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AN INVESTIGATION INTO THE SYNTHESIS AND PROPERTIES OF SOME FLUORINATED POLYCARBONATES.

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(St. Cuthbert's Society).

A thesis submitted for the Degree of Doctor of Philosophy (Ph.D.) to
the University of Durham.

1977.

Abstract

This thesis describes the synthesis and characterisation of several fluorinated aliphatic, aliphatic and aliphatic ether polycarbonates. The thesis is divided into four sections. In the first section the origins and motivation for the work are discussed, essentially the work forms part of a long term project concerned with the development of a predictively useful correlation between the structure of a polymer repeat unit and its glass transition temperature (Tg). In the second section the various methods for aliphatic polycarbonate synthesis are critically discussed together with the reason for selecting the method used in this work. The third section describes the progressive development of the eventually successful synthetic method and its application to the preparation of ten polycarbonates. The final section is concerned with the detailed characterisation of the polymers obtained, in particular with establishing that they were high polymers of the correct structure, and the measurement of their glass transition temperatures and thermal stabilities.

The results of this work suggest that the theoretical basis for the prediction of the glass transition temperatures of polymers is not presently particularly reliable. Part of the difficulty in developing a more predictively useful theory arises from the uncertainties associated with published values for Tg and a useful contribution of this work is to provide a further ten reliable data points for well characterised materials.

Acknowledgements.

I would like to thank Dr. W.J.Feast for his continued guidance and encouragement during the supervision of this work, also Professor W.K.R. Musgrave for his interest, and Mr. H.R.Thomas for running the ESCA spectra and helpful discussions. Assistance from various members of the technical and laboratory staff is also greatly appreciated.

I also acknowledge the Ministry of Defence for the provision of a grant to carry out this project.

Memorandum.

This thesis is based on my own work carried out in the University of Durham Chemical Laboratories between October 1st 1973 and Easter 1977. This work has not been submitted for any other degree, and is the original work of the author except where acknowledged by reference.

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Section 1.

Introduction.

1.1 Background.

The work to be reported in this thesis was carried out on a research agreement financed by the Ministry of Defence through the Materials Department of the Royal Aircraft Establishment at Farnborough. It is concerned with the synthesis and characterisation of new polymeric materials, and in particular with a long term attempt to develop a better understanding of the relation between structure at the molecular level and bulk physical properties.

The particular problem with which this research is concerned is that of extending the working range of high performance elastomers. These are used as sealants, for example O-ring seals in hydraulic systems, and in some specialist applications, notably aerospace, are required to withstand severe operating conditions. In order to perform the fluid containment sealing function of elastomeric O-ring seals reliably the polymers used or developed are required to show the following practical characteristics:-

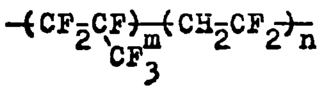
i) thermal and oxidative stability at elevated temperatures.
ii) chemical inertness towards likely service environments.
iii) adequate mechanical strength in the compound state.
iv) resistance towards oils, fuels and solvents.
v) retention of elastomeric behaviour at and below normal operating temperatures.

The increasingly higher performance of each generation of aircraft, has imposed successively more demanding standards on vital subsystems. In particular currently available elastomeric and sealant compounds do not adequately meet the specification of present and projected design requirements. This acts as a spur towards the development of new polymers capable of improved performance, and has led to considerable research interest is evidenced by the large number of new polymeric structures reported.

The value of fluorine in polymer chemistry has been well known since the discovery of poly(tetrafluoroethylene) (PTFE).[1] Highly fluorinated aliphatic polymers, which are usually insoluble in nonfluorinated solvents show the characteristics of high thermal and oxidative stability. This is attributed to the greater stability of a carbon-fluorine bond (as compared to a carbon-hydrogen bond), the increased strength of a carbon-carbon bond on successive replacement of hydrogen by fluorine, and the shielding of the carbon backbone by fluorine atoms.[2,3] The synthesis of elastomeric polymers containing enough fluorine to impart a significant degree of stability was not achieved until the mid 1950's. The first products reported being copolymers of vinylidene fluoride with chlorotrifluoroethylene (Kel F).[4-7]

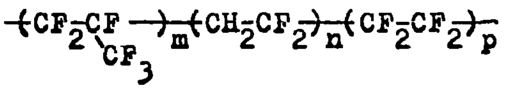
$$-(CH_2CF_2)_m-(CFCl-CF_2)_n-$$

Subsequently copolymers of vinylidene fluoride with hexafluoropropylene (Viton A),[8-10] and terpolymers of vinylidene fluoride with hexafluoropropylene and tetrafluoroethylene (Viton B)[11,12] were introduced by DuPont and became widely used.



$$-(CF_2CF(CF_3))_m-(CH_2CF_2)_n-$$

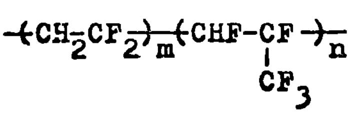
Viton A



$$-(CF_2CF(CF_3))_m-(CH_2CF_2)_n-(CF_2CF_2)_p-$$

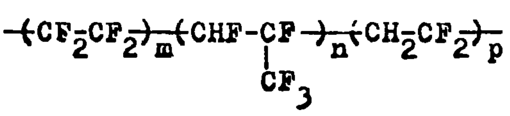
Viton B

Later other companies introduced essentially similar materials for example, the copolymer vinylidene fluoride and 1-hydropentafluoropropylene the terpolymer of vinylidene fluoride, 1-hydropentafluoropropylene and tetrafluoroethylene.



$$\text{-}(CH_2CF_2)_m(CHF\text{-}\underset{CF_3}{CF})_n\text{-}$$

Technoflon SL.

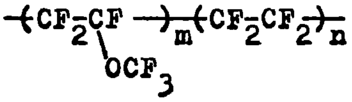


$$\text{-}(CF_2CF_2)_m(CHF\text{-}\underset{CF_3}{CF})_n(CH_2CF_2)_p\text{-}$$

Technoflon T.

These systems, prepared from monomeric fluorinated olefins, show relatively poor low temperature behaviour, and in most cases useful elastomeric properties are not maintained much below 0°.

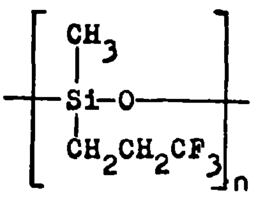
A copolymer of perfluoro(methyl vinyl ether) with tetrafluoroethylene has been reported recently,[16,18] possessing an even greater degree of high temperature stability than the poly(fluoro olefins) available so far.



$$\text{-}(CF_2\underset{OCF_3}{CF})_m(CF_2CF_2)_n\text{-}$$

It is said to be soluble in a few highly fluorinated solvents, insoluble in, unreactive toward and essentially unswollen by almost all organic solvents, inorganic acids, bases, oxidising and reducing agents; however again low temperature applicability is limited.

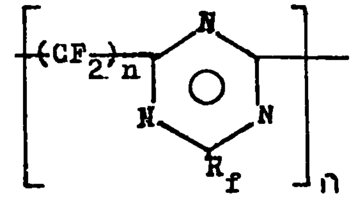
The excellence of fluorocarbon elastomers with respect to thermo-oxidative stability and solvent resistance stimulated efforts to impart these properties to silicone elastomers by introducing fluoroalkyl substituents whilst retaining the exceptional low and high temperature flexibility of the siloxane backbone. Fluoroalkyl siloxanes were developed after considerable synthetic difficulties had been overcome,[19,20] and proved to be solvent resistant elastomers with good low and high temperature flexibility.[21,23] Unfortunately their poor hydrolytic stability limits their usefulness despite the markedly improved low temperature characteristics which allows flexibility well below 0°.



$$\left[\text{-}\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}\text{-}O\text{-}\right]_n$$

Alternating copolymers of tetrafluoroethylene with perfluoronitrosomethane have been of considerable interest as elastomers; reported first in 1955[24] and later in patents,[25] the raw polymer has excellent low temperature behaviour, outstanding chemical resistance to strong acids and oxidants, is non inflammable and has good resistance to a range of hydrocarbon and some oxygenated hydrocarbon fluids. The principle deficiencies of this polymer are pyrolytic decomposition at 175° and sensitivity to degradation by organic bases; however vulcanizates have been used in some specialist applications not requiring thermal stability.

Another class of materials of interest because of their outstanding oxidative stability and high resistance to acids and bases, are poly-(perfluoroalkylenetriazine) elastomers.[26]



They represent the first real structural innovation fluorine chemistry has contributed to the field of polymers, predating perfluoronitroso polymers by several years. The triazine ring is however susceptible to hydrolytic attack by alkali, degrading to amides, and the process leading to polytriazine formation was not as effective as first anticipated.

Recently copolymers prepared from various prepolymers (polyesters, polyethers) and linked together with a low proportion of urethane linkages, have become commercially important materials, useful as elastomers, foams and coatings.[27] Some fluorinated polyurethanes have been prepared,[28] though the relationship between their structure and

$$-\!(\mathrm{NH}\text{-}\mathrm{R}_f\text{-}\mathrm{NH}\text{-}\mathrm{CO}\text{-}\mathrm{R}_f\text{-}\mathrm{OC})_p\!-$$

properties has not been reported in any detail; it is expected that many of the relationships valid for non fluorinated aliphatic polyurethanes will hold for the fluorinated cases, for example good low temperature flexibility, resistance to abrasion and solvents. Recent patents concerning different fluorinated polyurethanes claim excellent resistance to fuels and oils;[29] good low temperature flexibility;[30,31] and adhesive properties.[32] These properties, however are more dependent on the nature of the prepolymer, the urethane link being used as a method of fixing the prepolymer into a polymer chain using well established polymer reactions, and are not characteristic of polyurethanes. In addition they show considerable promise for extending the operating range of elastomers, particularly at low temperature.

Other fluorinated polymers of probable elastomeric character have been described,[33] including polyepoxides, polyketals, polyfluorals, and polythiocarbonyl polymers; but many of these have been shown to be quite unstable in a variety of ways.

Quite extensive research has been carried out on another system of interest, fluorinated polyesters, derived from fluorinated aliphatic diols (mainly hexafluoropentanediol) and various diacids or derivatives, a variety have been reported over the last 20 years.[34-40] Their physical properties have encouraged interest as potential solvent resistant, thermally stable elastomers, through thermal stability is not exceptional their capacity to retain elastomeric behaviour below 0° is considered useful and worthy of further research effort.

1.2 Bulk Properties of Polymers.

Differences in the mechanical properties of polymers are determined by variations in the types and rates of segmental motion, and the types and degrees of molecular ordering. Changes in these parameters are marked by transition temperatures, which are important in determining the temperature where physical properties alter in magnitude or temperature dependence, and also the form the polymer takes at a particular temperature (e.g. a glassy, rubbery, flexible or rigid solid, or a liquid). For elastomers the most important transition occurs at the glass transition temperature (Tg), which determines the lower temperature limit of usefulness of a non crystallising rubber and the upper temperature limit for an amorphous thermoplastic.

1.3 The Glass Transition Temperature.

The glass transition temperature (Tg) is readily defined phenomenologically as that temperature which divides glass from rubber like behaviour. In practise this is usually a narrow temperature interval during which the polymer undergoes a profound change of state, attempts to formulate a precise theoretical definition of Tg leads to complications which will be discussed later. The molecular interpretation of Tg is that it is the temperature at which large scale motion of molecular chain segments begins to occur when the temperature of the sample is raised from the glass to the rubber state. Thus, at very low temperatures, polymer atoms may only undergo low amplitude vibration (or rotation of substituents e.g. methyl groups). When the temperature is increased both the amplitude and the co-operative nature of these vibrations amongst neighbouring polymer atoms increases, until well defined transition at Tg occurs, and co-operative segmental motion of the polymer chains becomes possible, resulting in the qualitative change of state from glass to rubber. Above Tg, the polymer chain segments can undergo co-operative rotational, translational and diffusional motion, in the case of an uncrosslinked non-crystallising polymer, if the temperature is raised further (usually c.a. Tg + 100°) it eventually assumes liquid like behaviour.

A first order thermodynamic transition, such as crystalline melting point, is characterised by discontinuities in the heat content and specific volume (both first derivatives of free energy) associated with heat of fusion and volume change on fusion. Tg is characterised by an abrupt change in volume expansion coefficient and heat capacity. These second derivatives of free energy are often used to determine Tg, and in fact some older texts refer to this phenomenon as a second order or apparent second order transition. It is not a true thermodynamic transition however, because rate affects manifest themselves in most experimental determinations of Tg, and the thermal history of the sample is also significant. As theories of Tg suggest (see below), a polymer is not in thermodynamic equilibrium at Tg when cooled at any finite rate, and on subsequent heating after rapid cooling the specific volume versus temperature curve may loose its simple two straight line form, and becomes more complicated. Thus, for example figure 1 shows how samples cooled at different rates give apparently different Tgs as determined by dilatometry.

