-$
Polyester 2	$-CF_2CF_2CF_2-$
Polyester 3	$-CF_2CF_2CF_2CF_2-$
Polyester 4	$-CF_2OCF_2-$
Polyester 5	$-(CF_2)_4O(CF_2)_4O(CF_2)_4-$
Polyester 6	 $-\underset{CF_3}{\underset{\vert}{C}}FO(CF_2)_5O\underset{CF_3}{\underset{\vert}{C}}F-$
Polyester 7	 $-\underset{CF_3}{\underset{\vert}{C}}FO(CF_2)_5O\underset{CF_3}{\underset{\vert}{C}}FCF_2O\underset{CF_3}{\underset{\vert}{C}}F-$
Polyester 8	 $-\underset{CF_3}{\underset{\vert}{C}}F\left[OCF_2\underset{CF_3}{\underset{\vert}{C}}F\right]_pO(CF_2)_5O\left[\underset{CF_3}{\underset{\vert}{C}}FCF_2O\right]_q\underset{CF_3}{\underset{\vert}{C}}F-$

$p + q = 2$

Figure 5.4

Of the above polymers, six (Polyesters 1,2,3,6,7,8) were prepared during this work: the other two (Polyesters 4,5) had been prepared by earlier workers on this research project. The structures of Polyesters 1,2,3,4 and 5 are defined unequivocally by the repeat units shown in Figure 5.4. Polyesters 6,7 and 8, however, contain chiral centres, and the stereoisomeric possibilities mentioned in Chapter 4 with regard to the monomers are carried over into these polyesters. In addition, Polyester 7, and also Polyester 8 for the case $p=0$, $q=2$, are derived from monomers which are assymetric with respect to interchange of the functional endgroups. These polyesters may therefore be expected to contain structures derived from head-to-head, tail-to-tail, and head-to-tail assembly of the monomer units. None of the above isomeric possibilities were amenable to study, however, and it is difficult to see how the relative proportions of the various structures could be determined.

Polymer Characterisation - Fractionation and Molecular Weight Measurement

The three polymers derived from hexafluoropropene epoxide were fractionated to ensure that the plateau region of the T_g vs $\overline{M}$ curve had been reached. The polymers were dissolved in 1,1,2-trichlorotrifluoroethane, and precipitated by the addition of methanol. The resultant fractions were degassed ($150^{\circ}C/10^{-3}$ torr) and molecular weights determined by vapour pressure osmometry. The molecular weights and degrees of polymerisation for each fraction are shown in Table 5.1.

Molecular Weights of Fractions from some Fluorinated Polyesters

Fraction		A	B	C	D	Residue	Unfractionated
Polyester 6	$\bar{M}$	35,400				14,400	17,300
	DP	52				21	26
Polyester 7	$\bar{M}$	28,700	32,200	27,000	28,400	14,800	20,300
	DP	34	38	32	34	18	24
Polyester 8	$\bar{M}$	52,700	44,200				
	DP	52	44				

Table 5.1

It will be observed from the Table that the highest $\bar{M}$ fraction of each polymer displays a satisfactory DP, particularly Polyester 6 and Polyester 8. The fractions of Polyester 7 show an irregular order of $\bar{M}$, but the contrast between the $\bar{M}$ observed for the precipitated fractions, and for the low molecular weight residue shows that fractionation had occurred. It is therefore more likely that the molecular weight measurements are inaccurate in this case, possibly due to contamination of the sample in some way. If this is the case, the true molecular weights of the earlier fractions of this material may well be higher than shown in the Table. The polymers derived from fluoro butane, pentane and hexane diols (Polyesters 1, 2 and 3) were degassed, and the unfractionated polymers examined by vapour pressure osmometry, using DMF as solvent. The results obtained are shown in Table 5.2.

Molecular Weights of Some Fluorinated Polyesters

	Polyester 1	Polyester 2	Polyester 3
$\bar{M}$	4500	8300	4800
DP	15	24	12

Table 5.2

The observed DP of these polymers is rather lower than those observed for the polyesters derived from HFPO. This may be due in part to the different apparatus used for the polymerisation. In addition, DMF is a solvent which, because of its hygroscopic nature, is likely to give anomolously low apparent molecular weights. Unfortunately, no alternative solvent could be found for these polymers. The DP's given above all relate to the number of repeat units in the polymer chain. However, each repeat unit in these copolymers is derived from two monomer units, and the DP as related to the degree of completion of the polycondensation reactions used to form the polymer is double the above figures.

Glass Transition Temperatures

The glass transition temperatures of the six polymers prepared in this work were measured by differential scanning calorimetry. In order to ensure comparability between the results, the procedure was standardised as far as possible. The polymer samples were degassed by heating and pumping under vacuum (150 - 180°C/10^{-3} torr), then cooled, and small samples (ca.10mg.) transferred to aluminium sample pans, which were sealed in a press. The bottoms of the pans were flattened to provide good thermal contact between the sample and the sensing element of the DSC, then placed in the instrument.

Initial experience showed that when Polyester 3 was cooled slowly, it crystallised to such an extent that the glass transition became unobservable (T_m = 398K, 125°C). All samples were therefore quenched to -100°C from 200°C at the maximum cooling rate of the instrument (320°/min). The initial temperature of 200°C was intended not only to remove any crystallinity and strain from the samples, but also to allow them to flow into an even layer on the base of the sample pan. From -100°C, the temperature was raised to ca.50° below the glass transition region, which had previously been measured approximately. Recording of the output was then begun, and the temperature of the samples programmed up at 40°C/min over a 100°C range. This procedure was repeated for all the samples, and was found to give results reproducible to $\pm$ 1°C. It was found that temperature calibration of the instrument was somewhat unstable, so that readings taken on consecutive days could differ by 5 - 7°C. The results presented here were therefore obtained within the space of one working day, following recalibration of the temperature scale of the instrument.

In the case of fractionated polymers, all the fractions showed identical T_g ($\pm$ 1°C) showing that the plateau value had been reached. The results obtained are presented in Table 5.3 and the predicted T_g values for the non-ether containing polymers are shown in Table 5.4.

Observed T_g Values of Some Fluorinated Polymers

Polyester	1	2	3	6	7	8
T_g K	306	297	293	268	258	252
°C	33	24	20	-5	-15	-21

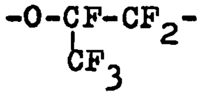
Table 5.3

Predicted T_g Values of Some Fluorinated Polymers

Polyester	1	2	3
T_g K	308	285	287
°C	35	12	14

Table 5.4

When comparing the figures given in these Tables, it is important to realise that the observed results are based on a heating rate of 40°C/min, whereas T_g values predicted by the additive parameter method are necessarily referred to a hypothetical zero heating rate, the correction being made to allow for comparison between data obtained in different laboratories and using different methods of T_g measurement. This correction could amount to <u>ca</u>. -10°C,[122] giving a closer fit between observed and predicted values. It was found that using the techniques and samples described above, changing the heating rate by a factor of X 2, led to a change in observed T_g of <u>ca</u>.2 - 3°C, but a proper study of this effect was not possible, due to instrument stability and sensitivity problems, and limited time. The polymer of hexafluoropentane diol has been synthesised previously, and the T_g observed here agrees well with the values of 25°C and 22°C reported by the earlier workers.[123,84]

By using the observed values of T_g for the ether-containing polymers, it is possible to obtain a value for the T_g contribution made by the  $-O-\underset{\displaystyle CF_3}{\underset{|}{CF}}-CF_2-$ group, i.e., the T_g of the hypothetical high molecular weight homopolymer of hexafluoropropene epoxide. The additive temperature parameter approach is used, the weighting being made according to the number of torsionally independant groups in the polymer chain, as described in Chapter 1 of this work. The division of the three polymers involved into their constituent groups is shown in Figures 5.5 - 5.7.

Decomposition of Polyester 6 into Torsionally Independant Groups

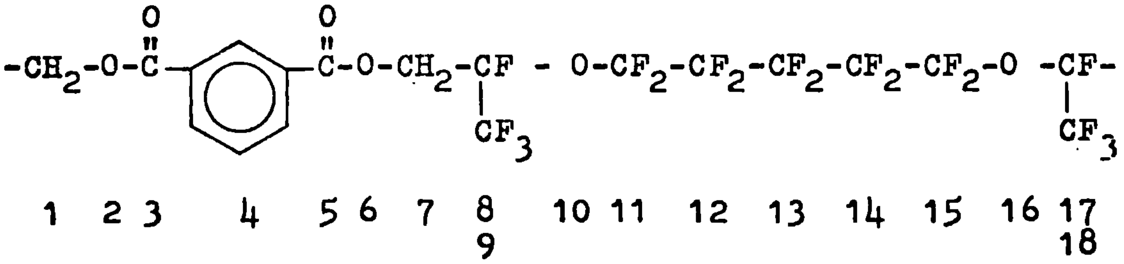


Figure 5.5

Decomposition of Polyester 7 into Torsionally Independant Groups

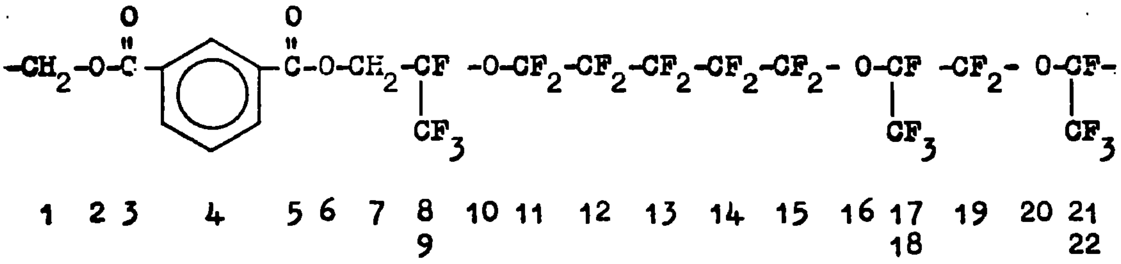


Figure 5.6

Decomposition of Polyester 8 into Torsionally Independant Groups

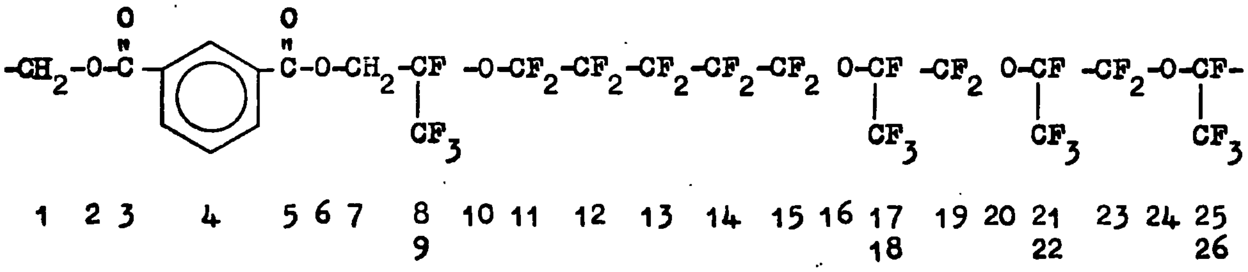


Figure 5.7

It will be noted that the eighteen groups present in Polyester 6 appear unchanged in Polyester 7 and Polyester 8. Now, for Polyester 6

$$\sum_{n=1}^{18} X_n T_{g_n}/18 = 268$$

For Polyester 7

$$\sum_{n=1}^{22} X_n T_{g_n}/22 = 258$$

Because each group has been explicitly labelled independantly, $X_n = 1$ for all values of n.

Therefore $$\sum_{n=1}^{22} T_{g_n}/22 = 258$$

or $$\sum_{n=1}^{18} T_{g_n}/22 + \sum_{n=19}^{22} T_{g_n}/22 = 258$$

But, $$\sum_{n=1}^{18} T_{g_n}/18 = 268$$

Substituting,

$$\frac{18}{22}.268 + \frac{4.}{22} T_g^{1} = 258$$

Where T_g^1 is the mean T_g contribution of the four independant groups -O-, $-CF_2-$, $-\underset{|}{C}F-$ and $-CF_3$. This yields T_g^1 = 213 K, which is the answer sought.

Proceeding in like manner with Polyester 6 and Polyester 8, we obtain

$$\frac{18}{26}.268 \quad + \quad \frac{8}{26}\, T_g^1 \quad = \quad 252$$

Giving $\quad T_g^1 = 216$ K

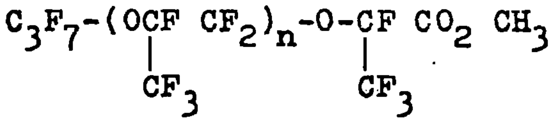
Finally, using the figures for Polyester 7 and Polyester 8, we obtain

$$\frac{22}{26}.258 \quad + \quad \frac{4}{26}.\, T_g^1 = 252$$

Which gives $\quad T_g^1 = 219$ K

The mean of these three values is 216 ± 5K, or -57 ± 5°C. The three equations are, in fact, not linearly independant, and a proper derivation of the value of T_g^1 would involve a least-mean-squares solution of a rather larger set of data than is used here, as well as incorporating the extrapolation or correction to 'zero heating rate' mentioned earlier. It is found, that a 1°C change in the observed T_g of a polymer produces a 5° change in T_g^1, giving the quoted limit on accuracy. Nevertheless, the value obtained, -57°C, is of sufficient value to be worth examining in the light of certain other measurements. Firstly, there are the observed T_g values for HFPO telomers; these were measured under the same conditions as the high polymers, the values obtained are shown in Table 5.5.