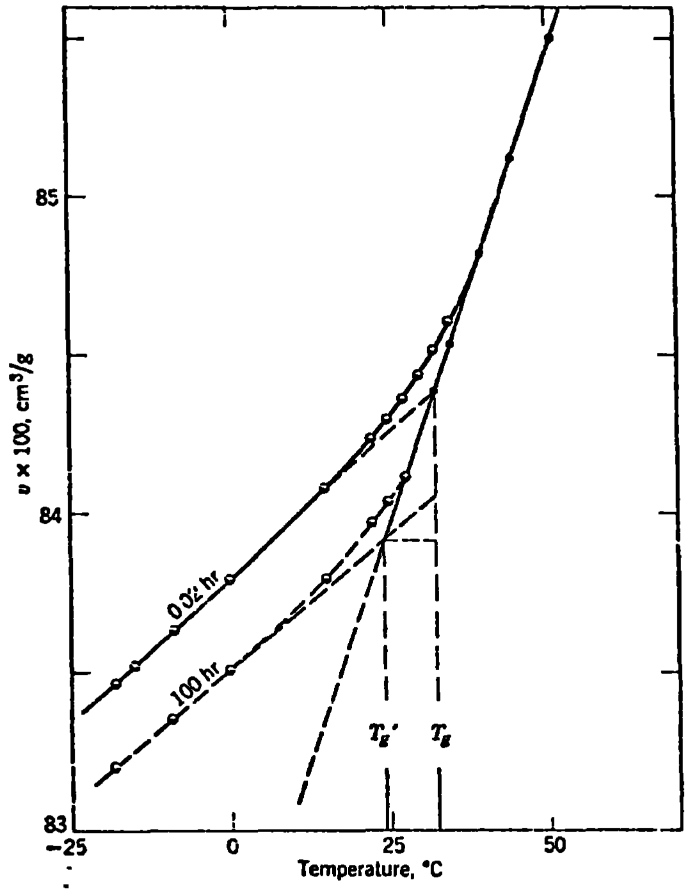
Rate effects in the measurement of Tg can be of three kinds :-

i) Rate of heat transfer to and from a sample.
ii) Rate of attainment of equilibrium at the imposed temperature.
iii) Rate of response to applied electrical or mechanical stress.

Use of fast heating or cooling rates may not allow temperature equilibriation of a polymer sample with its environment particularly ~~near~~ and below Tg where the relaxation processes involved are slow. Since isothermal drifts in volume and heat contents etc may occur over long periods of time near Tg, then true equilibrium determinations are difficult. In the interest of time saving, it is nearly always necessary to extrapolate[42-44] results in the region of Tg, but corrections for rate may be applied. Methods of determining Tg which involve high rates of application of electrical or mechanical stress often give Tg values approximately 20° higher than those determined at much slower rates e.g. dilatometrically. Various approximations to correct for frequency effects are available.

Figure 1.

The influence of thermal history on the glass transition temperature determination. Specific volume of poly (vinyl acetate), measured after cooling quickly from well above Tg. (after reference 41).



Since no measurement of Tg can be carried out at zero rate relatively slow methods are used, as opposed to dynamic or high frequency methods. With a very great number of physical properties of a polymer changing at Tg, a great variety of observational methods may be used to obtain values for Tg. A listing of these methods is recorded in the literature.[48] The most widely used techniques would appear to be dilatometry, differential scanning calorimetry (D.S.C.), penetrometry, and torsional braid measurements.

1.4 Theories Of The Glass Transition.

The above examination of the changes that occur at the glass transition shows that not only are static and thermodynamic properties affected, but that rate and relaxation properties are also markedly influenced. It is this dual characteristic of the glass transition that over the years has been the cause of considerable controversy over the development of a satisfactory theoretical explanation. Much of this difficulty has been in trying to adopt a quantitative approach to a phenomenon which affects thermodynamic quantities, and at the same time, shows a great or overriding dependence on rate effects. This has given rise to theories which have their origin in either thermodynamic or kinetic explanations. There are apparently three opposing but not mutually contradictory views of this phenomenon.

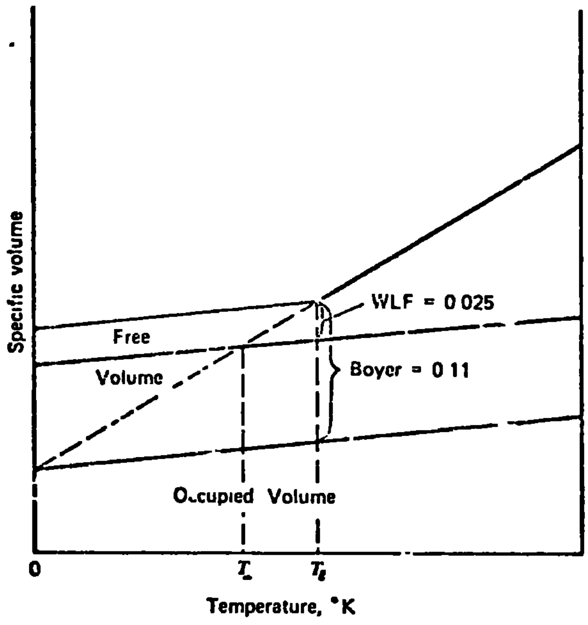
First, in the theory due to Gibbs and DiMarzio[49-52] (equilibrium theory), the observed glass transition is considered the result of kinetic manifestations of the approach to a true equilibrium thermodynamic transition. At infinitely long times, a second order thermodynamic transition could be achieved under equilibrium conditions. The approach to the transition is seen as the configurational entropy change of the material with temperature. As the temperature is lowered, the number of states available to the polymer decreases and the rate of approach to equilibrium also decreases. For a system in equilibrium being cooled, Tg is defined as the temperature at which the change in configurational entropy becomes zero.

Secondly the relaxation or hole theory of Hirai and Eyring[53,54] views vitrification as a process involving the passage of kinetic units (chain segments in which all the atoms move co-operatively) from one energy state to another. These units move into "holes" or empty spaces, formation of which requires a "hole" creation energy (the energy needed to overcome the surrounding molecules cohesive forces), and an activation energy to overcome the rearrangement potential barrier, via an activated state. All the holes in a polymer sample are characterised by a single mean volume. Description of the approach to equilibrium of a cooled rubbery liquid by this theory, defines the glass transition temperature as the half freezing of the hole equilibrium. This depends only on the cooling rate, since ample molecular motion in the liquid is possible for equilibrium to be achieved. In contrast as the glass is heated, then Tg depends not only on the heating rate, but also on the thermal history of the sample, since equilibrium cannot be reached below Tg. That is to say, glasses obtained by the use of differing cooling rates, represent different starting materials, having different enthalpies and time dependent heat capacities in the glass transition range.[55]

Lastly the free volume theory[56] based on a model proposed by Fox and Flory,[57] is the one outstanding successful approach to the problem. A liquid has it's volume partly occupied by molecules and partly by "free" or unoccupied volume. This free volume results from imperfections in the packing order of molecules arising from their random array. It is used in order to adjust from one configurational state to another, and is essential for molecular motion by rotation or translation to occur. The glass transition therefore occurs at a temperature at which the free volume reaches a critical value, such that below this point there is insufficient room for co-operative segmental molecular motion to occur. Below Tg, the free volume is frozen into the polymer, remaining constant as does the "hole" size and distribution. The volume expansion coefficient observed below Tg has the same origin as the thermal expansion coefficient of a crystalline solid. Above Tg, as well as this expansion mode, there will also be an expansion of the free volume, resulting in a larger expansion coefficient than that of the glassy state. This can clearly be seen in Figure 2 which shows the relationship of the increase in free volume to the volume expansion coefficients above and below Tg, and also the location of the pseudo equilibrium value of Tg at infinite time.

Figure 2

A diagram of specific volume around Tg as interpreted by the free volume theory.



More detailed analysis of glass transition theories have been reviewed[58-60] recently.

1.5 Glass Transition Temperature Prediction.

The development of new polymers with desired physical properties would be greatly facilitated by the availability of methods for predicting such properties from a knowledge of chemical structure alone; in particular, from the point of view of the present work, elastomers with extended low and high temperature performance. The incorporation of relatively short sequences of fluorinated aliphatic chains has been shown to enhance high temperature stability, whilst not adversely affecting low temperature flexibility (e.g. fluorinated polyesters and polyurethanes see section 1.1). The extension of low temperature performance, which is governed by Tg, may only be really satisfactorily achieved by the investigation and synthesis of new polymeric structures; although it may be possible to modify the observed properties of available materials to some extent by the incorporation of additives (e.g. plasticisers) or by preparing blends. The availability of methods for predicting Tg of polymers from chemical structures alone, would allow areas of potential interest (i.e. elastomers with a sufficiently low Tg prediction to allow significant extension of low temperature performance) to be detected and investigated. Such an approach would in principle, speed up the search for new materials although there is no guarantee that the predicted structures would be accessible by currently available synthetic techniques.

Several empirical methods for the prediction of glass transition temperatures have been proposed. Starting with equations describing the Tg dependence of copolymers on composition, additive temperature parameters (A.T.P.S) were calculated for individual structural units (groups of atoms).[61,62] In one of these treatments due to W.A. Lee of the Materials Department of the Royal Aircraft Establishment at Farnborough, consideration of the sequential arrangement of the groups in the polymer chain is taken into account.[63] A similar method has assumed the additivity of another parameter, density, as well as temperature in the empirical Tg calculation; whilst others have expressed the relationship of Tg and cohesive energy using the additive parameter approach.[64,65] Recent modifications to include a steric factor into this latter approach have been reported.[66]

The method due to Lee, has been developed and extended to consider the relationship between Tg and the molecular structure in fluoropolymers. For such a method to allow reliable estimates of Tg to be made, the data on which the computations are based must be as accurate as possible. Since, as explained earlier, the observed value of Tg is strongly dependent on the technique used in it's determination, there is a very real problem in acquiring a satisfactory data base on which to build the proposed parameterised predictive theory. In an attempt to overcome this problem Lee and Rutherford[67] have collected all the available data on fluoropolymers, critically assessed the reliability of the individual items, and taking into account differences in methods of determination have constructed a hopefully reliable table of glass transition temperatures. Such an operation however carefully carried out inevitably has an element of subjective assessment in it, which is of course undesireable in a quantitative approach; this limitation unfortunately appears unavoidable, but as more and more reliable data points become available the various parameters can be modified to obtain progressively better fits to the total data and therefore progressively better predictions. Using Tg data on a total of 144 fluoropolymers divided into 2 sets, one comprising of 51 aliphatic carbon chain polymers, and the other the remaining 93 polymers, a qualitative data analysis with respect to the effect of different bridging groups upon similar polymers, results in the observation that short sequences of fluoro-aliphatic and fluoroaliphatic ether diradicals promote low Tg values. Quantitatively, the Tg data on the fluoropolymers is seen to be self consistent, and the effects of various groups in raising or lowering Tg seem to be additive, provided that the groups are only regarded as identical if the neighbouring groups as well as the considered group are the same. That is to say that the Tg of a polymer is equal to the molar average of the Tg contributions of it's constituent neighboured groups, mathematically:-

$$Tg = \frac{\sum_{1}^{x} ni\ Tgi}{\sum_{1}^{x} ni}$$

where:- X = number of groups in the repeating units of the polymer.

ni = number of groups of the ith type.

Tgi = additive temperature parameter (ATP) associated with the ith group.

This method is called neighboured group analysis, applying it to a set of fluoropolymer Tgs gives rise to a set of simultaneous equations in which each reference Tg is expressed as a sum of ATPs appropriately weighted by the molar frequency of the group in the repeat unit. This set of simultaneous equations can, in principle, be satisfied by a unique set of ATPs, and it is these parameters which are required for predictive purposes. However, the data does not allow a unique solution and the best overall fit is obtained by computation. The resulting set of ATPs can then be used to recompute the base data, the difference between the original and recomputed Tgs gives a measure of the consistency of the approach. This has been done for two groups of fluoropolymers, the carbon chain, and the hetroatom chain types. The systematic errors in the method are listed in Table 1.

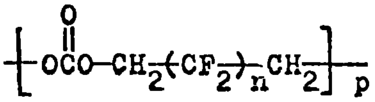
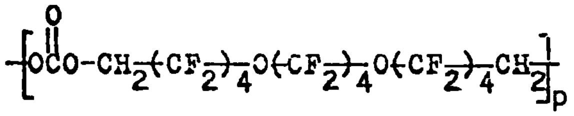
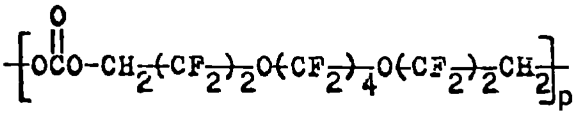
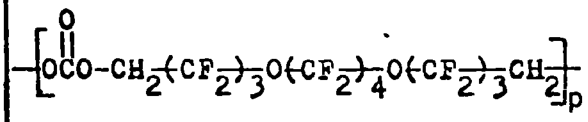
Table 1. Errors in neighboured group analysis of fluoropolymer Tgs.[68]

Polymer Type	Maximum Error (K)	R.M.S. Error (K)
Carbon Chain	21	4
Heteroatom Chain	17	6

The set of derived ATPs satisfactorily regenerates the Tg values from which they were calculated.

This approach can be applied to the prediction of Tg for other structures, with one proviso, that their constituent groups have appeared in the particular molar ratios required in other polymers for which Tg values are included. The results in Table 2 illustrate that the Tg values predicted by this approach for fluorinated aliphatic polycarbonates are considerably lower than those of materials currently available, for example Viton A Tg 250° K

<u>Table 2</u> Predicted Tg values for some fluorinated aliphatic polycarbonates.[68]

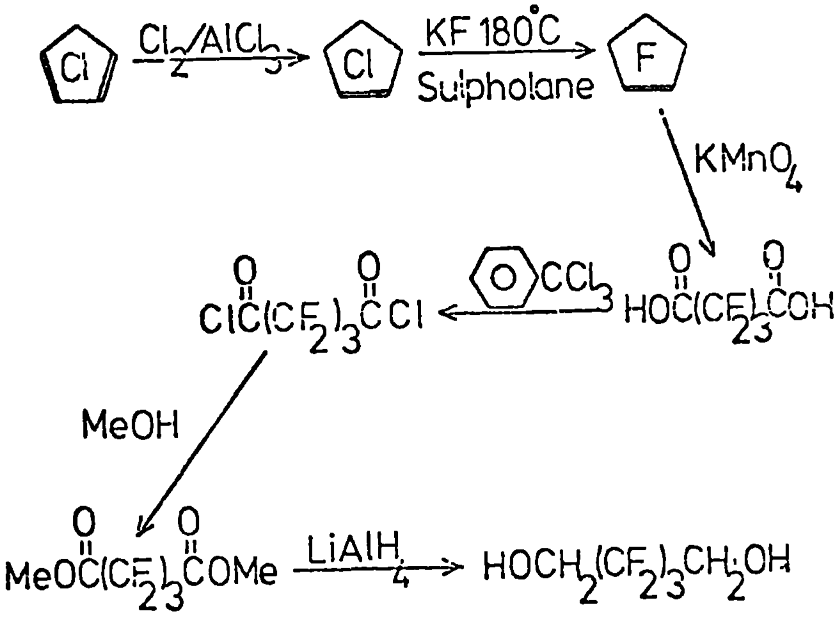
Structure		Tg (pred) K	Tg (obs) K
 $-\left[O\overset{O}{\overset{\|}{C}}O-CH_2(CF_2)_nCH_2\right]_p-$	n = 1	214	-
"	2	233	-
"	3	214	-
"	4	225	232
 $-\left[O\overset{O}{\overset{\|}{C}}O-CH_2(CF_2)_4O(CF_2)_4O(CF_2)_4CH_2\right]_p-$		217	-
 $-\left[O\overset{O}{\overset{\|}{C}}O-CH_2(CF_2)_2O(CF_2)_4O(CF_2)_2CH_2\right]_p-$		216	-
 $-\left[O\overset{O}{\overset{\|}{C}}O-CH_2(CF_2)_3O(CF_2)_4O(CF_2)_3CH_2\right]_p-$		217	-

A successful synthesis of these materials would therefore provide a useful check on the reliability of the predictive method, and possibly give rise to potentially useful new materials. Although it should be noted that even if the Tg is considerably lowered, a useful material will require satisfactory morphological characteristics (i.e. a low proportion of crystallinity), and satifactory chemical inertness, before it is considered for technological application.

The primary aim of this research has been to determine an effective synthesis of high molecular weight samples of fluorinated aliphatic polycarbonates, and to examine their physical properties, particlarly their glass transition temperatures and thermal stabilities, if successfully accomplished the work would then have extended the range of fluoropolymers known and provided data to test the validity of the predictive hypothesis advanced in other research establishments. The effect of introducing a flexibilising unit, the ether linkage, into the fluorinated main chain of the polycarbonates were also calculated, with a view to possible lowering of Tg values. This was a line of further research eventually not taken up.

Initial investigation of the synthesis of fluorinated aliphatic polycarbonates was to be performed using hexafluorpentanediol, since this is a readily available compound, which may be obtained by the following route.

<u>Figure 3</u> The Synthesis Of Hexafluoropentane Diol (HFPD)

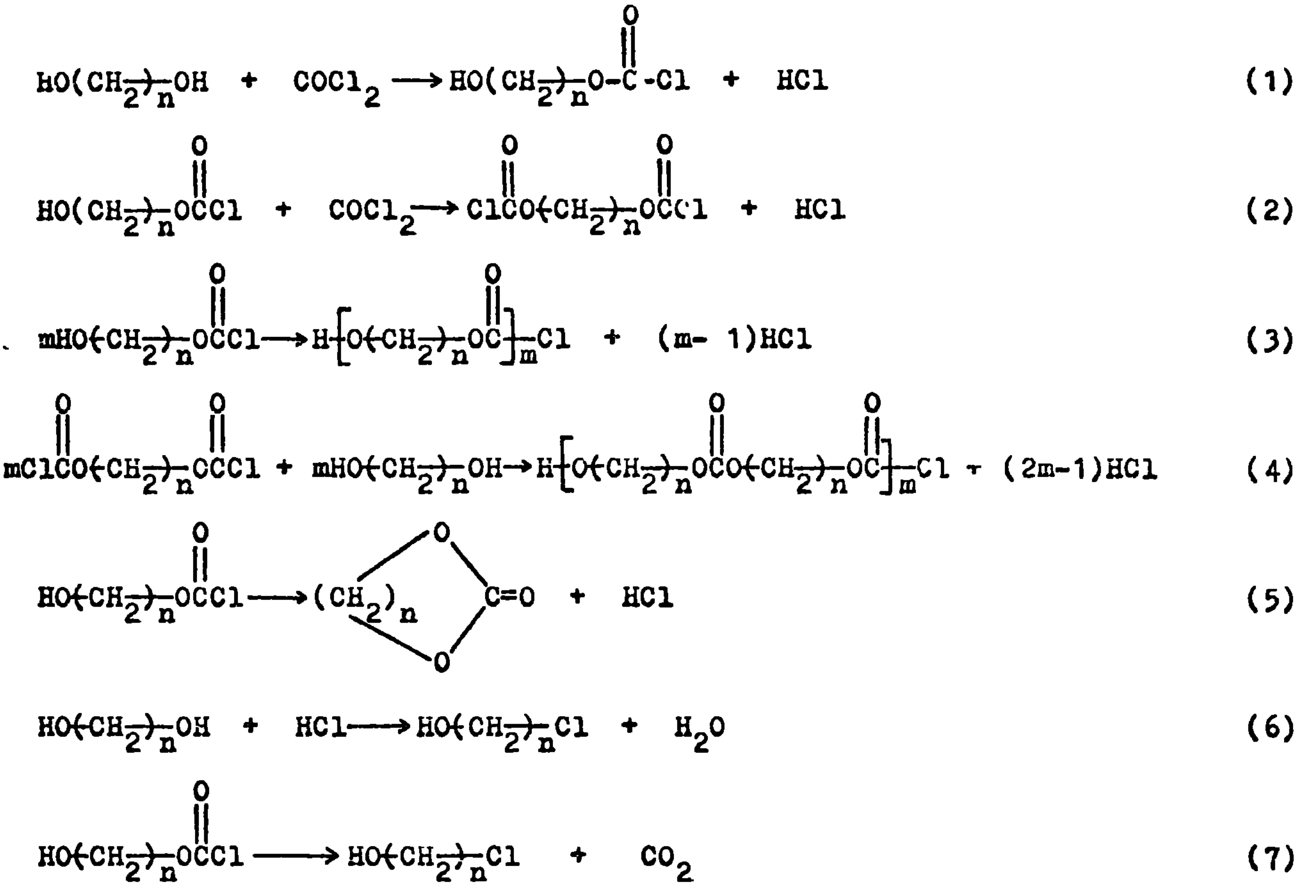


1.6 Preparation of Aliphatic Polycarbonates.

A literature survey of the available methods for polycarbonate synthesis was undertaken. By comparison with the information available for the synthesis of aromatic polycarbonates[69,70] the information concerning aliphatic polycarbonates is relatively meagre; never-the-less seven different approaches have been described and the main features of these are discussed below.

1.6 (i) Phosgenation of aliphatic diols.

When aliphatic diols and phosgene are mixed in inert solvents, the following reactions may occur:-



$$HO(CH_2)_nOH + COCl_2 \longrightarrow HO(CH_2)_nO\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + HCl \tag{1}$$

$$HO(CH_2)_nO\overset{O}{\overset{\|}{C}}Cl + COCl_2 \longrightarrow Cl\overset{O}{\overset{\|}{C}}O(CH_2)_nO\overset{O}{\overset{\|}{C}}Cl + HCl \tag{2}$$

$$mHO(CH_2)_nO\overset{O}{\overset{\|}{C}}Cl \longrightarrow H\left[O(CH_2)_nO\overset{O}{\overset{\|}{C}}\right]_mCl + (m-1)HCl \tag{3}$$

$$mCl\overset{O}{\overset{\|}{C}}O(CH_2)_nO\overset{O}{\overset{\|}{C}}Cl + mHO(CH_2)_nOH \rightarrow H\left[O(CH_2)_nO\overset{O}{\overset{\|}{C}}O(CH_2)_nO\overset{O}{\overset{\|}{C}}\right]_mCl + (2m-1)HCl \tag{4}$$

$$HO(CH_2)_nO\overset{O}{\overset{\|}{C}}Cl \longrightarrow (CH_2)_n\genfrac{}{}{0pt}{}{O}{O}C=O + HCl \tag{5}$$

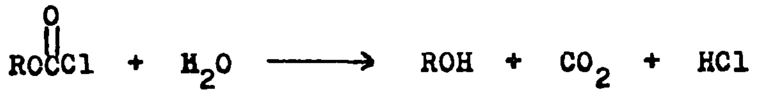
$$HO(CH_2)_nOH + HCl \longrightarrow HO(CH_2)_nCl + H_2O \tag{6}$$

$$HO(CH_2)_nO\overset{O}{\overset{\|}{C}}Cl \longrightarrow HO(CH_2)_nCl + CO_2 \tag{7}$$

The outcome of the reaction, will be determined by the diol used, and the detailed experimental conditions. The aliphatic hydrocarbon hydroxyl group usually reacts fast enough with the phosgene below 50° to form the chloroformate and HCl easily, frequently this is possible even below 0°. The bis-chloroformate of the diol may also be obtained in good yield via reactions (1) and (2), by adding the diol to liquid phosgene in an inert solvent.[71] However 1,2- and 1,3-diols have a great tendency to form cyclic carbonates via reaction (5), in addition to the bis-chloroformate;[72] this may be directly attributed to the stability of the 5- and 6-membered rings formed. If phosgene is added to these diols dissolved in an inert solvent good yields of the cyclic carbonates are obtained. Diols with hydroxyl groups separated by more than four carbon atoms give mixtures of bis-chloroformates and higher-boiling chlorine containing by-products.

In general high molecular weight chlorine free polycarbonates are not accessible by this route. This may be attributed to the different reactivities of phosgene and chloroformates towards the hydroxyl group. As seen above, phosgene reacts rapidly with the hydroxyl groups to form the chloroformates; however, these latter species react considerably slower with the hydroxyl group to form carbonic acid esters, i.e. polycarbonates. In order to carry out this latter reaction at a reasonable rate, the reaction temperature has to be elevated. However when the temperature is raised above 50° reactions (6) and (7) become important and some hydroxyl functionality is lost. The resulting chlorine containing mono-alcohols are, of course chain terminators for the overall polycondensation reactions (3) and (4), and consequently only low degrees of polymerisation can be obtained. A further source of chain-termination will be the water formed in reaction (6) which will hydrolyse both the phosgene and the chloroformates in the following manner:-

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl \qquad (8)$$

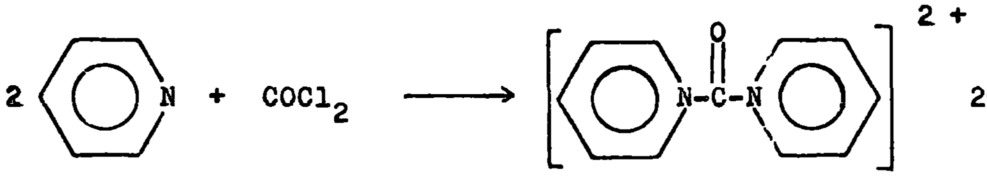


$$RO\overset{\overset{O}{\|}}{C}Cl + H_2O \longrightarrow ROH + CO_2 + HCl \qquad (9)$$

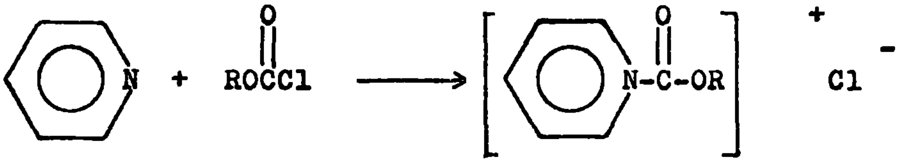
Both of the above reactions are faster than those with the alcohol, when carried out under the same conditions, it is therefore impossible to produce the chloroformates, cyclic carbonates or polycarbonates by this method in the presence of water or aqueous alkali, the desired products being obtained in very poor or zero yield.

Reactions of diols in inert solvents such as toluene, xylene, with phosgene at high temperatures in the presence of finely distributed carbonates, bicarbonates or hydroxides of alkali or alkaline earth metals yields low molecular weight hydroxyl terminated polycarbonates provided the water formed by neutralisation is quickly removed from the reaction mixture.[72]

The preparation of polycarbonates by phosgenating diols at a low temperature is catalysed by the addition of pyridine or tertiary amines. It has long been known that these compounds form ionic adducts with phosgene and chloroformates, and that these ionic compounds are more reactive towards the hydroxyl group, than the chloroformates.[74] The ionic adducts of pyridine, see (10) and (11) below, are especially suited to preparation of neutral formic acid esters and polycarbonates.[74]

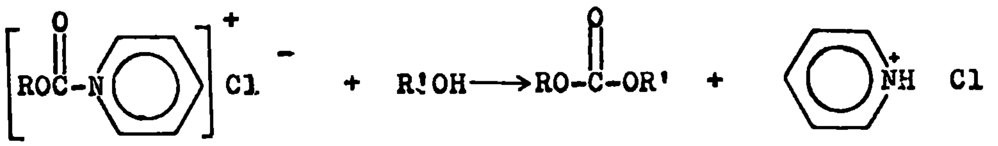


(10)



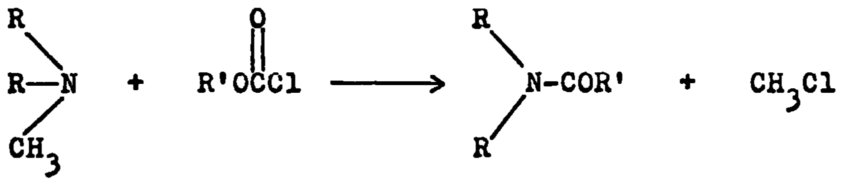
(11)

Since the adduct formed in reaction (11) is much more reactive than the chloroformate, the reaction of these adducts with the diols to give the carbonic acid esters and pyridine hydrochloride reaction (12) at a reasonable rate without elevating the reaction temperature is possible. This also reduces the extent of the chain termination reactions (6), (7), (8) and (9) resulting in a higher degree of polymerisation for the overall reaction.