Observed T_g of Low Molecular Weight HFPO Telomers



$$C_3F_7-(O\underset{\displaystyle CF_3}{\underset{|}{C}}F\ CF_2)_n-O-\underset{\displaystyle CF_3}{\underset{|}{C}}F\ CO_2\ CH_3$$

n		12	15
T_g	K	192	187
	°C	-71	-86

Table 5.5

The results plainly show that the plateau value of T_g has not been reached. As n increases, in fact, T_g decreases, an effect which can be explained if it is assumed that the glass transition is raised by association of the terminal groups of the molecules. In these samples, the terminal groups are n - C_3F_7, and $-\underset{\displaystyle CF_3}{\underset{|}{C}}FCO_2CH_3$, and the latter may be expected to associate much more strongly than the fluorinated polyether chains. Although these figures are of the expected order of magnitude, it is clearly dangerous to read great significance into figures obtained on such low molecular weight materials.

Of rather greater interest is the work reported by

Hill[53] who describes the preparation of cleanly bifunctional prepolymers from HFPO, having DP up to ca.50. The end groups of these prepolymers were chemically modified to allow curing by triazine ring formation. The product of the curing reaction is then a tough elastomer having a T_g between -50 and -60°C. The 3°C difference between the latter figure and the predicted T_g of the homopolymer is within the limits of accuracy of the above derivation. If the DP of the prepolymer is below 50, the triazine groups will be present in higher concentration, and T_g will be raised. In the light of these results, it appears that the oligomerisation of HFPO can yield bifunctional derivatives which, on copolymerisation, could be made to yield polymers having T_g in the range sought. Some additional support has been given to the additive temperature parameter approach to T_g prediction, and a fuller analysis of the T_g data presented here should enable predictions to be made of the glass transition temperatures of a wide range of HFPO derived polymers. Such an analysis, however, is dependant on the availability of a computer which already contains data from a large polymer set. This work, therefore, is outside the scope of this thesis, and will be carried out at R.A.E. Farnborough by the sponsors of the work reported here.

Thermal Degradation Analysis

The thermal and oxidative stability of polymers are routinely compared by thermogravimetric analysis (TG), but due to the differing interests and equipment of research workers, no standard procedure has been adopted. If samples are held at a constant temperature, it is possible to measure the weight loss after a convenient period of time. However, if samples of markedly different stability are under study, the differences in rate of weight loss become too large to be measured conveniently, and the apparent difference in thermal stability may vary widely according to the reference temperature chosen. It is therefore more common to program the temperature upwards through the decomposition range of the sample at a constant rate. The weight loss then follows an 'S' shaped curve for most polymers, and a decomposition temperature quoted, which may be the temperature of first weight loss, or when the loss of weight reaches some set percentage of the initial mass of the sample. These temperatures are dependant on the heating rate used, as well as the nature of the sample. Finally, a series of runs on a polymer under different conditions may be used to derive kinetic parameters for the polymer decomposition. Although equations describing a series of consecutive thermolytic reactions have been derived,[124] for the study of polymers a simpler analysis normally suffices, assuming a simple general rate equation for the decomposition. Several methods of processing the TG data have been described, and have been critically compared.[125] It appears that the traditional method of using isothermal conditions for each run is most advantageous, and this method is described more fully below.

Although the difference in polymer decomposition in inert and in oxidising atmospheres is clear, different workers have used significantly dissimilar environments for TG studies. Air is commonly used where an oxidative study is carried out; some workers have used dried or CO_2 free air, but in this work ordinary untreated air was used. Nitrogen, argon or helium have been used as inert atmospheres, while vacuum degradation has been suggested as a readily reproducible condition. However, the use of a vacuum is open to severe objections, in that it will tend to minimise thermal contact between the furnace, the sample, and the temperature measuring device. The inaccuracy could well be significant, as these degradations may be anticipated to have a high enthalpy of reaction, and a resultant temperature change of only a few degrees would produce a marked effect on the rate of degradation. In this study, dry, oxygen-free nitrogen was used.

Initial studies were carried out by the temperature program method. The samples were placed on the thermobalance, and the furnace temperatures adjusted to 200°C. The temperature was then programmed upwards at 1°C/min up to <u>ca</u>.600°C, by which temperature decomposition was essentially complete for all the polymers examined. It was found that an initial small (<u>ca</u>.1 - 3%) weight loss occurred for all polymers before the onset of rapid decomposition. This made the estimation of the temperature of first decomposition subject to considerable error, and the decomposition temperatures reported therefore correspond to 10% weight loss. Tests were carried out in nitrogen and air on the six polymers whose preparation is described in Chapter 4, and in addition, on Polyester 5, which had been prepared by an earlier worker on this project, and the synthesis of which has been described in Chapter 2. The reason for including this material, was to provide a fluorinated alkylene oxide polymer for comparison with the new polymers. Decomposition temperatures are tabulated below, and are quoted to the nearest 5°C.

Temperatures of 10% Weight Loss for Some Fluorinated Polymers (°C)

Polyester	1	2	3	5	6	7	8
N_2	410	420	420	425	375	375	375
Air	370	360	370	375	350	360	365

Table 5.6

It will be seen that within the different classes of polymer, members have essentially identical decomposition temperatures. The polymers derived from hexafluoropropene epoxide appear to have a significantly lower thermal stability than those from the straight chain fluorinated α, ω diols. However, this effect cannot be attributed to the presence of the ether links, since Polyester 5 shows a stability equal to or even greater than the non-oxygen containing polymers. The difference in stability between the polymers is less significant in air than in nitrogen, and the polymers decompose at a temperature ca.40°C lower in air than in nitrogen. However, the entire range of thermal stabilities observed only covers 75°C, and the temperatures quoted are probably only accurate to ca.± 5° - 10°C. In order to gain a greater knowledge of the decomposition of these polymers, a representative of each group was selected for further study of the kinetic parameters of the degradations.

For the more detailed kinetic study of thermal degradation, the polymers selected were Polyesters 3, 5 and 6. In addition, a further polymer, Polyester 4 was included. This polymer was intended to provide a closer comparison to Polyester 6, since they share an ether link β to the ester group. The preparation of this polymer is outlined in Chapter 2, and its thermal stability has been measured by a previous worker as 390°C for 10% weight loss in nitrogen.[45] This measurement was carried out at a heating rate of 4°C/min, but the result obtained for Polyester 2 under identical conditions accords well with the result obtained in this study.

For the purposes of the kinetic study, polymer weight loss is assumed to correspond with a degree of conversion, C, and to follow a general rate equation:

$$\frac{dC}{dt} = K\,(1 - C)^n\, e^{-E/RT}$$

where dC/dt is the rate of fractional weight loss, or rate of conversion, n is the order of reaction, E is the experimental activation energy for the degradation, R is the gas constant, and T is the absolute temperature. The pre-exponential constant K is a characteristic of the degradation. Taking natural logarithms,

$$\ln \frac{dC}{dt} = \ln K + n \ln (1 - C) - {}^{E}/_{RT}$$

When C = 0, then ln (1 - C) = 0, and

$$\ln \frac{dC}{dt} = \ln k - \frac{E}{RT}$$

A plot of $\ln \frac{dC}{dt}$ vs $\frac{1}{T}$ therefore gives a straight line of slope - ${}^{E}/_{R}$, and intercept ln K, and the activation energy for the degradation can thus be evaluated. Although K may also be found from the graph, it involves taking an exponential of an extrapolated result, and therefore will not be very accurate. The above equation relies on the condition C = 0 holding. Experimentally, therefore, polymer decompositions are carried out isothermally, and $\frac{dC}{dt}$ is measured at different values of C. Then ln $\frac{dC}{dt}$ is plotted against ln (1 - C), giving, theoretically, a straight line of slope n. When ln (1 - C) = 0, then C = 0 and the intercept therefore gives ln (dC/dt) at zero conversion. In practice, deviations from a straight line are observed at both high and low values of C. At low values of C, the sample has not yet reached thermal equilibrium with the furnace, and $\frac{dC}{dt}$ is lower than expected. At high values of C, and low values of T, $\frac{dC}{dt}$ is again lower than the theoretical, because a solid residue remains at the end of the degradation. This may in principal be allowed for by taking an 'infinity' reading of the residual fractional weight, W^1, and relating this to C by the equation

$$1 - C = \frac{W - W^1}{1 - W^1}$$

In practice, this correction is made very difficult because, at the low temperature where it is most important, a very long time interval is needed to obtain W^1. Furthermore, the solid residue appears to undergo slow weight loss at its own characteristic rate, i.e., a consecutive reaction analysis would be required for a proper treatment of results. It is found that the simple analysis outlined above gives satisfactory results, with the proviso that an apparent change in the order of reaction at low temperature does not necessarily reflect a true change in the reaction mechanism.

The results obtained by application of this method to the polymers stated, are tabulated below, and illustrated in the graphs. In order to explore the less arduous experimental procedure of measuring $\frac{dC}{dt}$ at constant $C \neq 0$, a plot is shown of $\ln \frac{dC}{dt}$ vs $\frac{1}{T}$ at $C = 0.5$. This obviates the necessity of extrapolating a series of readings to $C = 0$, and minimises the laborious measurement of reaction rates.

Then $$\ln \frac{dC}{dt} = \ln k + n \ln (1 - C) - \frac{E}{RT}$$

A plot of $\ln \frac{dC}{dt}$ vs $\frac{1}{T}$ should yield a straight line of slope $- E/R$, giving the activation energy for weight loss in the later part of the reaction, provided that n is independant of T.

As the essentially non-linear plots of ln (dC/dt) vs ln (1 - C) are not amenable to statistical analysis, lines were drawn by eye through the central portions of these graphs. The extrapolated values of ln (dC/dt) at $C = 0$ and the corresponding values of $\frac{1}{T}$ were then fitted to straight lines by standard statistical techniques,[126] which also allow estimation of the error in the slope of the lines, and therefore of the activation energy for the degradation.

Polyester 3 Degradation Data

		T = 451°C		T = 508°C		T = 552°C	
1 - C	ln(1-C)	$\frac{dC}{dt}(\text{min}^{-1})$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}(\text{min}^{-1})$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}(\text{min}^{-1})$	$\ln \frac{dC}{dt}$
0.9	-0.105	5.762×10^{-3}	-5.156	0.0785	-2.647	0.346	-1.062
0.8	-0.223	5.279×10^{-3}	-5.244	0.0634	-2.683	0.346	-1.062
0.7	-0.357	5.071×10^{-3}	-5.284	0.0600	-2.813	0.338	-1.086
0.6	-0.511	4.512×10^{-3}	-5.401	0.0567	-2.871	0.283	-1.261
0.5	-0.693	3.875×10^{-3}	-5.553	0.0500	-2.996	0.258	-1.354
0.4	-0.916	2.987×10^{-3}	-5.813	0.0383	-3.261	0.254	-1.370
0.3	-1.204	2.012×10^{-3}	-6.208	0.0275	-3.594	0.188	-1.674

Table 5.7

Polyester 4 Degradation Data

		T = 360°C		T = 403°C		T = 452°C		T = 462°C		T = 501°C		T = 521°C	
(1-C)	ln(1-C)	$\frac{dC}{dt}$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}$	$\ln \frac{dC}{dt}$
0.9	-0.105	3.54×10^{-3}	-5.64	0.0219	-3.82	0.0767	-2.57	0.160	-1.83	0.075	-0.255	0.80	-0.223
0.8	-0.223	3.85×10^{-3}	-5.56	0.0175	-4.05	0.0550	-2.90	0.105	-2.25	0.650	-0.431	0.50	-0.693
0.7	-0.357	3.65×10^{-3}	-5.61	0.0150	-4.20	0.0425	-3.16	0.0900	-2.41	0.488	-0.718	0.413	-0.886
0.6	-0.511	3.33×10^{-3}	-5.70	0.0119	-4.43	0.0338	-3.39	0.0625	-2.77	0.413	-0.886	0.283	-1.264
0.5	-0.693	3.12×10^{-3}	-5.77	9.38×10^{-3}	-4.67	0.0240	-3.73	0.0567	-2.87	0.283	-1.26	0.233	-1.456
0.4	-0.916	2.50×10^{-3}	-5.99	5.63×10^{-3}	-5.18	0.0150	-4.20	0.0288	-3.55	0.150	-1.90	0.125	-2.079
0.3	-1.204	1.67×10^{-3}	-6.40	2.81×10^{-3}	-5.87	-	-	8.75×10^{-3}	-4.74	0.043	-3.16	0.031	-3.466

Table 5.8

Polyester 5 Degradation Data

		T = 462°C		T = 496°C		T = 547°C	
1 - C	ln(1-C)	$\frac{dC}{dt}(min^{-1})$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}(min^{-1})$	$\ln \frac{dC}{dt}$	$\frac{dC}{dt}(min^{-1})$	$\ln \frac{dC}{dt}$
0.9	-0.105	8.33×10^{-3}	-4.79	0.0675	-2.70	0.70	-0.357
0.8	-0.223	8.33×10^{-3}	-4.79	0.0575	-2.86	0.675	-0.393
0.7	-0.357	8.33×10^{-3}	-4.79	0.0475	-3.05	0.55	-0.598
0.6	-0.511	8.33×10^{-3}	-4.79	0.0425	-3.16	0.45	-0.799
0.5	-0.693	7.92×10^{-3}	-4.84	0.0375	-3.28	0.35	-1.050
0.4	-0.916	6.67×10^{-3}	-5.01	0.0300	-3.51	0.30	-1.204
0.3	-1.204	5.42×10^{-3}	-5.22	0.0215	-3.84	0.21	-1.561
0.2	-1.609					0.15	-1.897
0.1	-2.303					0.05	-2.996

Table 5.9

Polyester 6 Degradation Data

		T = 354°C		T = 390°C		T = 440°C	
1 - C	ln(1-C)	$\frac{dC}{dt}(\text{min}^{-1})$	$\ln\frac{dC}{dt}$	$\frac{dC}{dt}(\text{min}^{-1})$	$\ln\frac{dC}{dt}$	$\frac{dC}{dt}(\text{min}^{-1})$	$\ln\frac{dC}{dt}$
0.9	-0.105	$1.528\text{x}10^{-3}$	-6.484	0.0258	-3.659	0.1575	-1.848
0.8	-0.223	$1.806\text{x}10^{-3}$	-6.317	0.0300	-3.507	0.1950	-1.635
0.7	-0.357	$1.806\text{x}10^{-3}$	-6.317	0.0233	-3.761	0.1830	-1.701
0.6	-0.511	$1.666\text{x}10^{-3}$	-6.397	0.0173	-4.060	0.1500	-1.897
0.5	-0.693	$1.389\text{x}10^{-3}$	-6.579	0.0150	-4.200	0.1200	-2.120
0.4	-0.916	$1.179\text{x}10^{-3}$	-6.743	0.0105	-4.556	0.0925	-2.381
0.3	-1.204	$7.625\text{x}10^{-4}$	-7.179	$5.5\text{x}10^{-3}$	-5.203	0.0675	-2.696

Table 5.10

Order of Reaction and Temperature in Polymer Degradations

Polyester 3

T°C	451	508	552
n	0.88	0.63	0.50

Polyester 4

T°C	360	403	452	462	501	521
n	0.50	1.5	2.0	2.1	2.0	2.0

Polyester 5

T°C	462	496	547
n	0.1	1.00	1.30

Polyester 6

T°C	354	390	440
n	0.86	1.54	1.25

Table 5.11

Polyester 3 Kinetic Data

T(°C)	$^1/T \times 10^3 (K^{-1})$	$\ln \frac{dC}{dt}(C = 0)$	$\ln \frac{dC}{dt}(C = 0.5)$
451	1.38	-5.0	-5.55
508	1.28	-2.6	-3.00
552	1.21	-0.95	-1.35

Table 5.12

Polyester 4 Kinetic Data

T(°C)	$^1/_T \times 10^3 (K^{-1})$	$\ln \frac{dC}{dt}(C = 0)$	$\ln \frac{dC}{dt}(C = 0.5)$
360	1.58	-5.4	-5.77
403	1.48	-3.7	-4.67
452	1.38	-2.4	-3.73
462	1.36	-1.6	-2.87
501	1.29	+0.1	-1.26
521	1.26	-0.1	-1.46

Table 5.13

Polyester 5 Kinetic Data

T(°C)	$^1/_T \times 10^3 (K^{-1})$	$\ln \frac{dC}{dt}(C = 0)$	$\ln \frac{dC}{dt}(C = 0.5)$
462	1.36	-4.75	-4.84
496	1.30	-2.6	-3.28
547	1.22	-0.15	-1.05

Table 5.14

Polyester 6 Kinetic Data

T(°C)	$^1/_T \times 10^3 (K^{-1})$	$\ln \frac{dC}{dt}(C = 0)$	$\ln \frac{dC}{dt}(C = 0.5)$
354	1.59	-6.0	-6.58
390	1.51	-3.1	-4.20
440	1.40	-1.3	-2.12

Table 5.15

Best Straight Line Fits to $\frac{1}{T}$ vs ln $^{dC}/dt$ at C = 0

	Slope $\times 10^{-3}$ ± Standard Error	Intercept ± Standard Error	r(correlation coefficient)
Polyester 3	-23.8 ± 0.1	27.9 ± 0.2	0.999
Polyester 4	-17.5 ± 1.3	22.2 ± 1.8	0.989
Polyester 5	-32.7 ± 2.1	39.8 ± 3.6	0.999
Polyester 6	-24.2 ± 5.6	32.9 ± 8.5	0.975

Table 5.16

Best Straight Line Fits to $\frac{1}{T}$ vs ln $^{dC}/dt$ at C = 0.5

	Slope $\times 10^{-3}$	Intercept	r(correlation coefficient)
Polyester 3	-24.8	28.6	0.999
Polyester 4	-14.5	16.9	0.976
Polyester 5	-27.1	32.0	0.999
Polyester 6	-23.2	30.5	0.991

Table 5.17

Activation Energies for Polymer Degradations

	Polyester 3	Polyester 4	Polyester 5	Polyester 6
E_a (kcals/mole) ± standard error	47.4 ± 0.26	34.8 ± 2.6	65.0 ± 4.3	48.1 ± 11.3