(12)

These adducts may be made in a solution of the diol in pyridine, or in a mixture of pyridine and an inert solvent. The pyridine hydrochloride will not react with phosgene or chloroformates to form reactive adducts. Therefore a slight excess of pyridine is required over and above the stoichiometric amount to act as catalyst for the reaction. Reactions (10) and (11) have to be carried out under dry conditions since the adducts decompose in the presence of water to give carbon dioxide and pyridine hydrochloride. In addition to reactions (1) to (5) side reactions have been observed, especially at higher temperatures, when tertiary amines are used as acid binding materials in the phosgenation, particularly when such amines contain one or several alkyl groups with a small number of carbon atoms. The side reactions may be attributed to the formation of alkyl chlorides and carbonic acid esters by reaction of the chloroformates with these amines[75] see (13).



(13)

Hence the preference of pyridine as the acid acceptor since this side reaction, restricting the extent of the polycondensation, is not available with pyridine.

Thus for the preparation of aliphatic hydrocarbon polycarbonates, the diol is dissolved in a mixture of an inert solvent and just over 2 moles of pyridine, one mole of phosgene being added at or below room temperature. The viscous solution is washed with diluted hydrochloric acid and then with water to remove traces of pyridine and finally dried, the polycarbonate being obtained by evaporation of the solvent.

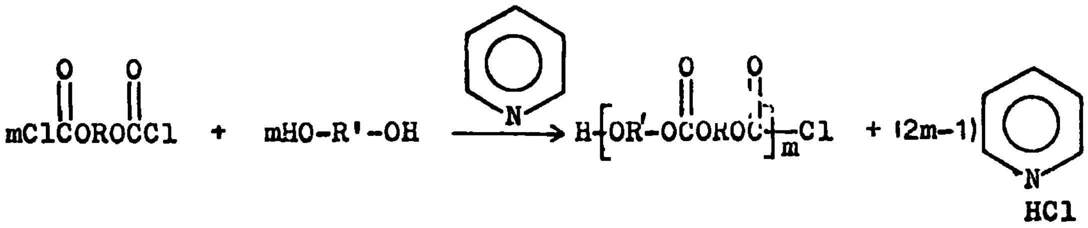
Phosgenation can also lead to good yields of cyclic carbonates, using tertiary amines and diols capable of forming 5- or 6-membered cyclic carbonates i.e. 1,2- and 1,3-diols. 1,4-diols can also form cyclic carbonates when the dilution principle is used, for example 7- and 14-membered cyclic carbonates, together with a low molecular weight polycarbonates were obtained on the addition of phosgene in toluene to a dilute solution of 1,4- butane diol and pyridine in chloroform at 40-50°.[77,78]

1.6(ii) Reaction of bis-chloroformates of aliphatic diols with aliphatic diols.

The reaction of bis-chloroformates of aliphatic diols and aliphatic diols, reaction (6) above, has to be carried out at elevated temperature for a reasonable reaction rate to be obtained. However, the side reaction leading to exchange of hydroxyl by chlorine takes place under these conditions. This can be partially eliminated by carrying out the reaction under vacuum, so that the HCl formed is immediately removed from the reaction mixture. In this manner low molecular weight aliphatic polycarbonates, have been obtained.[79]

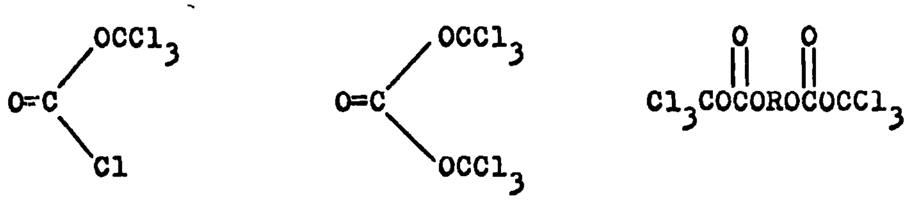
The reaction of bis-chloroformates with aliphatic diols in inert solvents at elevated temperatures in the presence of finely divided carbonates, bicarbonates or hydroxides of alkali or alkaline earth metals, has also been carried out yielding low molecular weight polycarbonates with terminal hydroxy groups, providing that water formed during the reaction is removed quickly from the reaction.[72]

Reaction of the bis-chloroformates with the aliphatic diols in the presence of tertiary amines, as seen in the previous section, is better suited to the preparation of high molecular weight polycarbonates. However, the thermal instability of the hydrocarbon bis-chloroformates has prevented the preparation of high purity samples, and therefore high molecular weight polycarbonates by this route. Regular alternating copolymer albeit of of relatively low degree of polymerisation can be prepared by this method,



(14)

A variation on this basic procedure may be effected by using compounds that react in the same way e.g. trichloromethyl chloroformate (diphosgene), bis (trichloromethyl) carbonate or the bis (trichloromethyl) carbonates of aliphatic diols[80] i.e.

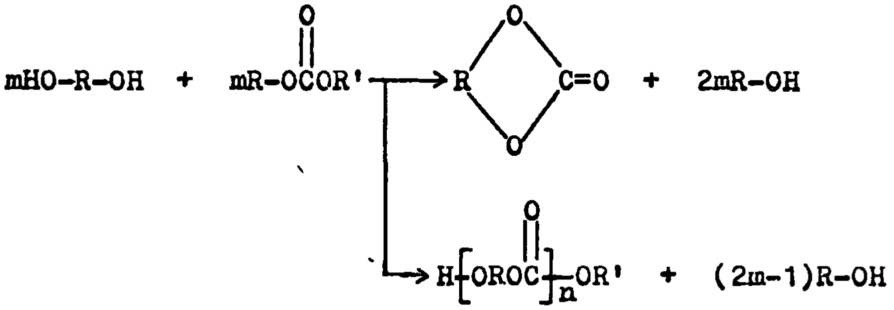


(15)

which may promote the polycondensation reaction by being much better elimination products.

1.6 (iii) Trans-esterification of aliphatic diols with dialkyl carbonates.

The reaction of aliphatic diols with equimolar amounts of the dialkyl carbonates is the most generally useful method for the preparation of high molecular weight aliphatic hydrocarbon polycarbonates.



(16)

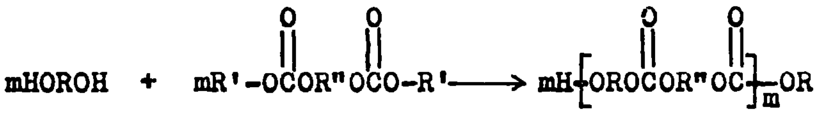
(17)

Depending on the diol and the reaction conditions, either cyclic carbonates, a mixture of cyclic carbonates and polycarbonates, or just polycarbonates may be obtained. Indeed this is the route Carothers[81,82] used to first synthesise polycarbonates in his classic investigation of polymer forming polycondensation reactions; the diols $HO(CH_2)_nOH$ (where n = 2—9,11—14,18), diethylene glycol, triethylene glycol, p-xylene glycol were trans esterified with diethyl or dibutyl carbonate, between 120-160°, using alkoxide catalysis. In many cases the pressure was reduced in the latter part of the polycondensation to effect complete removal of the alcohols formed. In the case of the 1,2- and 1,3- diols the cyclic carbonates were formed. Diols with the hydroxyl group separated by more than 3 carbon atoms gave polycarbonates of molecular weights lower than 3000. Later investigation of the influence of reaction conditions and the structure of the aliphatic diols on the formation of cyclic carbonates or polycarbonates during trans-esterification with dialkyl carbonates,[77,78] showed that the monoesters are formed first, and that the structure of the diols determine whether the monoesters form cyclic carbonates or polycarbonates. Increase in the rate of reaction and use of the dilution principle favour cyclic carbonate formation. Cyclic carbonate formation from 1,3-propane diol derivatives is favoured by bulky substituents on C_2 or substituents on C_1 and C_3.

The trans-esterification reaction is not possible in the absence of catalysts even at elevated temperatures, being only feasible in the presence of strongly basic catalysts, e.g. sodium alkoxides at temperatures between 120-220°. The use of these temperatures however create problems with the volatility of the dialkyl carbonates especially the lower alkyl derivatives resulting in a part of the dialkyl carbonates being lost from the reaction mixture together with the alcohol eliminated. This causes an excess of the diol to be present in the reaction mixture, which may act as a chain terminator, preventing the formation of high molecular weight polycarbonates. This problem may be overcome by adopting appropriate experimental techniques.[82] However high molecular weight polycarbonates are not obtained this way, because the highly alkaline catalysts present, tend to degrade and decompose the aliphatic polycarbonate at the temperatures necessary for its formation.

The trans-esterification procedure used by Carothers has been modified to remove the influence of the alkaline catalyst in the latter stages and at higher temperatures,[84] using sodium alkoxides and a non-volatile water insoluble carboxylic acid or ester in a concentration lower than that of the alkoxide catalyst. After the larger portion of the alcohol has been eliminated the low molecular weight polycarbonate is dissolved in an inert solvent, and washed with dilute HCl and water to remove the alkali. After removal of the solvent, trans-esterification was continued at temperatures up to 200° and under vacuum, using the catalytic action of the carboxylic acid, to give polymers of intrinsic viscosities 0.4-0.6 in chloroform.

The production of high molecular weight polycarbonates by this method is greatly simplified by the use of diaryl carbonates in the trans-esterification e,g. diphenyl carbonate which reacts without catalysts and relatively low temperatures.[85] This method gave a polycarbonate of relative viscosity 1.414 in dichloromethylene at 25°. It is also possible to produce aliphatic polycarbonates or polycarbonate copolymers by trans-esterification of diols with bis-alkyl or bis-arylcarbonates of the same or another diol e,g.

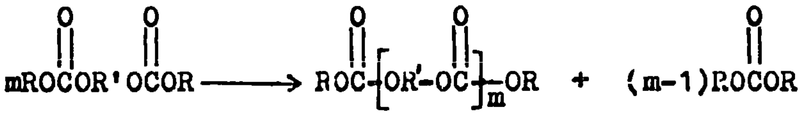


$$mHOROH + mR'{-}O\overset{\overset{O}{\|}}{C}OR''O\overset{\overset{O}{\|}}{C}O{-}R' \longrightarrow mH\left[ORO\overset{\overset{O}{\|}}{C}OR''O\overset{\overset{O}{\|}}{C}\right]_m OR + (2m-1)R'OH \qquad (18)$$

In the above reaction high molecular weight polymers have also been prepared where R and R" are cyclobutane rings.[86]

1.6 (iv) Polycondensation of bisalkyl or bisaryl carbonates of aliphatic diols.

This may be regarded as an extention of methods described in the preceding section, whereby the requirement for strict stoichiometic balance between the diol and bisalkyl or bisaryl carbonate is avoided. The polycondensation is carried out using just the bisalkyl or bisaryl carbonates of the aliphatic diols which form polycarbonates by eliminating dialkyl or diaryl carbonates, reaction (19). This reaction is catalysed by a whole range of basic catalysts, for example alkoxide ions-



$$m\mathrm{RO\overset{\overset{O}{\|}}{C}OR'O\overset{\overset{O}{\|}}{C}OR} \longrightarrow \mathrm{RO\overset{\overset{O}{\|}}{C}}\left[\mathrm{OR'{-}O\overset{\overset{O}{\|}}{C}}\right]_m\mathrm{OR} + (m-1)\mathrm{RO\overset{\overset{O}{\|}}{C}OR} \qquad (19)$$

This procedure has the advantages that correct stiochiometry is automatically maintained during the entire polycondensation, and the decomposition of the diols at elevated temperatures is also avoided. Polycarbonates of penta-, hexa-, decamethylene diol have been produced with highly alkaline trans-esterification catalysts, and high temperatures up to 240°, under reduced pressure. Intrinsic viscosities in the range 1.3 and 1.7 in chloroform[87] have been obtained.

Preparation of the monomers is effected from the diols by trans-esterification with an excess of dialkyl or diaryl carbonate, or by reaction of alkyl or aryl chloroformate with diols in pyridine.

1.6 (v) Polymerisation of cyclic carbonates.

Cyclic carbonates of aliphatic diols with ring size larger than 5 can be polymerised. These monomers are available by the following processes:

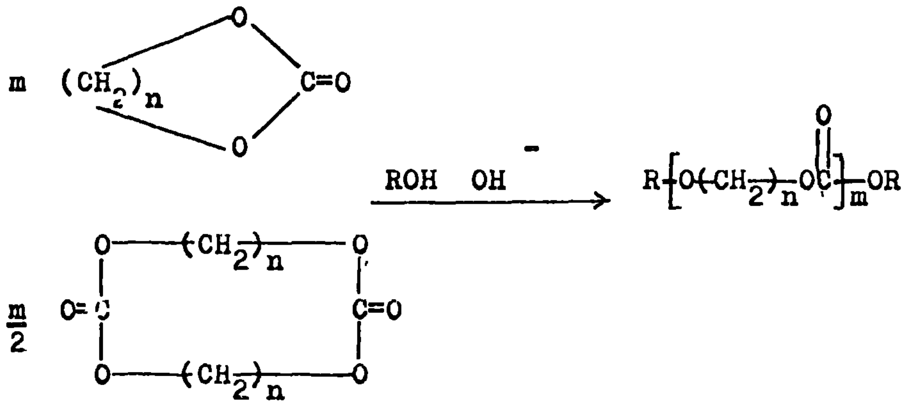
(i) phosgenation of aliphatic diols;

(ii) trans-esterification if aliphatic diols with diesters of carbonic acid;

(iii) depolymerisation of aliphatic polycarbonates.