Table 5.18

Decomposition Rates of Polyester 3

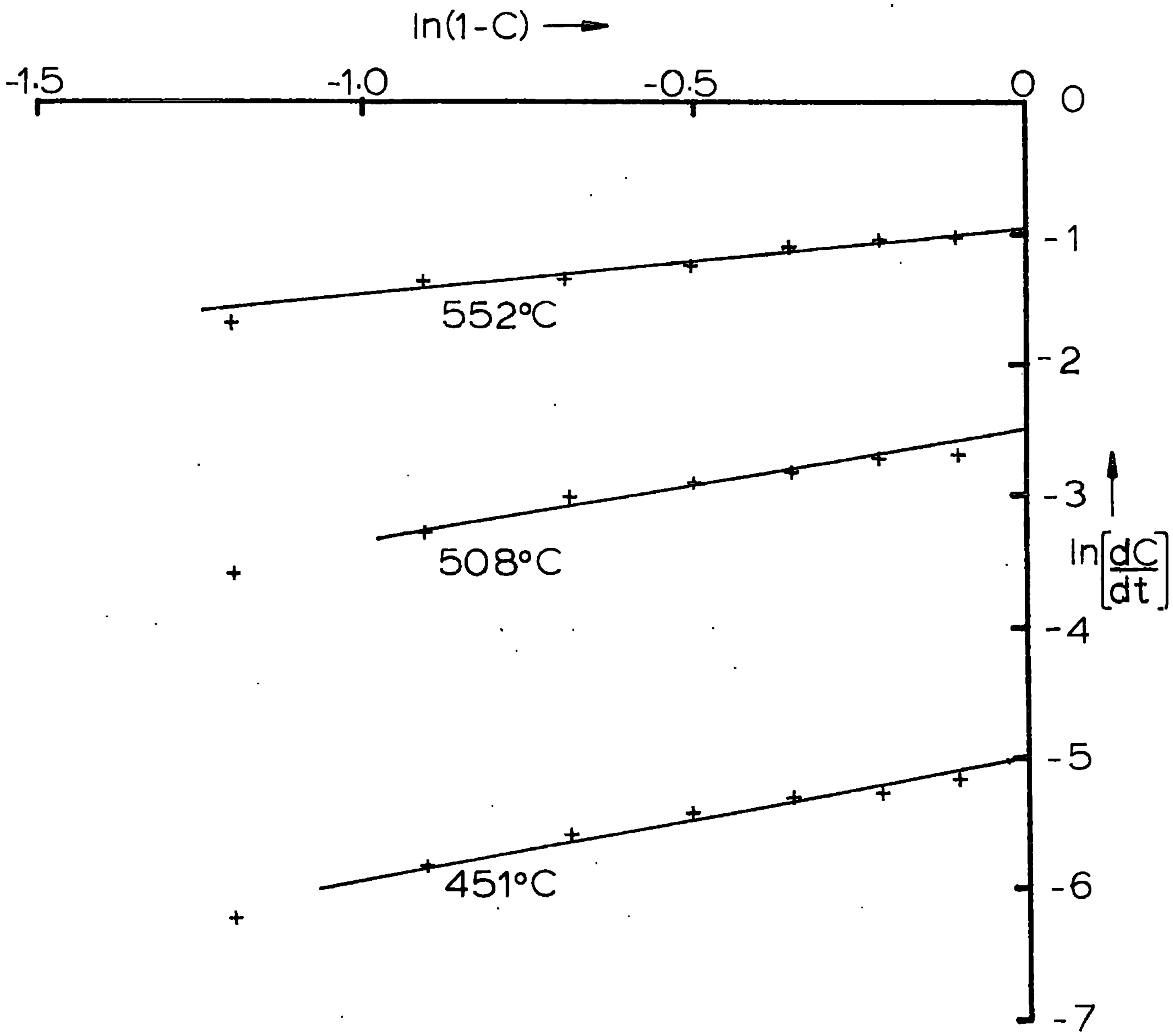


Figure 5.8

Decomposition Rates of Polyester 4

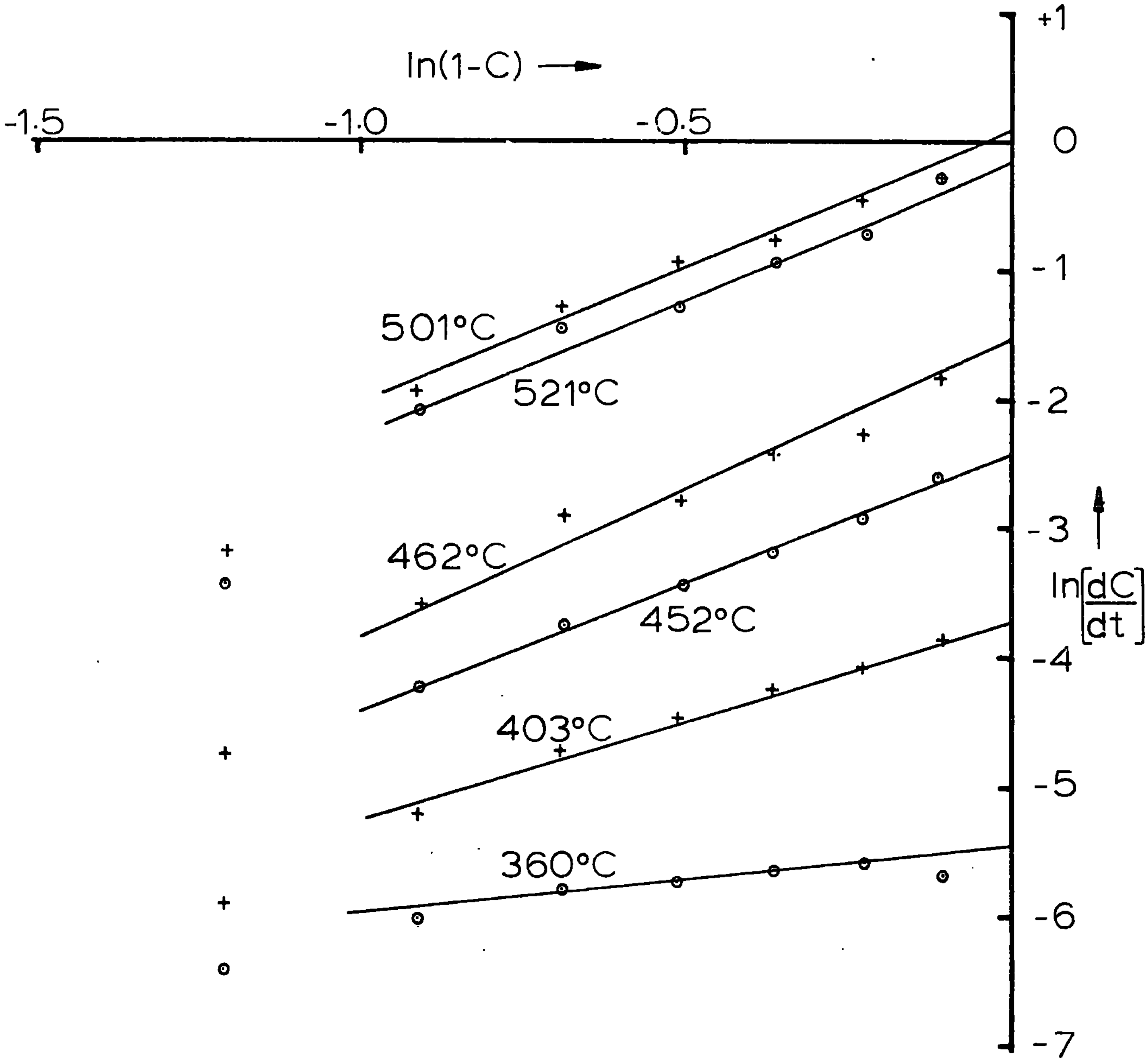


Figure 5.9

Decomposition Rates of Polyester 5

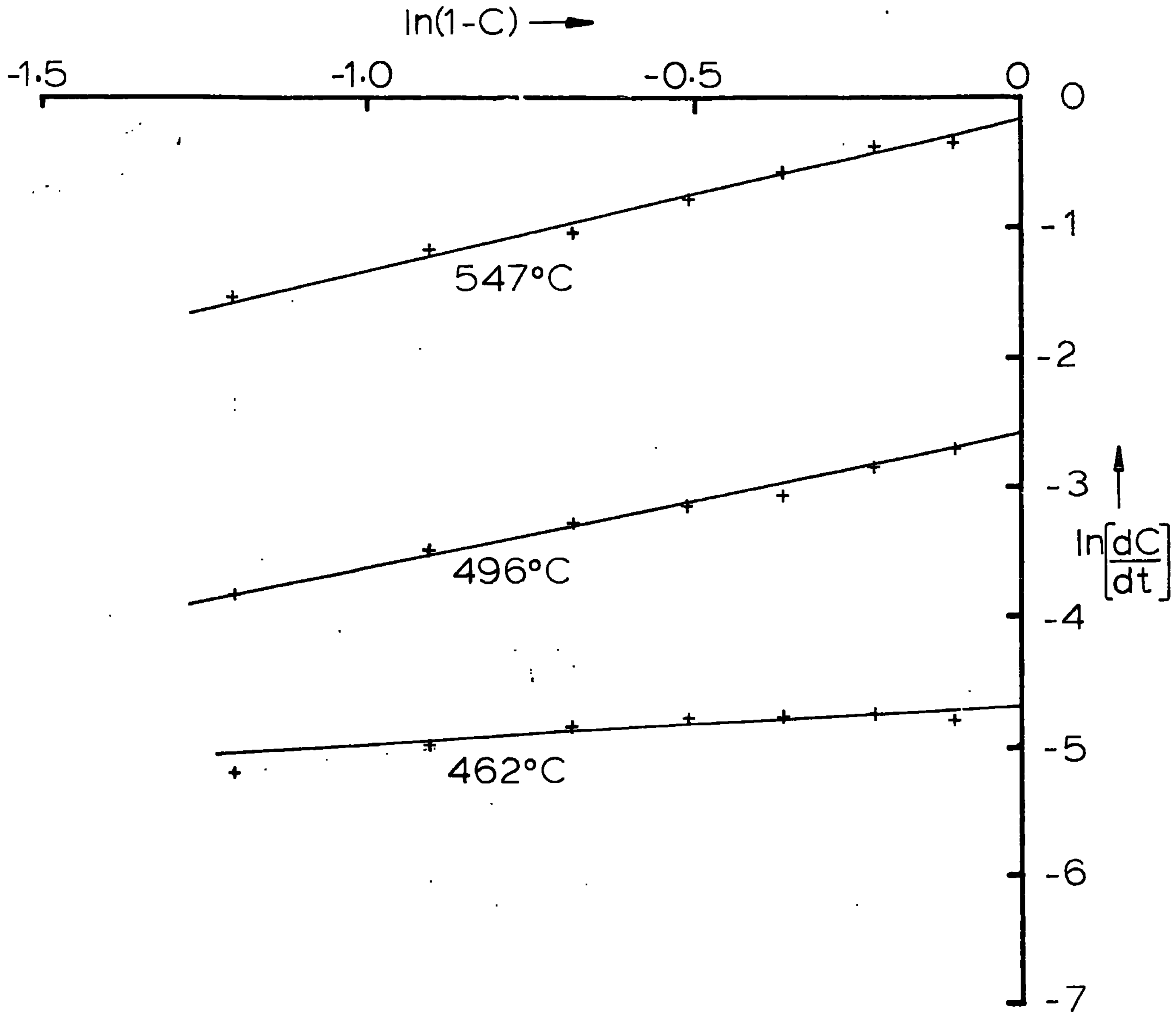


Figure 5.10

Decomposition Rates of Polyester 6

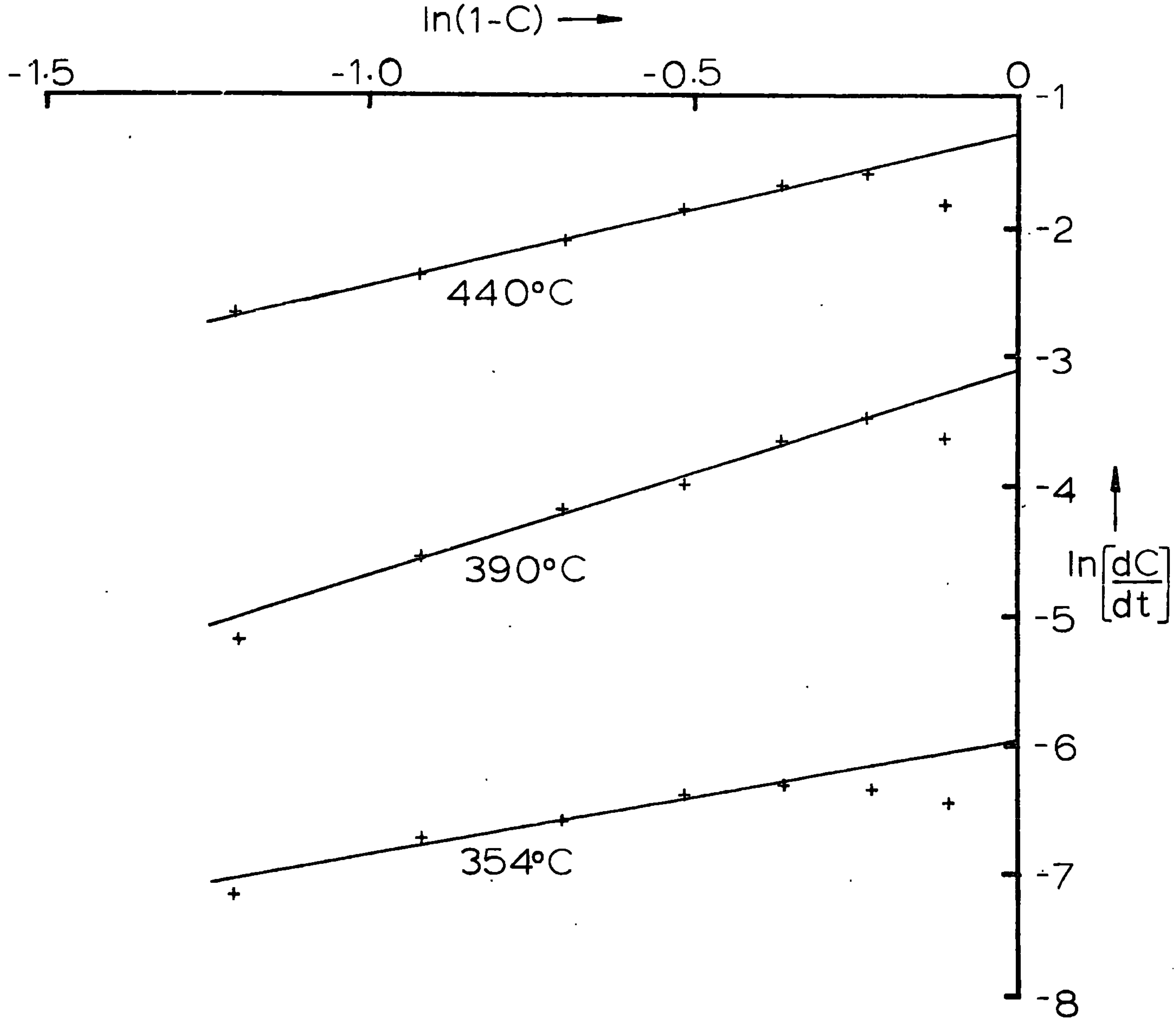
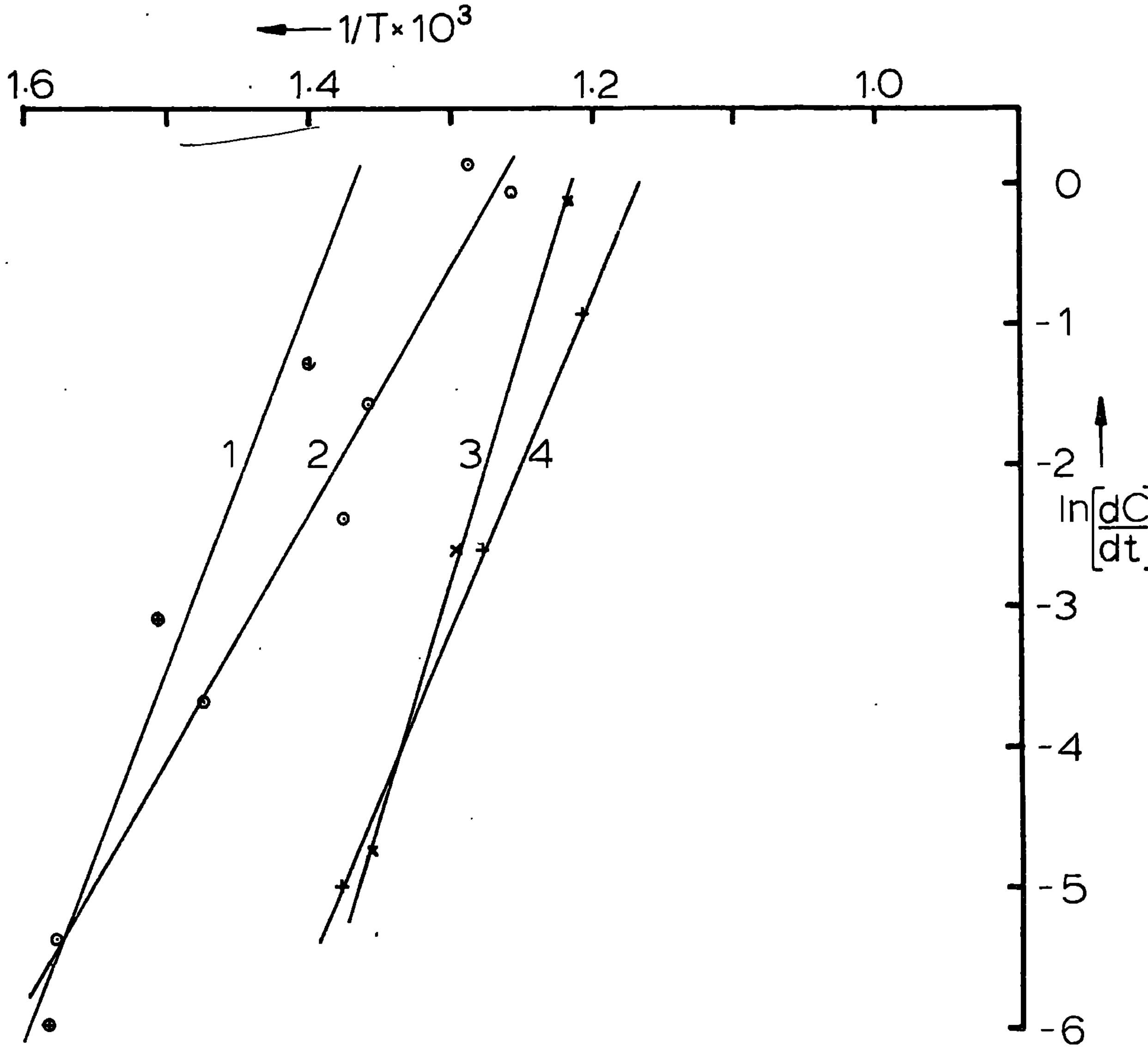


Figure 5.11

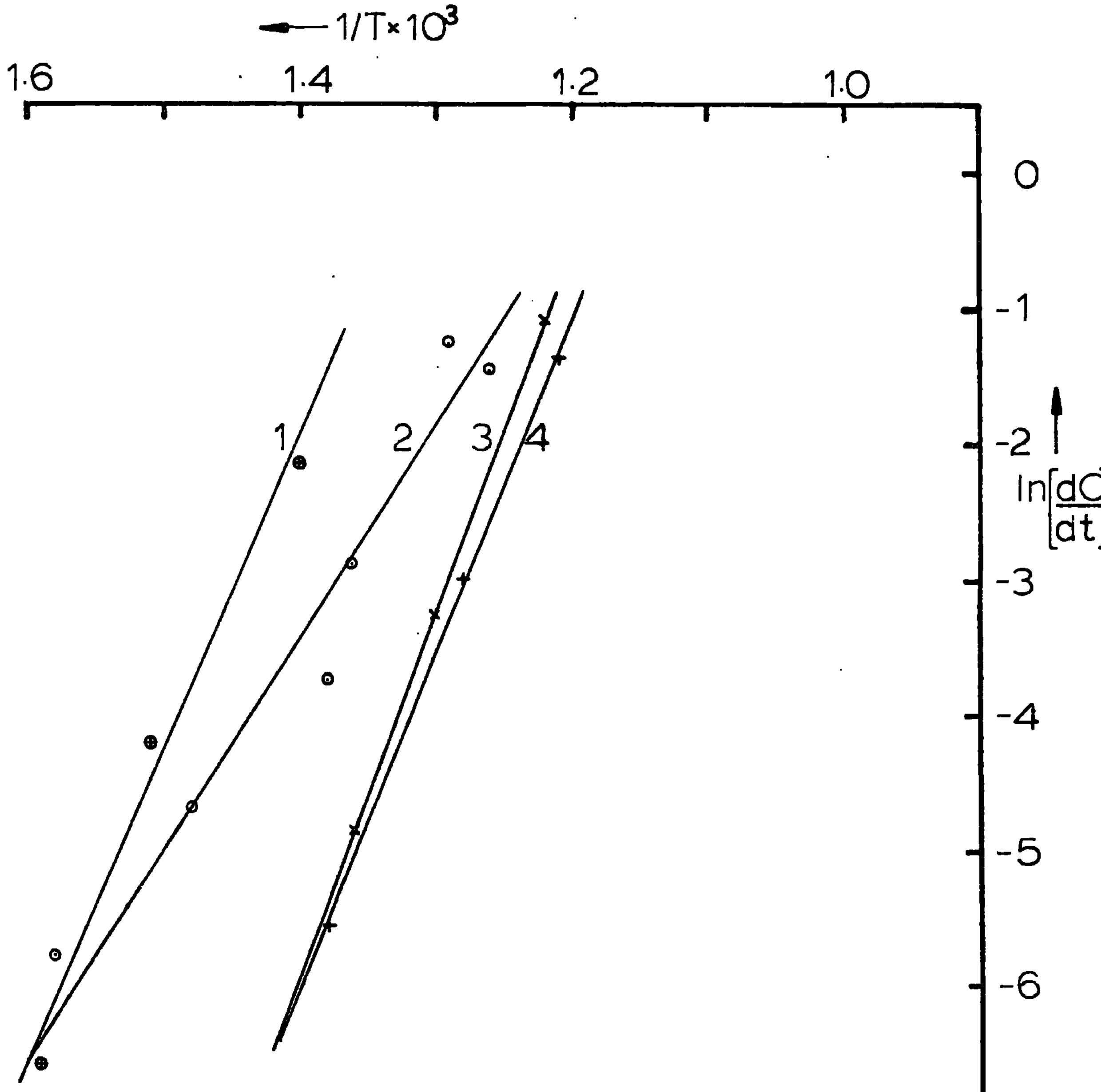
Thermal Degradation Rates of Polyesters at C = 0



Trace 1, ⊕ - Polyester 6
Trace 2, ⊙ - Polyester 4
Trace 3, × - Polyester 5
Trace 4, + - Polyester 3

Figure 5.12

Thermal Degradation Rates of Polyesters at C = 0.5



Trace 1, ⊕ - Polyester 6
Trace 2, ⊙ - Polyester 4
Trace 3, × - Polyester 5
Trace 4, + - Polyester 3

Figure 5.13

It will be seen from Table 5.11 that the apparent order of reaction for the polymer degradation is strongly temperature dependant, while only for Polyester 4 are enough results available for any confidence to be placed in the figures. For this polymer, the reaction appears to be second order at higher temperatures. Both Polyester 3 and Polyester 6 show peculiarities in the variation of reaction order with temperature, but it would be unwise to draw conclusions from the limited data available. This variation, however, means that E cannot be obtained from the measurements made at C = 0.5 alone.

Plots of $\frac{dC}{dt}$ vs $\frac{1}{T}$ give good straight lines both at C = 0, and at C = 0.5. The slope of the line at C = 0 gives $^{-E}/R$, and values of E derived in this way are presented in Table 5.18. However, of greater importance are the degradation rates at different temperatures, and the graphs allow a direct comparison of these figures.

In the temperature range studied, Polyester 6 is the least stable of the samples studied, while at low temperatures it appears to be more stable than Polyester 4. The instability is not intrinsic to the fluorinated ether link; Polyester 5 has a thermal stability comparable with a non-ether containing fluorinated polyester. It seems likely, rather, that the instability of both Polyester 4 and Polyester 6 is a consequence of the proximity of the ester and ether links. The apparent difference in thermal behaviour between these two polymers may be accounted for by two factors; the fluorinated methyl group in Polyester 6 is indicated by space-filling molecular models to be quite sterically significant and may cause destabilisation of this polymer. However, it seems likely that breakage of the ester link in Polyester 4 would be followed by complete fragmentation of the fluorinated ether diol chain, a route which is blocked by the $(CF_2)_5$ group in Polyester 6.

From the above study, it appears that the preparation of polyesters from fluorinated diols carrying ether groups β to the hydroxyl carrying carbon atoms yields products having markedly lower thermal stability than similar materials in which the ether links are remote from the ester groups. It will therefore be necessary, if an epoxide-derived polymer precursor is to be used, either to chemically modify the end-groups to yield a diol without β oxygen links, or to use an alternative polymer-forming reaction. Triazine-linked polyperfluoroepoxide polymers show excellent thermal stability at up to 400°C, the present problems with such materials being associated with hydrolytic instability of incompletely formed triazine rings.

It has been shown that polymers derived from hexafluoropropene epoxide could potentially provide materials having T_g's down to <u>ca.</u>-60°C. The use of tetrafluoroethylene epoxide would give a more flexible polymer chain having a still lower T_g. Nevertheless, the problem of obtaining a low T_g polymer while retaining maximum thermal stability in a fluorinated polyester structure is unresolved. Synthesis of closer model systems to I remains an elusive aim of synthetic chemistry. Nevertheless, the basic assumptions on which this project was based have been largely confirmed, and a continued effort toward the synthesis of perfluoroalkyleneoxide polymers of novel structure seems justified.

Experimental

Polymers were fractionated where indicated, by solution in 1,1,2-trichlorotrifluoroethane (2% solution) and fractional precipitation with methanol. The non-solvent was added until turbidity was observed in the solution, then the solution was stirred (24 hours), allowed to separate (24 hours), and the lower layer extracted by pipette. Removal of volatiles (150°/10^{-3} torr) afforded a polymer fraction, and the process was repeated with the remaining solution.

Molecular weights were measured using a Perkin-Elmer 115 Vapour Pressure Osmometer, and using 1,1,2-trichlorotrifluoroethane or DMF as solvent. Benzil was used as a calibration standard.

Glass transition temperatures were measured on a Perkin-Elmer DSC2 Differential Scanning Calorimeter. Results were recorded at a scanning rate of 40°C/min, and the temperature calibration of the machine was checked before use, against the melting point transitions of water and indium metal.

Thermogravimetric analyses were carried out on a Stanton Redcroft TG 750 Thermobalance operating in a percentage weight loss mode, using atmospheres of dry nitrogen or undried air. The temperature readout of temperature programmed runs was made on a chart recorder colaterally with the weight loss trace. The temperature of isothermal runs was measured by potentiometer to

± 1°C. The rates of weight loss of polymers were estimated by measurement of the slopes of lines drawn tangent to the degradation curves at the appropriate values of C.

APPENDIX

Characterisation Data of Important Products and Intermediates

Apparatus used in the characterisation of compounds prepared in the work described in this thesis was as follows:

IR spectra were recorded on Perkin-Elmer 137 or 157 spectrometers.

NMR spectra were measured on a Varian A56/60 spectrometer at 56.4 MHz or a Bruker spectrospin instrument at 84.67 MHz, using $CFCl_3$ as standard, either internally or by exchange.

Analytical g.l.c. analyses were carried out on a Pye 104 gas chromatograph using a flame detector. Columns of silicone gum rubber or 2-cyanoethyl methyl silicone were used as stationary phase.

Octadecafluoro-1,11-diiodo-3,9-dioxaundecane (V)

IR spectrum No.1

Analysis

	Calculated
C	14.68
F	46.46
I	34.51

(Sample liberated iodine on standing)

^{19}F NMR spectrum

Shift	Integrated Intensity
79.1	4
82.5	4
108.8	4
115.8	2
118.8	4

Octadecafluoro-3,9-dioxa-1,11-bis(3-methoxycarbonylphenyl) undecane (VI)

IR spectrum No.2

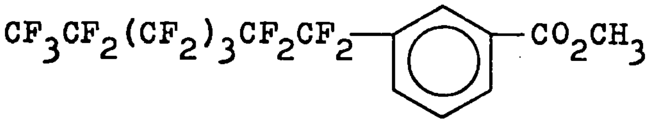
Analysis

	Calculated	Found
C	39.9	
H	1.86	
F	45.5	

^{19}F NMR spectrum

Shift	Integrated Intensity
79.1	4
82.5	4
108.8	4
115.8	2
118.8	4

Methyl (3-pentadecafluoroheptyl) benzoate



IR spectrum No.3

Analysis

	Calculated		Found
C	35.73	C	35.38
H	1.40	H	1.25
F	56.52		

^{19}F NMR spectrum

Shift	Integrated Intensity
74.9	3
105.7	2
116.7	6
119.2	2
121.1	2

Dimethyl dodecafluoro-3,9-dioxa-2,10-bis trifluoromethyl undecane-1,11-dicarboxylate (XIII)

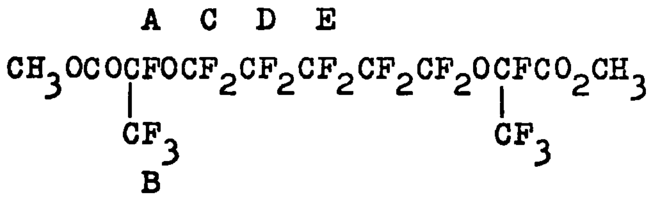
b.p. 66°C/0.6 torr

IR spectrum No.4

Analysis

	Calculated	Found
C	26.01	
H	1.01	
F	56.98	

^{19}F NMR spectrum



$CH_3OCO\underset{\underset{B}{CF_3}}{\overset{A}{C}F}O\overset{C}{CF_2}\overset{D}{CF_2}\overset{E}{CF_2}CF_2CF_2O\underset{CF_3}{C}FCO_2CH_3$

Shift	Integrated Intensity	Assignment
82.8		C
83.7		B
123.6	2	E
126.8	4	D
133.2	2	A

The following coupling constants were extracted -

$J_{C_1C_2}$	152 Hz
J_{AC_1}	6.8 Hz
J_{AC_2}	20 Hz
J_{C_1E}, J_{C_2E}	10 Hz

The nonequivalence of fluorines C_1 and C_2 implies a preferred conformation of the endgroup.

Mass spectrum

m/e	Possible Fragment
600	$C_{13}H_6F_{18}O_6$
569	$C_{12}H_3F_{18}O_5$
541	$C_{11}H_3F_{18}O_4$
441	$C_9H_3F_{14}O_4$
425	$C_9H_3F_{14}O_3$
325	$C_7H_3F_{10}O_3$
159	$C_4H_3F_4O_2$

Dimethyl pentadecafluoro-3,9,12-trioxa-2,10,13 tris trifluoromethyl tetradecane-1,14-dicarboxylate (XIV)

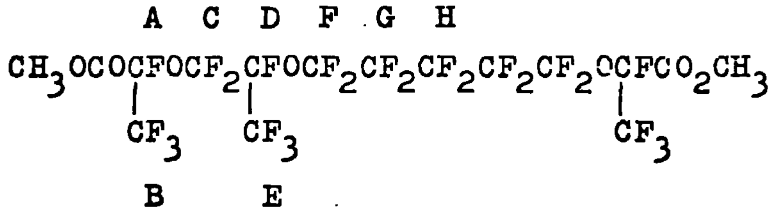
b.p. 87°C/0.6 torr

IR spectrum No.5

Analysis

	Calculated	Found
C	25.07	
H	0.78	
F	59.51	

^{19}F NMR spectrum



$CH_3OCO\underset{CF_3}{C}FOCF_2\underset{CF_3}{C}FOCF_2CF_2CF_2CF_2CF_2O\underset{CF_3}{C}FCO_2CH_3$

Peak Position	Integrated Intensity	Assignment
80.1		E
82.6		B
122.9	2	H
126.2	4	G
132.7	2	A
146.1	1	D
Submerged Peaks		C,F

Mass spectrum

m/e	Possible Fragment
766	$C_{16}H_6F_{24}O_7$
735	$C_{15}H_3F_{24}O_6$
707	$C_{14}H_3F_{24}O_5$
607	$C_{12}H_3F_{20}O_5$
557	$C_{11}H_3F_{18}O_5$
491	$C_{10}H_3F_{16}O_4$
391	$C_8H_3F_{12}O_4$
325	$C_7H_3F_{10}O_3$
225	$C_5H_3F_6O_3$
159	$C_4H_3F_4O_2$
69	CF_3
59	$C_2H_3O_2$

Dimethyl octadecafluoro-3,9,12,15-tetraoxa-2,10,13,16-tetrakis trifluoromethyl heptadecane-1,17-dicarboxylate and/or dimethyl octadecafluoro-3,6,12,15-tetraoxa-2,5,-13,16-tetrakis trifluoromethyl heptadecane-1,17-dicarboxylate (XV and/or XVI)

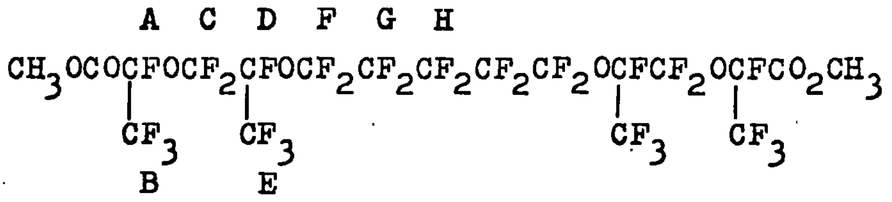
b.p. 103°C/0.5 torr

IR spectrum No.6

Analysis

	Calculated	Found
C	24.48	
H	0.65	
F	61.14	

^{19}F NMR spectrum



$CH_3OCO\underset{CF_3}{CF}OCF_2\underset{CF_3}{CF}OCF_2CF_2CF_2CF_2CF_2O\underset{CF_3}{CF}CF_2O\underset{CF_3}{CF}CO_2CH_3$

Peak Position	Integrated Intensity	Assignment
82.4		E
85.2		B
123.6	2	H
126.8	4	G
133.2	2	A
146.7	2	D
Submerged peaks		C,F

Mass spectrum

m/e	Possible Fragment
932	$C_{19}H_6F_{29}O_8$
901	$C_{18}H_3F_{29}O_7$
873	$C_{17}H_3F_{29}O_6$
773	$C_{15}H_3F_{25}O_6$
607	$C_{12}H_3F_{20}O_5$
557	$C_{11}H_3F_{18}O_5$
491	$C_{10}H_3F_{16}O_4$
391	$C_8H_3F_{12}O_4$
325	$C_7H_3F_{10}O_3$
225	$C_5H_3F_6O_3$
159	$C_4H_3F_4O_2$
69	CF_3
59	$C_2H_3O_2$

Methyl undecafluoro-3,6-dioxa-2,5-bis trifluoromethyl nonanoate

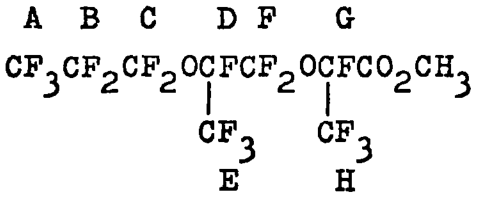
b.p. 88°C/16 torr

IR spectrum No.7

Analysis

	Calculated	Found
C	23.54	
H	0.59	0.67
F	63.32	63.17

^{19}F NMR spectrum



$$\overset{A}{\mathrm{CF_3}}\overset{B}{\mathrm{CF_2}}\overset{C}{\mathrm{CF_2}}\mathrm{O}\overset{D}{\underset{\underset{\mathrm{E}}{\mathrm{CF_3}}}{\underset{|}{\mathrm{C}}}}\mathrm{F}\overset{F}{\mathrm{CF_2}}\mathrm{O}\overset{G}{\underset{\underset{\mathrm{H}}{\mathrm{CF_3}}}{\underset{|}{\mathrm{C}}}}\mathrm{FCO_2CH_3}$$

Peak Position	Integrated Intensity	Assignment
81.6		E
83.2		A
84.3		H
132.1	2	B
134.1	1	G
147.7	1	D
Submerged peaks		C,F

Mass spectrum

m/e	Possible Fragment
510	$C_{10}H_3F_{17}O_4$
479	$C_9F_{17}O_3$
451	$C_8F_{17}O_2$
351	$C_6F_{13}O_2$
185	C_3F_7O
159	$C_4H_3F_4O_2$
100	C_2F_4
69	CF_3
59	$C_2H_3O_2$