The latter process was discovered by Carothers. Heating the polycarbonates he obtained by trans-esterification method under reduced pressure, he prepared monomeric and dimeric cyclic carbonates[82] together with some decomposition products. 2,2-Disubstituted 1,3-propane diol derivatives also form corresponding cyclic carbonates readily and in good yield when heated at atmospheric pressure.[77,78]

This method of polymer formation was first used by Carothers and Van Natta[81] who obtained poly(trimethylene carbonate) on heating the cyclic trimethylene carbonate with potassium carbonates. Latter, Hill and Carothers[82] prepared the corresponding polycarbonates from the cyclic carbonates of deca-, dodeca-, trideca-, and tetradeca-methylene diol, and from the dimeric cyclic carbonates of hexa- and deca-methylene diol.



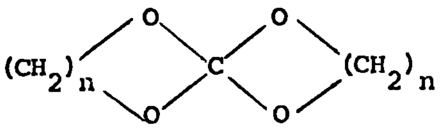
(20)

Water or alcohols are necessary for chain termination, if they are not present in the monomer or formed during heating, they have to be added.

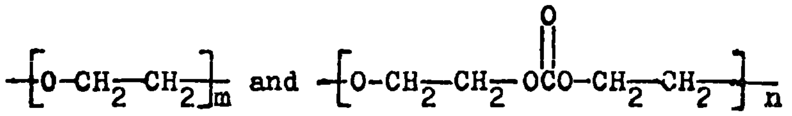
Polymerisation of cyclic carbonates can be hindered by certain substituents on the ring carbon atoms, as has also been shown for other cyclic monomers which can polymerise by ring opening. The readily formed cyclic carbonates of 2,2-disubstituted 1,3-propane diols show only a negligible tendency to polymerise.[77,78]

1.6 (vi) Spiro orthocarbonate ring opening polymerisation.

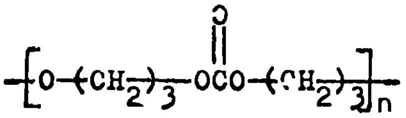
A recently developed technique[88] depending on the successful development of novel methods of preparing the spiro ortho carbonates of the general formula:



and using cationic initiators e.g. boron trifluoride etherate, leads to ring opening polymerisation where n = 2 to 4. When n = 2 a mixture of cyclic ethylene carbonate and a polymer containing poly(oxyethylene) and poly(diethylene glycol carbonate) units, i.e.

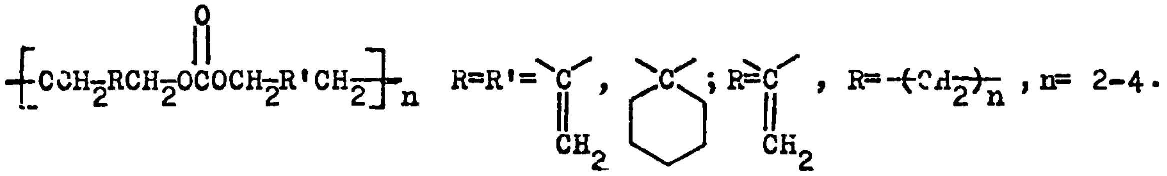


$\left[O-CH_2-CH_2 \right]_m$ and $\left[O-CH_2-CH_2-O\overset{O}{\overset{\|}{C}}O-CH_2-CH_2 \right]_n$ is obtained; where n = 3 the polyether carbonate



$$\left[O-(CH_2)_3-O\overset{O}{\overset{\|}{C}}O-(CH_2)_3 \right]_n$$

results; and where n = 4 poly(tetramethylene carbonate) results. This method has been developed more recently to give polyethercarbonates of the following structures:-[89,90]



$\left[OCH_2RCH_2O\overset{O}{\overset{\|}{C}}OCH_2R'CH_2 \right]_n$ R=R'= $\underset{CH_2}{\overset{\|}{C}}$, ; R= $\underset{CH_2}{\overset{\|}{C}}$, R= $-(CH_2)_n-$, n= 2-4.

1.6 (vii) Copolymerisation of an epoxide with carbon dioxide.

In a method developed by Japanese workers,[91] propylene epoxide has been reacted with carbon dioxide in the presence of a diethylzinc/water catalyst to give poly(propylene carbonate) with an intrinsic viscosity of 4.60 in chloroform at 30°. Further development of the technique has lead to the use of a diethylzinc/aromatic carboxylic acid catalyst, leading to a polymer intrinsic viscosity of 1.21 in benzene at 30°.[92] This method however is limited by the ring opening step which is only possible for three membered ring cyclic ethers, i.e. epoxides, larger ring ethers do not react to form polycarbonates at all.[92]

The suitability of the various methods of synthesis to the preparation of high molecular weight sample of polycarbonates can be summarised briefly in the following manner;

Method (i)

Because of the great number of side reactions, chain terminations and the stringent requirements of dryness, catalyst and equimolar quantities of reactants, this method would be expected to show poor high polymer forming characteristics. In practice the intrinsic viscosities of the polycarbonates obtained is relatively low.

Method (ii)

Here the two reactants may be prepared in good yield, although the purity of the bis-chloroformate may be in question due to its thermal instability. Again high purity, dryness, exactly equimolar quantities of reactants and catalyst, are restraints on the degree of polymerisation possible using this method. Although a general improvement on the previous method, high molecular weight polycarbonates are not obtained. Although the route does offer some synthetic utility, where a polycarbonate with alternating aliphatic main chain components is desired, and high molecular weight is not critical; for example, in the preparation of prepolymers, for some formulations.

Method (iii)

This is the most important method for the preparation of aliphatic polycarbonates, products with high degree of polymerisation are obtained, e.g. specific viscosity for 1% solution in chloroform at 25° = 2.75.[86] Although it has been shown that special procedures are required to achieve these high degrees of polymerisations. This route is therefore of obvious significance and utility, especially where polymers with alternating aliphatic chains may be required.

Method (iv)

This may be regarded as a modification of the third method, over which it holds certain theoretical advantages namely, the need for exact molar equivalence of reactants is automatically maintained throughout the reaction;

the avoidance of diols, potential terminators at elevated temperature; and low catalyst concentrations. This is reflected in the high intrinsic viscosity of the polymers obtained,[87] for example 1.75 in chloroform. This method is therefore of obvious synthetic utility, for the production of homo,polymers and random copolymers.

Method (v)

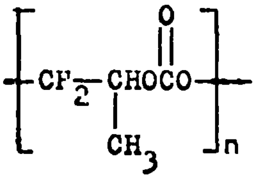
Little research has been carried out in this area since Carothers initial investigation, the monomers being readily obtainable and polymerisable however the polymers obtained have only low degrees of polymerisation.[77,78,81,82,95] Although the theoretical possibilities for this method suggest much higher values ought to be attainable. This method therefore seems attractive on theoretical grounds but the lack of practical examples must be regarded as a drawback.

Method (vi)

The dependence on the synthesis of new compounds using novel reactions, and also the degree of variability of the structure of the polycarbonate produced on polymerisation, must both be regarded as serious drawbacks to the synthetic utility of this approach.

Method (vii)

With this method, although high degrees of polymerisation are available, it is limited in its practical applications to hydrocarbon epoxides, producing polycarbonates of the structure



$$\left[-CF_2-\underset{\displaystyle CH_3}{\underset{|}{C}}HO\overset{\displaystyle O}{\overset{\|}{C}}O- \right]_n$$

i.e. the aliphatic carbon chain of the polycarbonate is only two atoms long. Therefore this route is of limited application at present.

1.7 Previous syntheses of fluorinated aliphatic polycarbonates.

It was found during the course of this literature survey, that several reports of the synthesis of fluorinated aliphatic polycarbonates existed, these are reviewed here. Using method (i) hexafluoropentane -1,5-diol has been reacted with phosgene, on its own and in admixtures with various dihydric phenols. The poly(hexafluoropentamethylene carbonate) obtained having an intrinsic viscosity of 0.3 in dioxane at 30°.[95] Method (ii) has been used to produce poly(hexafluoropentamethylene carbonate)[96,97] and also poly(octafluorohexamethylene carbonate)[98] both of relatively low molecular weights, 1000-1800 and 5000 respectively. The poly(hexafluoropentamethylene carbonate) was used as a prepolymer for preparation of highly fluorinated polyurethanes for use as structural adhesives.[99] Poly(octafluorohexamethylene carbonate) was synthesised in the course of an investigation into this particular method synthesis, centering on the experimental variables and their effects on the degree of polymerisation obtained.[98] A patent[100] has reported the use of method (iii) to prepare a polycarbonate of propane -1,3-diol with pendant fluorinated side chains.

From this literature survey and more importantly the survey of methods of making aliphatic polycarbonates, it was concluded that the most favourable routes to high molecular weight samples of fluoroaliphatic polycarbonates were likely to be:-

a) Transesterification of fluorinated diols with dialkyl or diaryl carbonates.

b) Polycondensation of bisalkyl or bisaryl carbonates of fluorinated diols.

It was therefore decided to initially investigate the latter of these two methods, because of the simpler experimental requirements.

Section 2.

The development of an effective synthesis of fluorinated aliphatic polycarbonates.

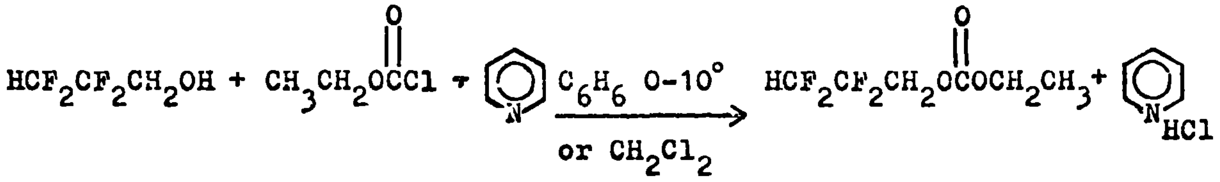
Section 2: The Development of an Effective Synthesis of Fluorinated Aliphatic Polycarbonates.

2.1 Introduction.

This section consists of a description of the sequence of events leading to the development of the synthetic route to fluorinated aliphatic polycarbonates which was eventually successful and which will be described in greater detail in Section 3. The order of presentation is chronological, mistakes and false starts have been included to show how the approach was successively modified in the light of experience. To some extent the sequence of events was dictated by the availability of materials.

2.2 Discussion.

The methods of synthesising polycarbonates were reviewed earlier (Section 1.6) and the route chosen was via the alkoxide ion catalysed ester exchange reaction. Initially it was thought appropriate to examine this reaction using monomeric system, in order to obtain a good understanding of the factors affecting the proposed polymer forming reaction. It was expected that such an approach would also provide a set of spectral parameters on simple well defined compounds which would prove useful in subsequent polymer characterisations. The alcohol used for this exercise was 1,1,3-trihydrotetrafluoropropan-1-ol (I), this is commercially available resulting from the radical telomerisation of tetrafluoroethylene with methanol. Alcohol (I) was converted in good yield (~80%) to the 2,2,3,3,-tetrafluoropropylethyl carbonate using ethylchloroformate and pyridine in an inert solvent as indicated in reaction 21.

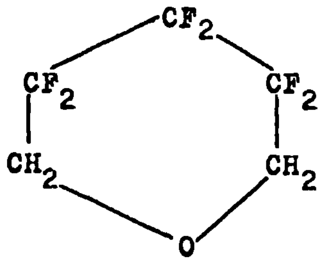


(21)

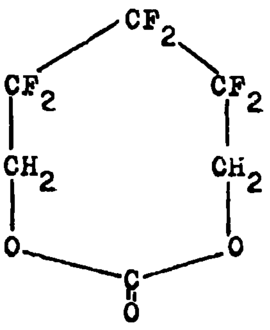
(I) (II)

Attempts to investigate the thermal and alkoxide ion catalysed ester exchange reactions of this compound were frustrated by the fact that the starting materials and reaction products were of very similar volatility and effective separation could not be achieved. This approach was therefore abandoned in favour of a direct attempt to prepare fluorinated aliphatic polycarbonates by the ester exchange reaction of bisalkyl carbonates of hexafluoropentane-1,5- diol (HFPD), where the volatility problems associated with the seperation of products were not anticipated.

Thus the bis(methyl) carbonate of HFPD was prepared by a method analogous to that described above for alcohol I (see reaction 21). After purification and characterisation of this monomer several attempts were made to polymerise it, thermally and by alkoxide ion catalysed ester exchange. The catalyst used was a solution of sodium methoxide in methanol prepared by dissolving sodium in rigorously dried and purified methanol, following the procedure described in the patent.[87] Several experiments were carried out varying the temperature, pressure (atmospheric or lower) and duration of reaction and the time at which the catalyst solution was added (i.e. either prior to heating, or to the hot monomer). These attempted polymerisations were unsuccessful, in general the monomer was finally distilled from the reaction vessel in essentially quantitative yield. On some occassions low yields (∼5%) of volatile products were also obtained. An analysis of the product mixture using a gas chromatograph coupled with a mass spectrometer allowed a tentative assignment of two of the products as (III) and (IV).



(III)



(IV)

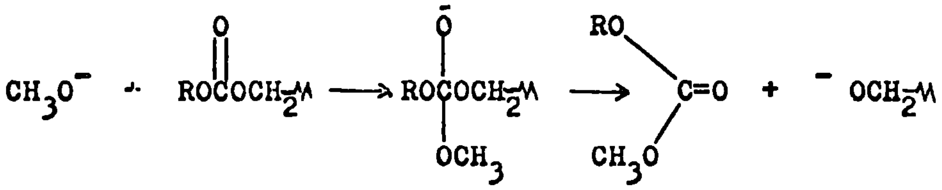
At this stage, it was thought necessary to eliminate any doubts concerning the experimental procedure being used, and to this end the synthesis of poly(hexamethylene carbonate) by ester exchange from the bis (ethyl) carbonate of hexamethylene -1,6-diol was undertaken following the literature procedure.[87] The catalyst system used was sodium ethoxide in ethanol, prepared as described in the patent,[87] and somewhat disconcertingly polymerisation was not observed. A careful consideration of the various factors which might have been responsible for this failure lead to an examination of alternative methods of obtaining the required alkoxide catalyst. A sample of solid sodium methoxide was obtained and on substituting this for the catalyst solution used previously a satisfactory polymerisation followed giving poly(hexamethylene carbonate), a tough white solid Mn~7100,(D.P.~49). Having eliminated questions concerning experimental technique and obtained an active alkoxide catalyst, the polymerisation of a bisalkyl carbonate of a fluorinated diol was re-examined.

The bis(ethyl) carbonate of HFPD was therefore prepared, purified, characterised and then submitted to attempt polymerisation under conditions closely analogous to those successful with the bis(ethyl) carbonate of hexamethylene-1,6-diol, without any detectable reaction in several attempts. Variation of the reaction conditions and substitution of calcium hydride for sodium methoxide as the base catalyst also failed to effect any polymerisation.

In the light of this result and the previous failure with the bis (methyl) carbonate of HFPD, a re-examination of the reaction was undertaken, especially with respect to the proposed mechanism.

The alkoxide ion catalyst polymerisation of bis-carbonates may be rationalized as follows.

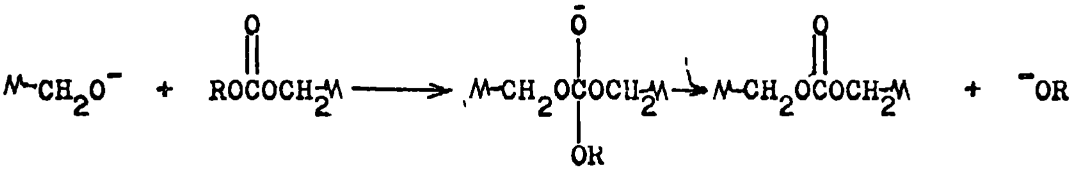
Initiation



$$CH_3O^- + RO\overset{O}{\overset{\|}{C}}OCH_2\sim \longrightarrow RO\overset{O^-}{\underset{OCH_3}{C}}OCH_2\sim \longrightarrow (RO)(CH_3O)C{=}O + {}^-OCH_2\sim \quad (22)$$

(V) (VI)

Propagation



$$\sim CH_2O^- + RO\overset{O}{\overset{\|}{C}}OCH_2\sim \longrightarrow \sim CH_2O\overset{O^-}{\underset{OR}{C}}OCH_2\sim \longrightarrow \sim CH_2O\overset{O}{\overset{\|}{C}}OCH_2\sim + {}^-OR \quad (23)$$

(VII)

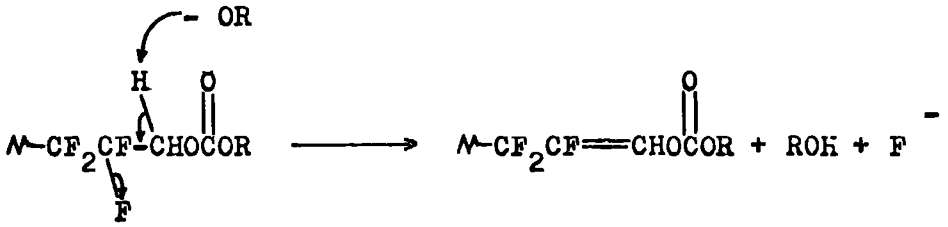
The initiation step involves attack by the initiating alkoxide at the carbonyl carbon of the monomer, subsequent elimination of a dialkyl carbonate from the intermediate anion (V) results in an alkoxide chain end (VI). Propagation occurs when this alkoxide chain end (VI) attacks another carbonate group to displace an alkoxide anion (RO^-) rather than a chain end alkoxide. Where the initiating and chain end alkoxide species are of similar reactivity, then the reactions 22 and 23 should properly be represented as equilibria, the overall reaction being driven towards polymerisation by removal of the volatile eliminated dialkyl carbonate. It is reasonable to enquire if an explanation of the failure to observe polymerisation in the fluoro-carbon case can be constructed on the basis of this mechanistic rationalisation. The expected effect of the electronegative fluoro-alkylene sequence on the reactivity of the carbonyl group is to enhance it's susceptability to nucleophilic attack; thus, the initiation step would reasonably be expected to be easier in the fluoro-carbon case than in the hydrocarbon analogue. However, having formed the alkoxide chain end (VI) will the fluorocarbon species (VII) formed in the subsequent propagation step react in the same way as the analogous hydrocarbon?, the answer to this question will depend on the relative stabilities of the alternative alkoxide anions. Some indication of these stabilities can be obtained from the pKa values of the appropriate alcohols (see Table 3) and from this it is clear that the more acidic fluoroalcohol is expected to give rise to the more stable anion, consequently it is to be expected that in the fluorocarbon case (reaction 22) will proceed in the direction of the formation of the chain end alkoxide (VI) without difficulty.

Table 3: pKa Values for Various Alcohols

Alcohol	pKa	Reference
- CF_2CH_2OH	11-12	102
- CH_2CH_2OH	18	103
OH	9-11	104

It is also reasonable to assume that reaction of this alkoxide with a carbonate group (reaction 23) will occur to give the intermediate anion (VII), however at this point the propagation reaction requires the elimination of a less stable hydrocarbon alkoxide anion (RO^- in reactions 22 and 23). This is clearly in conflict with the above arguement which would expect the preferential elimination of the fluoroalkoxide species from this intermediate with resultant prevention of propagation.

This prediction is in agreement with the observed results, not only the failure to observe polymerisation, but also the low yield byproducts actually detected fit in with the proposed rationalisation. Thus, the analysis presented above proposes that the reaction proceeds as far as the formation of the alkoxide $ROCOOCH_2(CF_2)_3CH_2O^-$, but that the intermolecular reaction between this and another alkylfluoroalkylene carbonate unit does not occur; the two minor products actually observed (III and IV) being conceiveably products of the intramolecular reaction of the initially formed anion (VII). An alternative reason for the lack of reaction in the fluorocarbon case, namely that the alkoxide initiator is consumed in dehydrofluorination reactions of the type indicated below in reaction 24, was not supported by any experimental observations and was subsequently



$$\sim CF_2\overset{\overset{^{-}OR}{H}}{\underset{F}{CF}}-CHO\overset{O}{\overset{\|}{C}}OR \longrightarrow \sim CF_2CF{=}CHO\overset{O}{\overset{\|}{C}}OR + ROH + F^- \qquad (24)$$

excluded by the successful synthesis of high polymers from a closely analogous systems.

In the light of the arguement presented above, preparation of the bis-fluoroalkyl carbonate of HFPD would be the most obvious case to pursue, since in this case it would be expected that thermodynamic and/or electronic factors introduced by the synthesis of bis-alkyl carbonates of HFPD would be eliminated, and the polymerisation reaction would revert to the fluoroalkyl analogue of the process described in the patent.[37]

In fact the next step undertaken in the investigation of this proposed polymerisation was the synthesis, purification, characterisation of the bis(phenyl) carbonate of HFPD, and its attempted polymerisation. This monomer was investigated since considerations of pKa (Table 3) suggested that it would be more readily polymerised than the bis-alkyl carbonates investigated previously and thus establish the viability of investigating polymerisation via the bis(fluoroalkyl) carbonates of HFPD. Its synthesis using the readily available phenyl chloroformate was a straight forward extension of established procedure. Initial polymerisations using solid sodium methoixde catalyst, lead to elimination of diphenyl carbonate under reduced pressure to give a viscous liquid which was characterised by integrating the signals in the ^{1}H n.m.r. spectrum due to methylene protons and aromatic protons their relative intensities giving an estimation of the overall degree of polymerisation (DP). Eventually after several trial polymerisations and with improving techniques the maximum DP obtained was 6. The main practical restriction was that of removing the relatively involatile diphenyl carbonate (b.p. 162° at 0.2mm Hg) quickly and efficiently enough to promote rapid polymerisation.

This result established the feasibility of the proposed polymerisation via the alkoxide ion catalysed ester exchange reaction of bis carbonates, despite the low D.P.s obtained. It was concluded that the best route to the fluorinated aliphatic polycarbonate objective would require the synthesis of bis fluoroalkyl carbonates of fluorinated diols and their reaction with alkoxide ion initiators since the use of such systems was expected to eliminate problems encountered eariler arising from relative alkoxide reactivities and/or the volatilities of the eliminated dialkyl or diaryl carbonate. This eventually successful method, is reported in greater detail in Section 3.

EXPERIMENTAL

2.3 Preparation of Hydrocarbon Alkyl Carbonates of Fluoroalcohols

General Method.

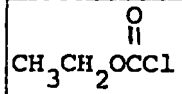
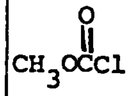
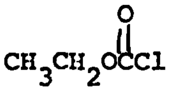
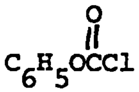
A mixture of the fluoroalcohol (1 molar proportion), dry ($CaCl_2$) pyridine (1·2 molar proportions) and an inert solvent (CH_2Cl_2) contained in a three necked round bottomed flask, equipped with mechanical stirrer, thermometer and dropping funnel, was stirred vigorously and cooled to 0-5° by the use of an external ice/salt bath. The chloroformate (1·2 molar proportions) was added at a rate such that the reaction temperature did not exceed 5°. As the reaction proceeds a precipitate of pyridine hydrochloride is formed. On completion of addition of the chloroformate, stirring was continued overnight, to ensure complete reaction. Pyridine hydrochloride was then filtered off and the solution washed approximately five times with an equal volume of water to remove excess pyridine. After drying over magnesium sulphate, the solvent was evaporated and the product carbonate purified by distillation.

A similar method was applied to synthesis of the bis-alkyl and bis-phenyl carbonates of hexafluoropentane-1,5-diol with suitable adjustments in the amount of pyridine and chloroformate used. Exact experimental details and analyses are included in Table 4.

2.4 Investigation of the Ester Exchange Reaction Using 2,2,3,3, Tetrafluoropropylethyl Carbonate.

Two drops of a solution prepared by dissolving sodium (0.7762g, 0.0337 moles) in methanol (10g, 0.312 moles, dried (Mg), distilled and stored over molecular sieve 3A) was added to 2,2,3,3,-tetrafluoropropylethyl carbonate (6g, 0.03 moles) in a round bottom flask (25ml), the operation being carried out in an atmosphere of dry nitrogen in a dry box. The flask was removed from the dry box and heated to 120° (oil bath), with stirring while maintaining the dry nitrogen atmosphere, for 6 hrs. Analysis of the

TABLE 4. Experimental details of the preparation of alkyl/aryl carbonates of fluoroalcohols.

Reactants and Quantities			Boiling Ranges of products				Yield %	IUPAC NAME	Elemental Analysis		
Alcohol g (moles)	Chloroformate g (moles)	Pyridine g (moles)	Experimental		Literature			COMMON NAME	Found (Required)		
			°C	mm Hg	°C	mm Hg			C	H	F
$HCF_2CF_2CH_2OH$ 29.60 (0.225)	 $CH_3CH_2O\overset{\overset{O}{\Vert}}{C}Cl$ 29.20 (0.269)	21.25 (0.269)	144	760	-	-	89	2,2,3,3-tetrafluoropropoxycarbonyloxyethane	35.5	4.1	37.0
								2,2,3,3-tetrafluoropropyl ethyl carbonate	(35.3)	(3.9)	(37.3)
$HOCH_2(CF_2)_3CH_2OH$ 50 (0.239)	 $CH_3O\overset{\overset{O}{\Vert}}{C}Cl$ 53.86 (0.57)	45.03 (0.57)	170	0.2	-	-	89	bis(methoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene	33.1	3.0	35.0
								bis methyl carbonate of hexafluoropentane-1,5-diol	(32.9)	(3.0)	(34.8)
$HOCH_2(CF_2)_3CH_2OH$ 50 (0.239)	 $CH_3CH_2O\overset{\overset{O}{\Vert}}{C}Cl$ 61.84 (0.57)	45.03 (0.57)	290	760	94-8	0.2[101]	85	bis(ethoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene	36.9	3.8	32.2
								bis ethyl carbonate of hexafluoropentane-1,5-diol	(37.1)	(3.9)	(32.0)
$HOCH_2(CF_2)_3CH_2OH$ 50 (0.239)	 $C_6H_5O\overset{\overset{O}{\Vert}}{C}Cl$ 89.77 (0.57)	45.03 (0.57)	176	0.1	-	-	91	bis(phenoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene	50.04	3.13	25.30
								bisphenyl carbonate of hexafluoropentane-1,5-diol	(50.4)	(3.1)	(25.2)

product by g.l.c. (Column '0', 150°) showed one major component with a slight tail, separation of these components for identification could not be achieved due to their similar volatilities and retention times.