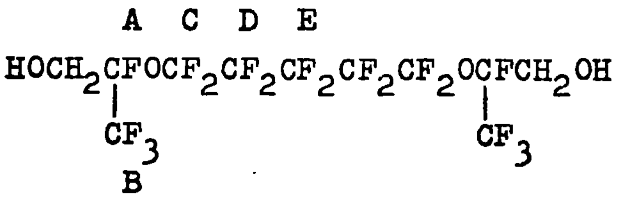
Pentadecafluoro-3,9,12-trioxa-2,10,13-tris trifluoromethyl tetradecane-1,14-diol (XVIII)

IR spectrum No.8

Analysis

	Calculated	Found
C	24.28	24.10
H	1.11	0.86
F	62.85	63.19

^{19}F NMR spectrum



$$\mathrm{HOCH_2\underset{\underset{B}{CF_3}}{\overset{A}{CF}}O\overset{C}{CF_2}\overset{D}{CF_2}\overset{E}{CF_2}CF_2CF_2O\underset{CF_3}{CF}CH_2OH}$$

Peak Position	Integrated Intensity	Assignment
79.5		C
80.2		B
121.9	2	E
124.8	4	D
135.9	2	A

The following coupling constants were extracted

$J_{C_1C_2}$	150 Hz
J_{AC_1}	16 Hz
J_{AC_2}	21 Hz
J_{C_1E}, J_{C_2E}	10 Hz

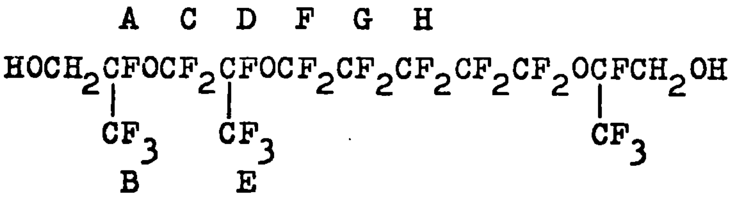
Dodecafluoro-3,9-dioxa-2,10-bis trifluoromethyl undecane-1,11-diol (XVII)

IR spectrum No.9

Analysis

	Calculated	Found
C	23.68	23.39
H	0.85	0.68
F	64.21	64.80

^{19}F NMR spectrum



$$HOCH_2\overset{A}{\underset{\underset{B}{CF_3}}{CF}}O\overset{C}{CF_2}\overset{D}{\underset{\underset{E}{CF_3}}{CF}}O\overset{F}{CF_2}\overset{G}{CF_2}\overset{H}{CF_2}CF_2CF_2O\underset{CF_3}{CF}CH_2OH$$

Peak Position	Integrated Intensity	Assignment
79.4		E
81.3		B
121.9	2	H
124.7	4	G
133.5	2	A
144.1	1	D
Submerged peaks		C,F

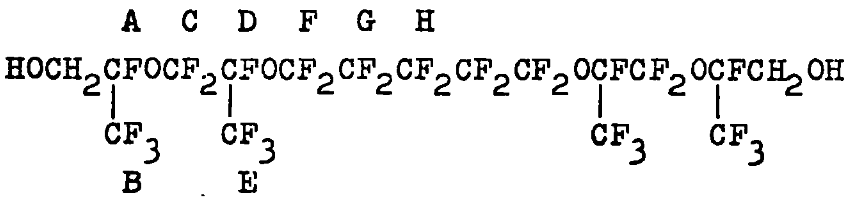
Octadecafluoro-3,9,12,15-tetraoxa-2,10,13,16-tetrakis trifluoromethyl heptadecane-1,17-diol and/or octadecafluoro-3,6,12,15-tetraoxa-2,5,13,16-tetrakis trifluoromethyl heptadecane-1,17-diol (XIX and/or XX)

IR spectrum No.10

Analysis

	Calculated	Found
C	23.30	23.51
H	0.69	0.36
F	65.05	65.52

^{19}F NMR spectrum



$$\mathrm{HOCH_2\underset{\underset{\underset{B}{CF_3}}{|}}{\overset{A}{C}}FO\overset{C}{CF_2}\underset{\underset{\underset{E}{CF_3}}{|}}{\overset{D}{C}}FO\overset{F}{CF_2}\overset{G}{CF_2}\overset{H}{CF_2}CF_2CF_2O\underset{\underset{CF_3}{|}}{C}FCF_2O\underset{\underset{CF_3}{|}}{C}FCH_2OH}$$

Peak Position	Integrated Intensity	Assignment
80.2		E
81.9		B
122.4	2	H
125.5	4	G
134.4	2	A
145.0	2	D
Submerged peaks		C,F

Polyester 1

IR spectrum No.11

Analysis

Calculated	Found
C 49.33	C 49.08
H 2.76	H 2.36
F 26.01	F 25.87

Polyester 2

IR spectrum No.12

Analysis

	Calculated	Found
C	45.63	44.55
H	2.36	2.13
F	33.31	33.5

Polyester 3

IR spectrum No.13

Analysis

	Calculated	Found
C	42.87	41.80
H	2.06	1.60
F	38.76	38.5

Polyester 6

IR spectrum No.14

Analysis

	Calculated	Found
C	33.84	35.14
H	1.20	1.44
F	50.72	52.86

Polyester 7

IR spectrum No.15

Analysis

	Calculated	Found
C	31.44	31.76
H	0.96	1.20
F	54.27	54.70

Polyester 8

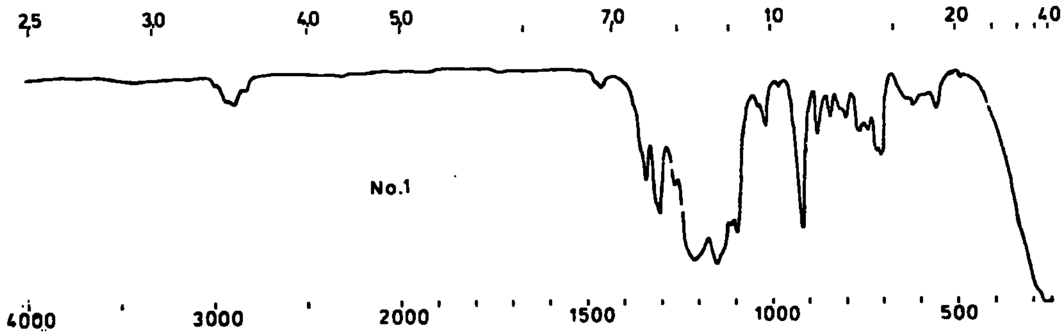
IR spectrum No.16

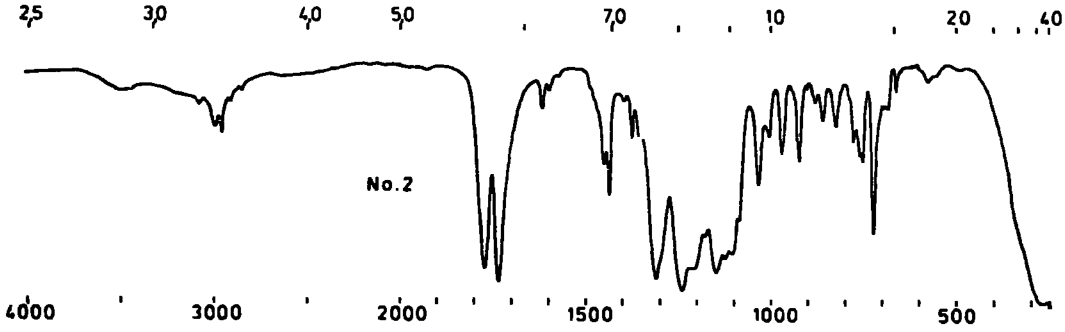
Analysis

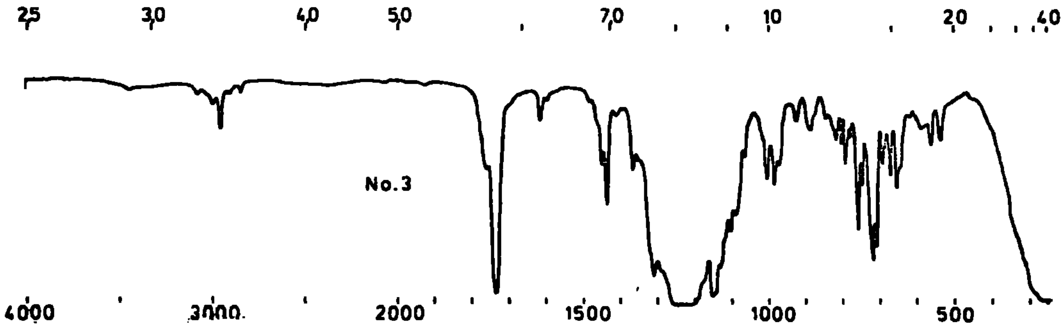
	Calculated	Found
C	29.84	30.98
H	0.80	0.35
F	56.64	55.73