2.5 Attempted Polymerisations of the Bismethyl Carbonates of Hexafluoropentane-1,5-diol (HFPD).

a) The apparatus shown in figure 4 was assembled with the bismethyl carbonate of HFPD (6.7g, 0.02 moles) stirred by a teflon coated stirrer bar and heated (oil bath) initially at 100° for 12 hrs and then at 270° for 12 hrs. Analysis of the reaction product by g.l.c. (Column '0', 200°), i.r., m.s., and elemental analysis showed no detectable reaction to have taken place.

b) A catalyst solution of sodium methoxide in methanol was prepared as described in 2.4. and two drops of this solution added to the bismethyl carbonate of HFPD (6.7g, 0.02 moles) contained in an apparatus described in 2.5.a. The reaction mixture was then heated (oil bath) to 200° for 8 hrs and then 270° for 2 hrs, the flask was then allowed to cool and the pressure was progressively reduced, monomer distillation occuring quantitatively at 170°, 0.2mm Hg. Analysis of the distillate by g.l.c. (Column '0', 200°) showed no detectable reaction.

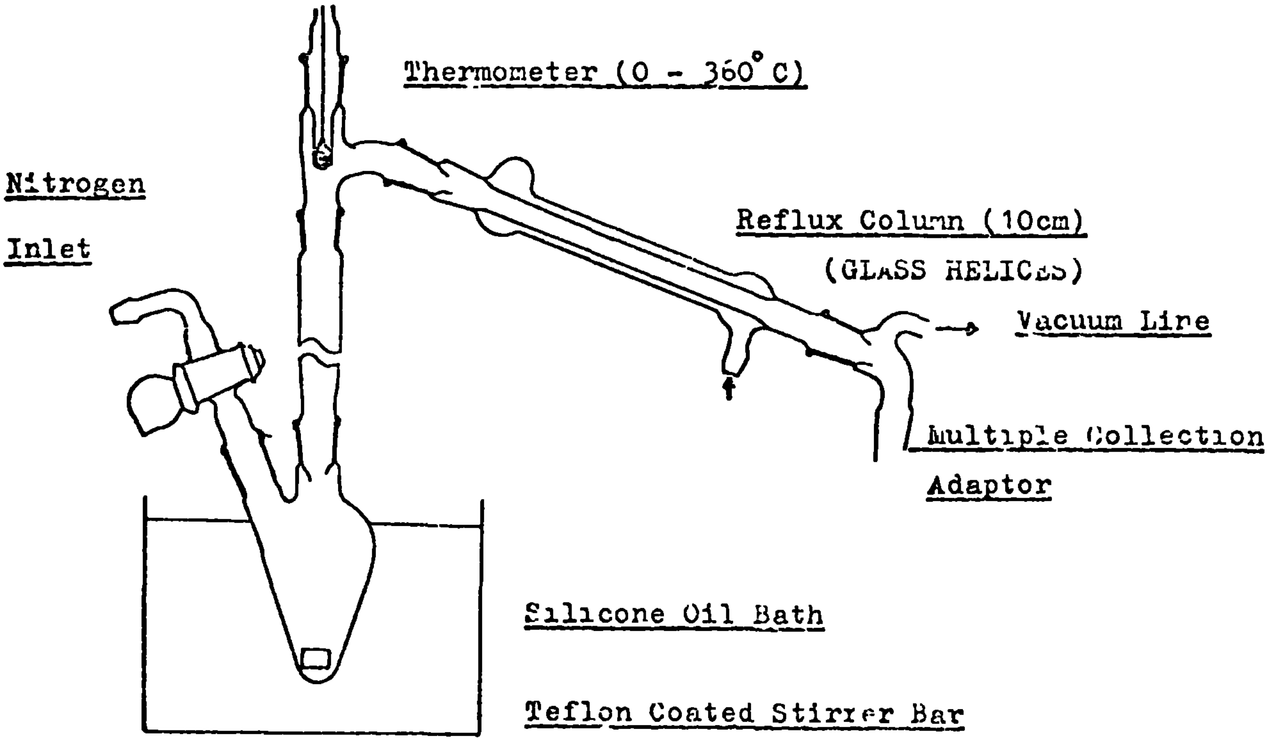
c) Using the procedure described in 2.5.b 20μl of the prepared catalyst was added to the bismethyl carbonate of HFPD (5.0g, 0.015 moles), which was maintained at 220° (Woods metal bath), after addition of the catalyst heating was continued for 6hrs. Analysis of the reaction product by g.l.c. coupled to m.s. (Column '02½', 150°) showed small amounts (~5%) of degradation products (III) and (IV) to have been formed.

d) A fresh sample of sodium methoxide catalyst was made up, as described in 2.4, removal of excess methanol was achieved by evaporation under reduced pressure (vacuum line), to give a concentrated mixture of sodium methoxide and methanol. A small sample (0.0646g) of this was added to the bismethyl carbonate of HFPD (5.0g, 0.015 moles) contained in the apparatus shown in Figure 4 under a dry nitrogen atmosphere. Following the experimental procedure given in 2.5.c., analysis of the distilled fractions showed small amounts of the degradation products (III) and (IV) to be present.

2.6 Preparation of the Bisethyl Carbonate of Hexamethylene 1,6-diol (HMD).

Using the experimental procedure given in 2.3, ethylchloroformate (112ml, 1.179 moles) was added to a solution of hexamethylene-1,6-diol (58g, 0492 moles), dry ($CaCl_2$) pyridine (95ml, 1.185 moles) and dry (Na) benzene (500ml) to give after distillation (86° /0.1mm Hg) bisethyl carbonate of HMD as a colourless liquid. Found: C, 56.26; H, 8.90; required for $C_{12}H_{22}O_6$; C, 56.24; H, 8.65. ^{1}H n.m.r. showed two regions

Figure 4. The initial polymerisation apparatus.



of absorption, a triplet at 8.9τ (J = 7Hz), broad multiplet at 8.65τ, and a quartet at 6.01τ (J = 7Hz), triplet at 6.07τ (J = 5Hz) using external T.M.S. reference, in the relative group intensity ratio 1.75: 1

v max 1745 (C=O), 1465, 1405, 1370, 1255, 1010, 790cm.$^{-1}$.

2.7 Attempted Polymerisations of Bisethyl Carbonate of Hexamethylene-1,6diol.

a) Sodium methoxide catalyst solution (0.1ml) made up as described in 2.4 was added to bis-ethyl carbonate of HMD (5.7g, 0.022 moles) as described in the experimental procedure. in 2.5.c. No reaction was detected on analysis by g.l.c. (Column '02½', 200°)

b) A sample of commercially available solid sodium methoxide (K and K Industries, supplied through Kodak) (0.05g, 0.001 mole) was added to bisethyl carbonate of HMD (20g, 0.076 moles) in a dry box which was then transferred to the apparatus shown in Figure 4. The reaction mixture was then heated (Wood's metal bath) at 220° for 2hrs with gradual distillation of a liquid at 126°, this was later characterised by n.m.r., i.r., and m.s. as diethyl carbonate (6.1g, 70% polycondensation), and gradual increase in the viscosity of the reaction mixture. Gradual reduction of the pressure in the system (vacuum line) over the next 2hrs to approximately 1mm Hg, resulted in the reaction increasing in viscosity until the teflon coated stirrer bar stopped rotating. On cooling to room temperature, the residue in the reaction flask was a tough white solid which was soluble in chloroform and had a number average molecular weight (determined by vapour phase osmometry) of 7100 (DP ~ 49).

2.8 Attempted Polymerisations of Bisethyl Carbonate of Hexafluoropentane-1,5-diol.

a) Using the experimental procedure described in 2.7.b solid sodium methoxide (0.05g, 0.001 moles) was added to bisethyl carbonate of HFPD (14.3g, 0.04 moles). Heating of the mixture for 2hrs, followed by distillation and analysis of the product by g.l.c. (Column '02½', 200°) showed no reaction.

b) Repeating the experimental sequence of 2.8 but refluxing the reaction mixture at 290° lead to no reaction that could be detected by g.l.c. (Column '02½', 200°)

c) The method given in 2.8.b was repeated using calcium hydride (0.05g, 0.01 moles) as the catalyst, again with no detectable reaction by g.l.c.

2.9 Attempted Polymerisation of Bisphenyl Carbonate of Hexafluoropentane-1,5-diol.

a) Using the experimental procedure described in 2.7.b bisphenyl carbonate of HFPD (10g, 0.022 moles) and solid sodium methoxide (0.05g, 0.001 moles) were heated at 250° for 4hrs, during which time a distillate turning to a white solid was obtained, this was characterised by i.r., mass spectroscopy as diphenyl carbonate. Gradual reduction of the system pressure over the next 2hrs results in the easier removal of more diphenyl carbonate from the reaction mixture, which was characterised by taking the ^1H n.m.r. spectrum and integrating the absorbtions due to the methylene and aromatic protons, the relative ratio of these indicated an overall degree of polymerisation of (~2).

b) Modifying the experimental procedure given in 2.9.a the system pressure was reduced (vacuum line) after 2hrs, diphenyl carbonate distilling at 140° (1-10mm Hg), allowing the reaction to proceed for another 2hrs at this pressure resulted in the collection of 3.9g (83% polycondensation) of diphenyl carbonate. Analysis of the reaction residue by ^1H n.m.r. indicated an overall degree of polymerisation of 5 - 6 (80 - 83% polycondensation).

Section 3.

The preparation of some fluorinated aliphatic and aliphatic polycarbonates.

Section 3. The Preparation of some Fluorinated Aliphatic and Aliphatic Polycarbonates.

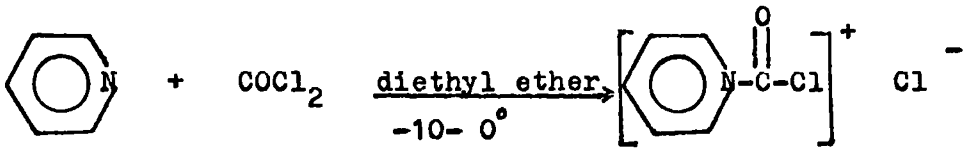
3.1 Introduction.

In the previous section attempts to prepare fluorinated aliphatic polycarbonates via alkoxide ion catalysed ester exchange reaction using various bisalkyl and bisaryl carbonates of hexafluoropentane-1,5-diol were described, together with the mechanistic rationalisation of this polymerisation process. It was concluded that the method of synthesizing these polymers most likely to give genuine high D.P. products would use the bisfluoroalkyl carbonates of HFPD as starting material. The synthesis and reaction of this compound, and the development of the experimental technique is presented here, again in chronological order. The technique, once developed, was applied to the synthesis of the polycarbonates derived from 2,2,3,3-tetrafluorobutane-1,4-diol, 2,2,3,3,4,4,5,5,-octafluorohexane-1,6-diol, and a variety of hydrocarbon diols.

3.2 Discussion.

3.2.(i)Fluoroalkyl Chloroformates.

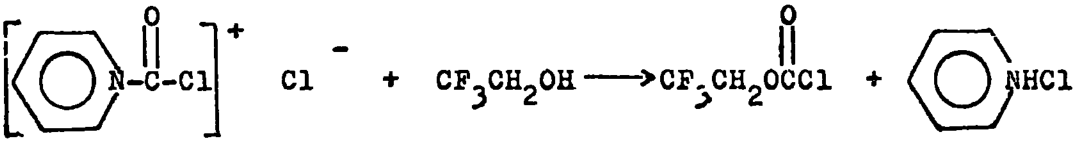
In the preparative reactions leading to the bisalkyl and bisaryl carbonates of HFPD described in the previous section, the chloroformates used were commercially available, however the fluoroalkyl chloroformates required in this section were not available and a synthetic route to these compounds had to be devised. The chemistry of chloroformates is well established and has been quite recently reviewed,[105] chloroformates are prepared by reaction of phosgene and hydroxy compounds at or below room temperature (see Section 1.6). Low temperatures in this reaction are preferred to minimise the formation of dialkyl carbonates, and it is also advantageous to carry out the reaction in the presence of a tertiary amine, for example pyridine to absorb the eliminated HCl. Previous attempts[99] to prepare fluoroalkyl chloroformates have encountered problems due to the relatively low reactivity of fluorinated alcohols with phosgene alone, and the relatively high reactivity of fluorinated alcohols with their chloroformates, which generally resulted in difluoroalkyl carbonate formation rather than isolation of the required chloroformate. This dictated a new approach to fluoroalkyl chloroformate preparation, the reaction of phosgene with pyridine in an inert solvent gives a solid crystalline compound, chlorocarbonyl pyridinium chloride (VIII) (Reaction 25).



(VIII)

(25)

As mentioned in section 1.6, this compound reacts much more readily with alcohols than does phosgene itself, and the addition of one molecular equivalent a fluorinated alcohol (2,2,2,trifluoroethanol) to a dilute solution of one molecular equivalent of this reagent gives the chloroformate in good yield (75%) (Reaction 26). A patent describing this synthesis[106] has been published recently.