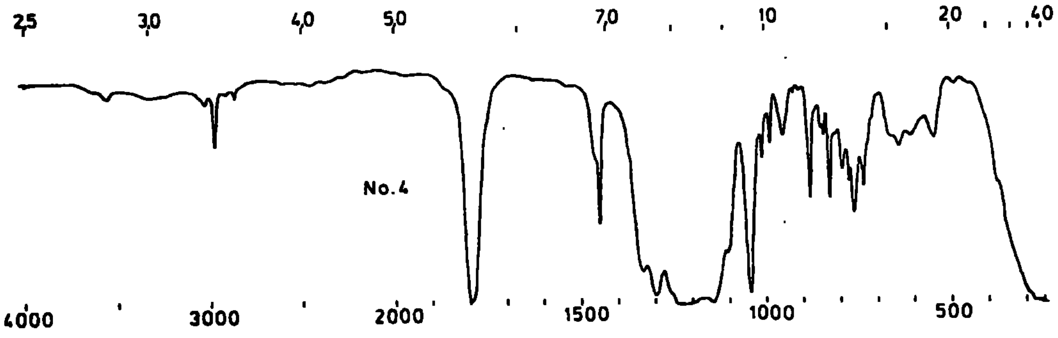
IR Spectra

Upper Scale-Microns Lower Scale Wavenumbers

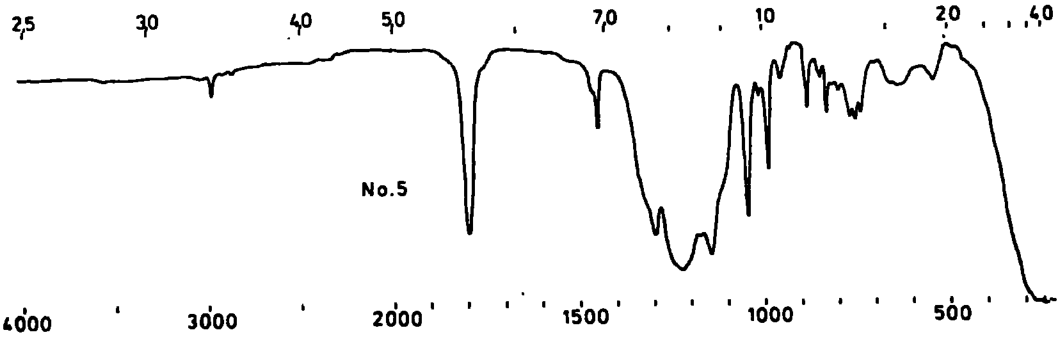

No.1

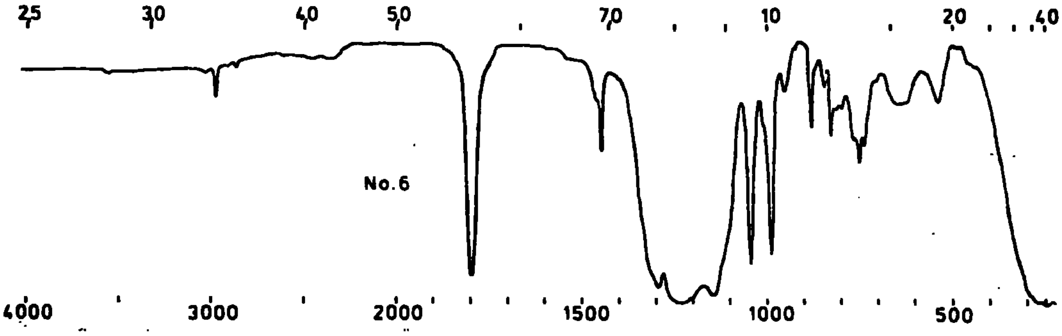

No.2

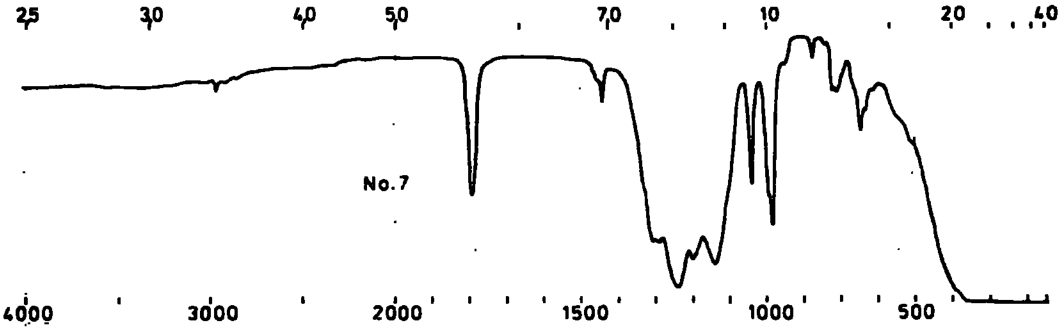

No.3

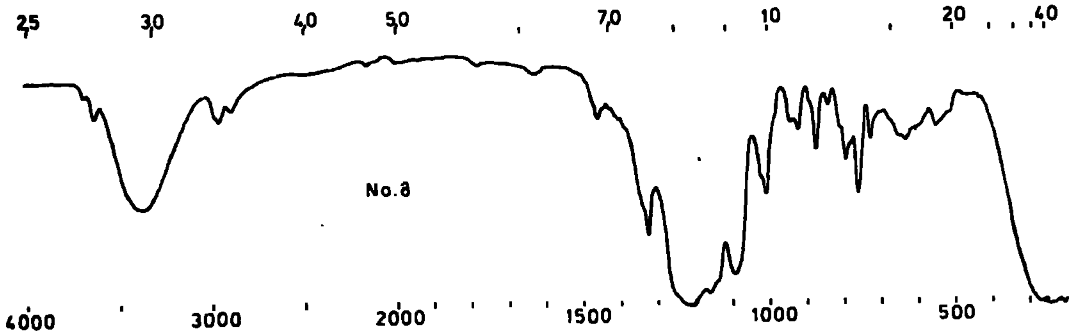

No.4

Upper Scale-Microns Lower Scale Wavenumbers

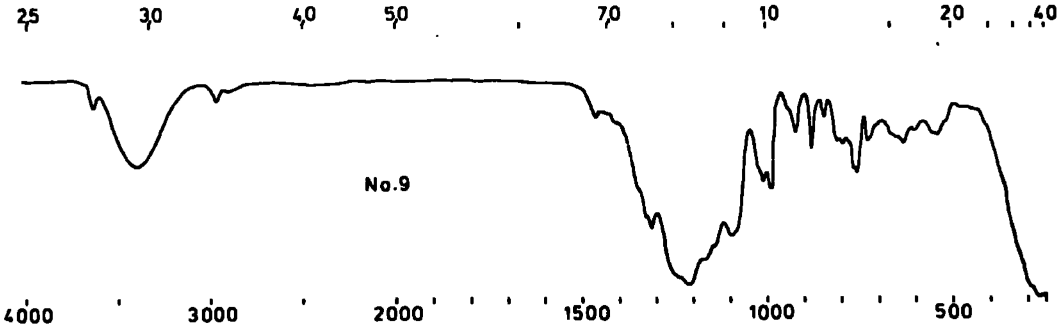

No.5

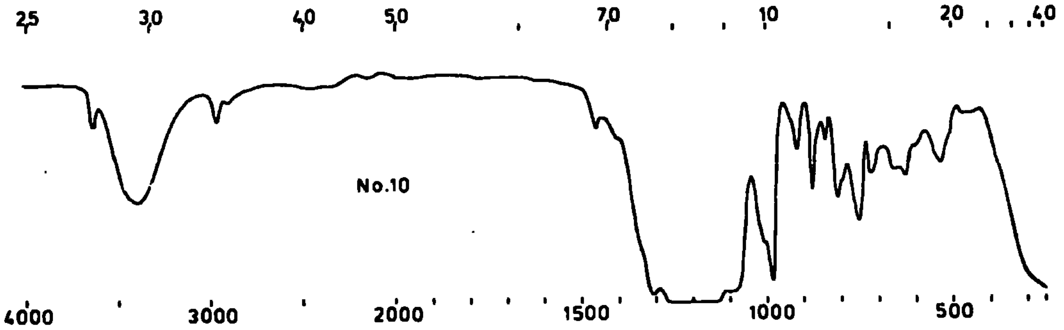

No.6

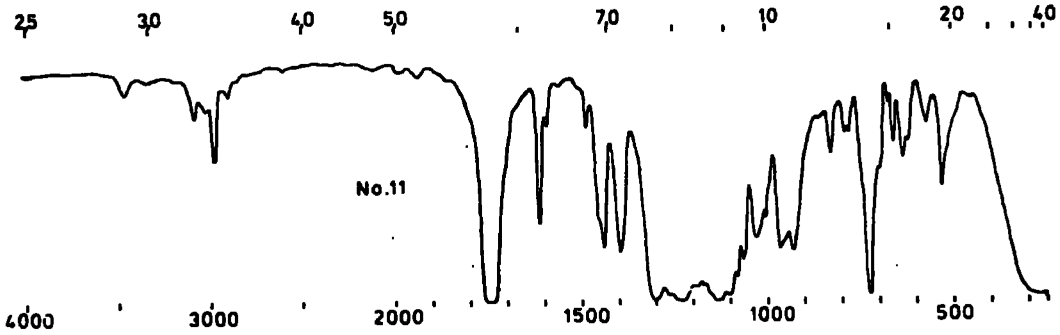

No.7

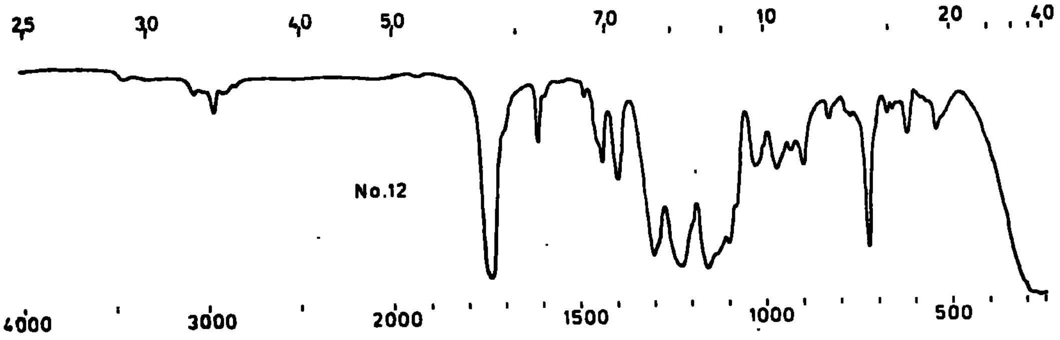

No.8

Upper Scale-Microns Lower Scale Wavenumbers

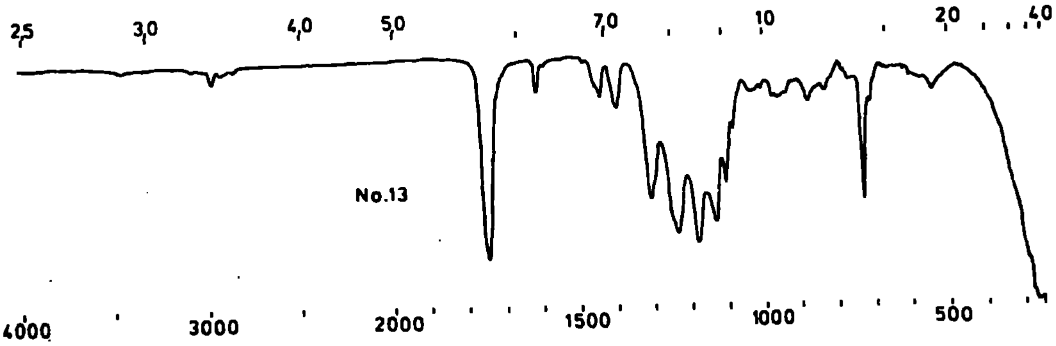

No.9

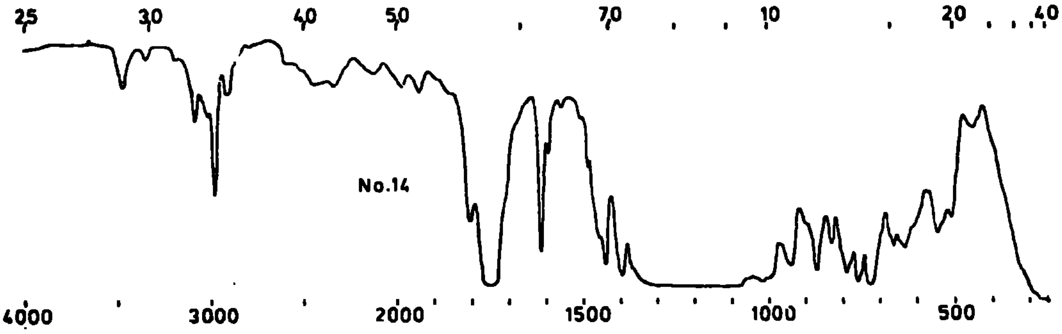

No.10

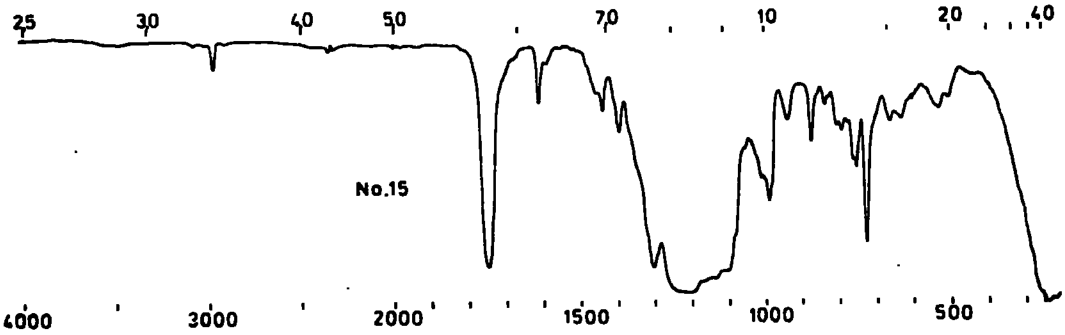

No.11

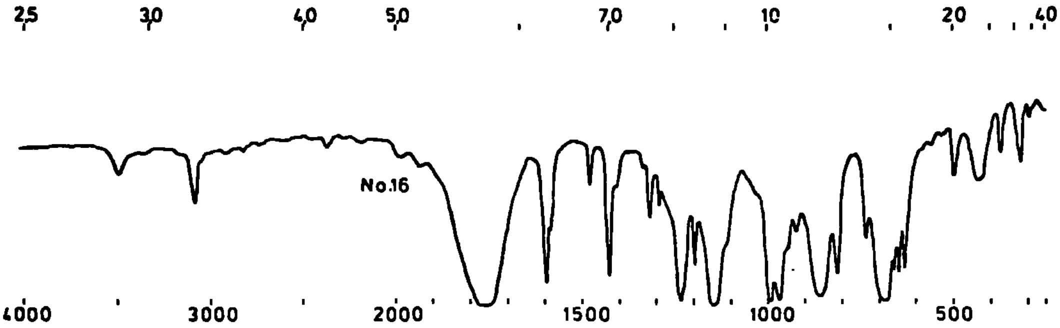

No.12

Upper Scale-Microns   Lower Scale Wavenumbers


No.13


No.14


No.15


No.16

REFERENCES

1. R.A.E. Tech. Memo MAT 120 (1971) Fear, E.J.P., White, I.M., Lee, W.A.

2. For further detail on the various aspects of the glass transition discussed here, and for details of the original publications, the reader is referred to treatments of the topic in:
   a) Molecular Behaviour and the Development of Polymeric Materials. Ed. Ledwith and North.
   b) Physical Properties of Polymers. Bueche, F.
   c) R.A.E. Tech. Report 66090 (1966) Allen, G., Lee, W.A.
   d) The Physics of Glassy Polymers. Ed. Hayward.

3. R.A.E. Report CPM8 (1964) Lee, W.A.

4. J. Appl. Chem. <u>14</u> 1 (1964). Allen, J.

5. Tet. <u>27</u> 2133 (1971) Gourot-Leray, A., Bodot, H.

6. R.A.E. Tech. Report 65112 (1965) Lee, W.A., Sewell, J.H.

7. See Ref. 2d, Ch. 1.

8. Chem. Rev. <u>43</u> 219 (1948) Kauzmann, W.

9. J. Chem. Phys. <u>28</u> 373 (1958) Gibbs, J.H., Di Marzio, E.A.

10. See Ref. 2b, Ch. 4.

11. J. Appl. Phys. <u>25</u> 825 (1954) Boyer, R.F.

12. J. Polym. Sci. <u>9</u> 470 (1952) Beamann, R.G.

13. Preparative Methods of Polymer Chemistry, p.48
Sorenson, W., Campbell, T.W.

14. Brit. Polym. J. <u>2</u> 73 (1970) Lee, W.A., Knight, G.J.

15. J. Appl. Chem. <u>2</u> 493 (1952) Gordon, H., Taylor, R.B.

16. J. Polym. Sci. <u>40</u> 121 (1959) Di Marzio, E.A.,
Gibbs, J.H.

17. J. Polym. Sci. B <u>1</u> 223 (1963) Ellerstein, S.M.

18. J. Appl. Polym. Sci. <u>9</u> 3945 (1965) Beamann, R.G.

19. J. Appl. Polym. Sci. <u>5</u> 318 (1961) Hayes, R.A.

20. Polymer <u>11</u> 79 (1970). Weyland, H.G., Hoftyzer, P.J.,
Van Krevelen, D.W.

21. R.A.E. Tech. Report 66292 (1966) Lee, W.A.,
O'Mahony, D.

22. J. Polym. Sci. A <u>8</u> 555 (1970) Lee, W.A.

23. R.A.E. Tech. Report 74060 (1974) Lee, W.A.

24. R.A.E. Tech. Memo MAT 195 (1974) Lee, W.A.

25. J. Appl. Polym. Sci. <u>8</u> 2935 (1964) Cox, J.M.,
Wright, B.A., Wright, W.W.

26. J. Polym. Sci. A <u>7</u> 971 (1969) Trischler, F.D.,
Hollander, J.

27. J. Polym. Sci. A 9 2733 (1971) Feast, W.J., Reeves, N., Musgrave, W.K.R.

28. J. Res. Nat. Bur. Standards A 3 261 (1959) Madorsky, S.L., Straus, S.

29. J. Polym. Sci. A 7 2969 (1969) Ehlers, G.F.L., Fisch, K.R., Powell, W.R.

30. Usp. Khim. 33 1409 (1964) Korshak, V.V., Krongaus, E.S.

31. J. Polym. Sci. B 6 335 (1968) Rice, D.E.

32. R.A.E. Tech. Report 72205 (1972) Knight, G.J.

33. R.A.E. Tech. Report 66409 (1966) Lee, W.A.

34. J. Chem. Soc. 2505 (1957) Smith, K.P., Tatlow, J.C.

35. J. Appl. Chem. 5 589 (1955) Fear, E.J.P., Thrower, J., Veitch, J.

36. Private Communication, Holmes, T.

37. Canadian Pat. 625287 (1961) Baranauckas, C.F., Gelfand, S.

38. Khim. Nauk. i Prom. 4 675 (1959) Okatov, M.A.

39. Russ. Chem. Reviews 32 461 (1963) Knunyants, I.L., Chih-Yuan, Li, Shokina, V.V. and cited refs.

40. R.A.E. Tech. Report 69048 (1969) McLoughlin, V.C.R., Hewins, M.A.H., Pippett, J.S.

41. J. Gen. Chem. USSR 36 1799 (1966) Ya Kazakov, V., Dzerinskaya, R.A., Tsimbalist, V.I., Shishkin, E.A.

42. J. Chem. Soc. 6077 (1965) Banks, R.E., Burling, E.D.

43. J. Chem. Soc. C 2585 (1969) Burdon, J., Chivers, G.E., Tatlow, J.C.

44. Abstracts, Div. Fluor. Chem., 156th Meeting Am. Chem. Soc. (1968).

45. Ph.D. Thesis, University of Durham (1970) Reeves, N.

46. J. Am. Chem. Soc. 75 5750 (1953) Henne, A.L.

47. Tet. 25 5921 (1969) McLoughlin, V.C.R., Thrower, J.

48. R.A.E. Tech. Report 70160 (1970) McLoughlin, V.C.R. et. al.

49. R.A.E. Tech. Report 71111 (1971) McLoughlin, V.C.R. et. al.

50. J. Org. Chem. 33 1839 (1968) Evans, F.W., et. al.

51. J. Fluor. Chem. 10 75 (1977) Denson, D.D., et. al.

52. J. Macromol. Sci. A 6 1027 (1972) Eleuterio, H.S.

53. J. Macromol. Sci. A 8 499 (1974) Hill, J.T.

54. Polym. Prep. Am. Chem. Soc. Div. Polym. Chem. 12 411 (1971) Sianesi, D.

55. Report AD 747257 on U.S. Navy Contract NOO019-71-C-0331 Doorenbos, H.E., Frick, H.R.

56. J. Macromol. Sci. A 3 1443 (1969) Zollinger, J.L., et. al.

57. J. Org. Chem. 30 2182 (1965) Harris, J.F.

58. J. Org. Chem. 35 2816 (1970) Mitsch, R.A., Ogden, P.H., Stoskopf, A.H.

59. U.S. Pat. 3,515,701 (1970) Tiers, G. Van D.

60. J. Polym. Sci. 44 9 (1960) Brown, H.C.

61. Rubber. Chem. Technol. 39 1175 (1966) Dorfman, E., et. al.

62. Russ. Chem. Rev. 40 679 (1971) Gitina, R.M., Zaitsova, E.L., Yakubovitch, A. Ya.

63. Russ. Chem. Rev. 40 301 (1971) Malichenko, B.F.

64. Zh. Org. Khim. 5 2192 (1969) Malichenko, B.F., Prikhod'ko, Z.S.

65. Final Research Report (1973) Ditchfield, G.

66. J. Fluor.Chem. 11 601 (1978) Soloski, E.J., Tamborski, C.

67. U.S. Pat. 3846376 (1974) Evers, R.C.

68. U.S. Pat. 3903166 (1975) Evers, R.C.

69. Can. J. Chem. 45 389 (1967) Redwood, M.E., Willis, C.J.

70. J. Org. Chem. 33 1837 (1968) Evans, F.W., Litt, M.H., Weidler-Kubanek, A.M., Avonda, F.P.

71. Private Communication, McLoughlin, V.C.R.

72. Private Communication, Tamborski, C. to White, I.M.

73. Research Agreement AT/2051/09MAT Minutes of Meeting 28th June, 1974.

74. J. Org. Chem. 31 392 (1966) Prager, J.H.

75. J. Phys. Chem. 70 618 (1966) Heicklen, J.

76. Zh. Org. Khim. 9 2038 (1973) Skoblikova, V.I. et. al.

77. Reagents for Organic Synthesis. Fieser, L. and Fieser, M.

78. J. Appl. Chem. 6 3199 (1956) Fear, E.J.P., Thrower, J., Veitch, J.

79. Organic Fluorine Chemistry (1969) Sheppard, W.A., Sharts, C.M.

80. J. Org. Chem. 31 2316 (1966) Pittman, A.G., Sharp, D.L.

81. Tech. Report AFML-TR-71-208 Anderson, R., Psarras, T.

82. Chim. et Ind. 55 208 (1973) Sianesi, D. et. al.

83. J. Chem. Soc. C (1971) 925 Camaggi, G., Gozzo, F.

84. J. Polym. Sci. A1 7 3020 (1969) Evers, R.C., Ehlers, G.F.L.

85. J. Org. Chem. 30 3009 (1965) Ward, R.B.

86. Canadian Patent 960222 (1974) Mitsch, R.A., Zollinger, J.L.

87. U.S. Pat. 3,755,265 (1973) Fletcher, J.C. et. al.

88. U.S. Pat. 3,772,251 (1973) Brown, H.A.

89. U.S. Pat. 3,772,248 (1973) Brown, H.A., Vogel, H.A., Sandberg, C.L.

90. Am. Chem. Soc. Symp. Ser. 6 185 (1974) Rosser, R.W. et. al.

91. U.S. Pat. 3933767 (1976) Nottke, J.E.

92. J. Appl. Polym. Sci. 20 1035 (1976) Cochoy, R.E.

93. U.S. Pat. 3250806 (1966) Warnell, J.L.

94. U.S. Pat. 3250807 (1966) Fritz, C.G., Moore, E.P.

95. U.S. Pat. 3274237 (1966) Selman, S.

96. U.S. Pat. 3303145 (1967) Carlson, D.P.

97. U.S. Pat. 3317484 (1967) Fritz, C.G.

98. U.S. Pat. 3322826 (1967) Moore, E.P.

99. U.S. Pat. 3412148 (1968) Arbogast, F.L.

100. U.S. Pat. 3637842 (1972) Stump, E.C., Rochow, S.E.

101. U.S. Pat. 3660315 (1972) Hill, J.T.

102. NASA Report CR 102259 (1968) Trischler, F.D., McLeod, A.

103. NASA Report CR 119740 (1971) Webster, J.A., Morrow, T.J.

104. NASA Report CR 130552 (1973) Watts, R., Tarrant, P.

105. NASA Report CR 120104 (1973) Harrison, E.S.

106. NASA Report CR 87156 (1967) Hollander, J. et. al.

107. NASA Report CR 61743 (1967) Hollander, J.

108. AFML TR67-271 (1967) Brown, H.A., Sandberg, C.L.

109. AFML TR-70-70 (1970) Schuman, P.D., Padgett, C.D.

110. AFML TR-71-114 (1971) Psarras, T., Schuman, P.D., Ringler, H.R.

111. AFML TR-72-123 (1972) Baucom, K.B., De Pasquale, R.J.

112. AFML TR 73-144 (1974) De Pasquale, R.J., Padgett, C.D.

113. Zh. Org. Khim. <u>11</u> 296 (1975) Skoblikova, V.I. et. al.

114. J. Fluor. Chem. <u>7</u> 581 (1976) Anderson R. et. al.

115. Personal Communication, Hughes, R.H.

116. Zh. Org. Khim. 11 315 (1975) Gubanov, V.A. et. al.

117. J. Chem. Soc. (C) (1969) 1706 Banks, R.E., et. al.

118. J. Org. Chem. 34 3438 (1969) Throckmorton, J.R.

119. J. Chem. Soc. (C) 2333 (1967) Banks, R.E., Mullen, K.

120. J. Polym. Sci. 24 33 (1957) Schweiker, G.C., Robitschek, P.

121. J. Am. Chem. Soc. 74 1426 (1952) Henne, A.L., Pelley, R.L.

122. Research Agreement AT/2051/09Mat. Proposals for Continuation June 1973.

123. Unpublished Results. McLoughlin, V.C.R.

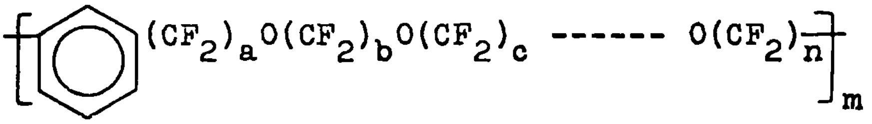
124. J. Polym. Sci. A 3 4253 (1965) Chatterjee, P.K.

125. Eu. Polym. J. 6 907 (1970) MacCallum, J.R., Tanner, J.

126. Errors of Observation and their Treatment. Topping, J. Sections 46-48.

ENDPAPERS

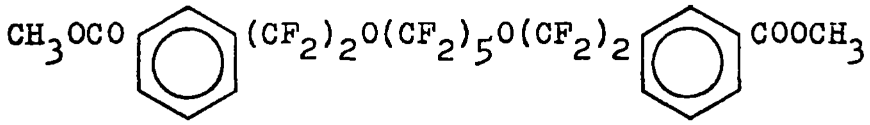
Endpaper 1



I

$I(CF_2)_2O(CF_2)_5O(CF_2)_2I$

V

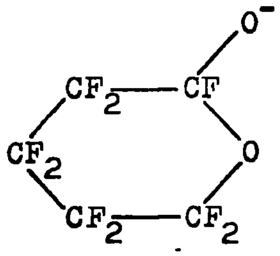


VI

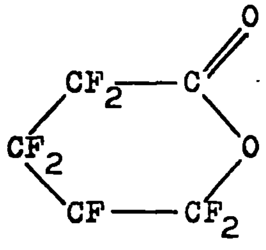
$I(CF_2)_2O(CF_2)_4CO_2H$

VII

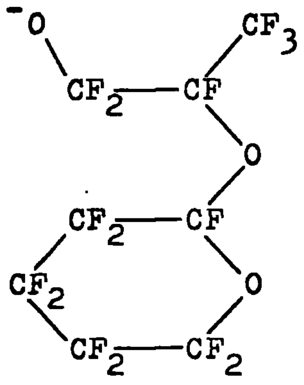
(IX-XX) - See over



XXI

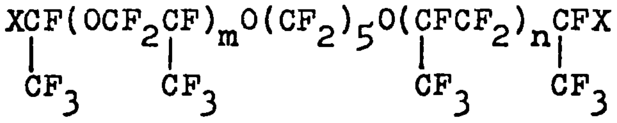


XXII



XXIII

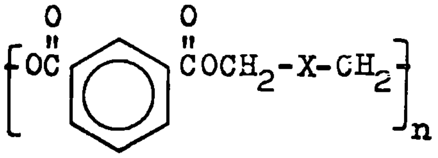
Endpaper 2

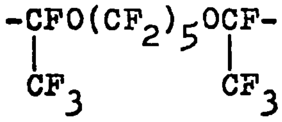
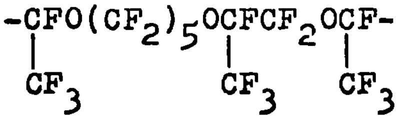
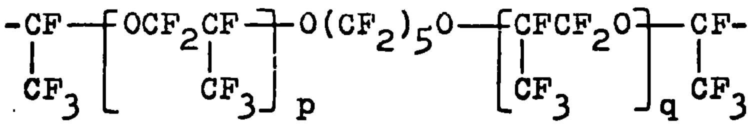


$$\mathrm{X}\underset{\mathrm{CF_3}}{\mathrm{C}}\mathrm{F(OCF_2}\underset{\mathrm{CF_3}}{\mathrm{C}}\mathrm{F)_mO(CF_2)_5O(}\underset{\mathrm{CF_3}}{\mathrm{C}}\mathrm{FCF_2)_n}\underset{\mathrm{CF_3}}{\mathrm{C}}\mathrm{FX}$$

			Compound
m = 0	n = 0	X = COF	IX
m = 0	n = 1	X = COF	X
m = 0	n = 2	X = COF	XI
m = 1	n = 1	X = COF	XII
m = 0	n = 0	X = $COOCH_3$	XIII
m = 0	n = 1	X = $COOCH_3$	XIV
m = 0	n = 2	X = $COOCH_3$	XV
m = 1	n = 1	X = $COOCH_3$	XVI
m = 0	n = 0	X = CH_2OH	XVII
m = 0	n = 1	X = CH_2OH	XVIII
m = 0	n = 2	X = CH_2OH	XIX
m = 1	n = 1	X = CH_2OH	XX

Endpaper 3



	X
Polyester 1	$-CF_2CF_2-$
Polyester 2	$-CF_2CF_2CF_2-$
Polyester 3	$-CF_2CF_2CF_2CF_2-$
Polyester 4	$-CF_2OCF_2-$
Polyester 5	$-(CF_2)_4O(CF_2)_4O(CF_2)_4-$
Polyester 6	 $-\underset{CF_3}{CF}O(CF_2)_5O\underset{CF_3}{CF}-$
Polyester 7	 $-\underset{CF_3}{CF}O(CF_2)_5O\underset{CF_3}{CF}CF_2O\underset{CF_3}{CF}-$
Polyester 8	 $-\underset{CF_3}{CF}-\left[OCF_2\underset{CF_3}{CF}\right]_p-O(CF_2)_5O-\left[\underset{CF_3}{CF}CF_2O\right]_q-\underset{CF_3}{CF}-$

$p + q = 2$