(26)

Due to the toxic nature of phosgene, a specialised apparatus for its handling in a laboratory fumes hood was devised and this is illustrated in Figure 5. As well as the phosgene inlet point, a nitrogen inlet was provided to enable dry flushing of the apparatus, gas handling to the reaction vessel was via a concentrated sulphuric acid bubbler, a safety trap to retain any acid spray and minimise any fluctuations in the flow rate, and a heavy white oil bubbler; from the reaction vessel the gases were lead via a heavy white oil bubbler to a scrubbing tower filled with broken glass down which a solution of sodium hydroxide was circulated to

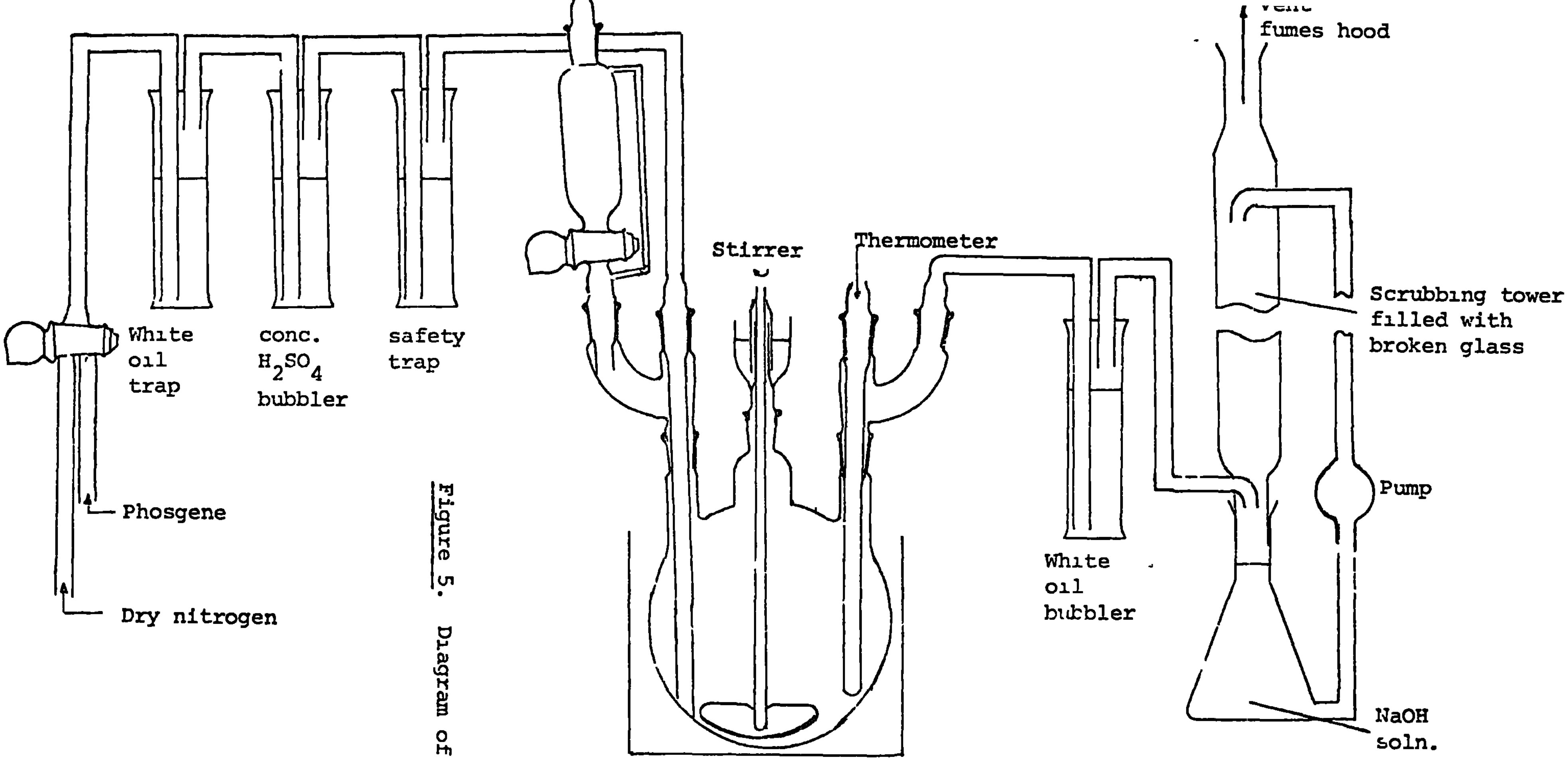


Figure 5. Diagram of the phosgenation apparatus.

destroy any accidental escape of phosgene from the reaction vessel. All experiments using phosgene and chloroformates were carried out with the ready availability of breathing apparatus. All these precautions were required due to the known or expected toxic nature of the compounds being used.

3.2.(ii) Initial Development of the Alkoxide Ion Catalysed Ester Exchange Reaction of Bis(2,2,2-trifluoroethyl)-Carbonate of Hexafluoropentane-1,5-diol.

Using the 2,2,2-trifluoroethyl chloroformate obtained, the synthesis of the bis(2,2,2-trifluoroethyl)-carbonate of HFPD was carried out in a manner analogous to that previously outlined for the bisalkyl carbonates of HFPD in section 2.3. The expected biscarbonate was obtained in good yield (77%) and characterised by elemental analysis, i.r., ^1H and ^{19}F n.m.r. and m.s. (see experimental section). The product was rigorously purified by distillation using a concentric tube column of 90 theoretical plates. Investigation of the alkoxide ion catalysed ester exchange polymerisation of this monomer was then undertaken using a catalyst made by dissolving sodium in a solution of 2,2,2-trifluoroethanol and dry diethyl ether and then removing the ether and excess alcohol by distillation under reduced pressure and finally pumping dry on a vacuum line. The catalyst was added to the monomer within a range of molar proportions outlined in the source patent,[87] and the reaction mixture heated to 150°, initially in an experimental apparatus similar to that described in 2.9. After two hours the system pressure was gradually reduced and a clear liquid distilled from the reaction vessel; this was characterised by n.m.r., i.r. and m.s. as di(2,2,2-trifluoroethyl) carbonate. The final system pressure was 0.01mm Hg after 5hrs reaction time. The extent of the condensation reaction could be assessed by the amount of di(2,2,2-trifluoroethyl) carbonate eliminated, and also by ^{19}F n.m.r. spectroscopy, a convenient method since the chemical shift of the trifluoromethyl group fluorine atoms (77.1 p.p.m.

with respect to external $CFCl_3$) is quite distinct and seperate from that of the difluoromethylene group fluorine atoms (122.3 and 127.9 p.p.m. with respect to external $CFCl_3$), the ratio of their intensities being a measure of the extent of the condensation reaction. The two methods of estimating the extent of reaction were not in agreement, in this case ~ 82% and ~94% respectively, presumeably some loss of the volatile di(2,2,2-trifluoroethyl) carbonate had occured in the vacuum system.

This promising initial result lead to an investigation of the effect of reaction variables on the extent of reaction as monitored by ^{19}F n.m.r. in a series of polymerisation experiments. The effect of temperature was examined first, this established that the optimum reaction temperature occured in the interval 140-150°. At lower temperatures, for example 120°, there was no evolution of di(2,2,2-trifluoroethyl) carbonate when the system pressure was lowered and when the pressure was sufficiently reduced the monomer distilled unchanged; presumably the exchange reaction is very slow at this temperature. At higher temperatures, for example 190°, again no elimination of di(2,2,2-trifluoroethyl) carbonate occured when the pressure was lowered and the unchanged monomer eventually distilled; in this case it seems reasonable to propose that the lack of exchange reaction results from rapid decomposition of the alkoxide initiator, the thermal instability of these anions has been reported previously.[107] The next factor to be examined was the catalyst concentration, which had up to this point been ~ 2 mole-%, this being the upper limit suggested in the source patent.[87] The concentration was progressively reduced, and it was found that 0.8 mole-% initiator gave satisfactory polymerisation at 150°. Another factor of importance, since anions of the type $-CF_2CH_2O^-$ are known to be thermally unstable,[107] is the duration of reaction. Ideally the reactants should be heated to the selected reaction temperature as rapidly as possible with the catalyst efficiently dispersed in the mixture.

Also the eliminated compound should be removed as quickly as possible and at as low a temperature as is consistent with a useful rate of reaction. Over the course of the examination of the effect of catalyst concentration, the overall reaction time was reduced, by improvement of experimental technique, to approximately two hours.

Thus far it had been established that the elimination of di-(2,2,2-trifluoroethyl) carbonate from the bis(2,2,2-trifluoroethyl) carbonate of HFPD could be reproducibly carried out in reaction conversions of the order of 95% or greater, in the temperature range 140—150° at an effective catalyst concentration of the order of 1 mole—% with system pressure reduction over the second hour of polymerisation to ~ 0.1mm Hg.

The catalyst used up to this point, solid solvent free alkoxide was stored under a dry nitrogen atmosphere in a dry box where addition of it to the monomer also took place, this was considered neccessary to preserve the activity of the catalyst. The solid nature of the catalyst caused problems with respect to the efficient dispersal through the monomer. A liquid catalyst as described in the source patent would facilitate the intimate dispersal of the catalyst throughout the liquid monomer, whilst also allowing a more convenient method of catalyst addition to the monomer i.e. this might be achieved in a more accurate manner by use of a syringe and gas inlet tap or serum cap system on the polymerisation apparatus. It was therefore decided (in spite of the previous failure with catalysts made up by dissolving sodium metal in the alcohol of choice, see Section 2.1) to prepare a solution of catalyst for this polymerisation by dissolving sodium in 2,2,2-trifluoroethanol under a dry nitrogen atmosphere. This catalyst was syringed into the monomer prior to heating and proved successful in initiating reaction when the mixture was heated to 150°, as judged by the recovery of di(2,2,2-trifluoroethyl) carbonate (37%) when the system pressure was lowered. The next step in the development of the technique aimed at reducing any effect of thermal degradation of the initiator by injecting the initiator into the preheated monomer. This resulted in very rapid reaction, with 85% of the theoretical amount of the eliminated product being recovered and an overall extent of reaction of 94% as indicated by the ^{19}F n.m.r. of the crude reaction product. Thus, progressive modification of the reaction conditions had resulted for the fluorocarbon case in a technique analogous to that outlined in the source patent[87] for hydrocarbon polycarbonates.

3.2 (iii) The Relationship Between Extent of Reaction and Molecular Weight.

The next phase in the investigation of the reaction was to establish unambiguously whether a polymer was being formed or not. This required the measurement of the molecular weights of the products obtained and the method chosen was vapour phase osmometry (v.p.o.) using dimethyl formamide (DMF) as a solvent in a Perkin-Elmer 115 Molecular Weight Apparatus. The choice of DMF as a solvent for these determinations was influenced by previous work of Russian workers on this class of polymers,[98] the solvent used by them was chosen in order that results might be directly comparable. Measurements of the molecular weights of various crude reaction products in DMF solutions gave disappointingly low values, for all samples there was a considerable discrepancy between the molecular weights calculated from ^{19}F n.m.r. intensity ratios of the trifluoromethyl and difluoromethylene groups and those measured by v.p.o., the latter invariably being much lower. There are two plausible explanations for this discrepancy; if the products were contaminated with low molecular weight impurities this would result in a pessimistically low estimate of the polymer molecular weight by v.p.o., alternatively the product might consist of a mixture of linear and cyclic polycarbonates in which case the v.p.o. measurements would be an accurate measure of the molecular weight. At this stage some irreproducibility in the v.p.o. measurements prompted a complete dismantling, overhaul and recalibration of the instrument; no faults were detected and the calibration curve was substantially the same as before.

One method of separating a high molecular weight sample of a polymer from a product with a broad molecular weight distribution is fractional precipitation. This can be accomplished at a variety of levels of sophistication, in the simplest method, a concentrated solution of the product is dripped into a large excess of vigorously stirred non-solvent. The higher molecular weight material precipitates from solution first, whilst the lower molecular weight material remains in solution. This technique was applied to the samples discussed above using DMF as the solvent and chloroform as the non solvent. The precipitated fraction of polymer was collected by filtration, and the soluble fraction recovered by evaporation of the solvents. These fractions, after removal of the last traces of solvent by heating under reduced pressure on a vacuum line, were submitted to molecular weight determination by the v.p.o. and n.m.r. techniques outlined above. During the determination of the molecular weights of the fractions by v.p.o. an odd effect was noted; namely, that the molecular weight value obtained depended on the length of time the polymer solution remained in the instrument, the value obtained falling steadily with time over a period of three days. The obvious conclusion being that the polymer in solution was being degraded by the solvent at the temperature at which the instrument was operating (57°). This imposed some restrictions on the method; thus, in preparing solutions heating the solvent to increase the rate at which the sample dissolves has to be avoided; for sensitivity reasons the instrument cannot be operated at a lower temperature with DMF, yet the sample has to be in the instrument long enough to be thermally equilibriated. However, it was found that for samples dissolved in DMF at room temperature and measured as soon after introduction to the instrument as possible, reasonably consistent values were obtained for solutions stored at room temperature for two days. It was concluded that the degradation was a very slow process at room temperature and that providing heating was avoided in the preparation of the solutions and their storage, the molecular weight values obtained could be taken as reasonable lower limits for the materials examined.

Carothers derived a simple equation relating the degree of polymerisation (DP) to the extent of reaction for reactions leading to the formation of linear condensation polymers. Application of this equation to the reaction

$$DP = \frac{1}{1 - P}$$ where DP = number average degree of polymerisation
P = reaction conversion

under consideration here, enables a direct correlation between the extent of reaction determined via n.m.r. and expressed using Carothers- equation as DPs, and the molecular weight, expressed in terms of DP, as determined by v.p.o. The correlation between the results of the two methods used to obtain the DPs of the products obtained in the work to this point was dissappointingly poor, this is illustrated in Figure 6. where it can be seen that DPs determined by n.m.r. are generally higher than those determined by v.p.o. Since both methods yield number averages there should be a one to one correlation. The problems encountered with the v.p.o. measurements have been discussed earlier, and when the n.m.r. technique is considered in detail considerable reservations emerge. The method depends on the accurate integration of the intensities of two well seperated signals, and thus on the reliability of the electronic integrator of the instrument used. Experience shows that the reliability of instrument integrator for well characterised low molecular weight compounds decreases with increasing peak width and decreasing signal noise ratio. The inevitable low signal to noise ratio for the dilute polymer solutions obtainable therefore mitigated against good integrations, and at the time of this work facilities for improving the signal to noise ratio by CAT (Computer Averaging of Transients) or FT (Fourier Transform) techniques were not available. Since these

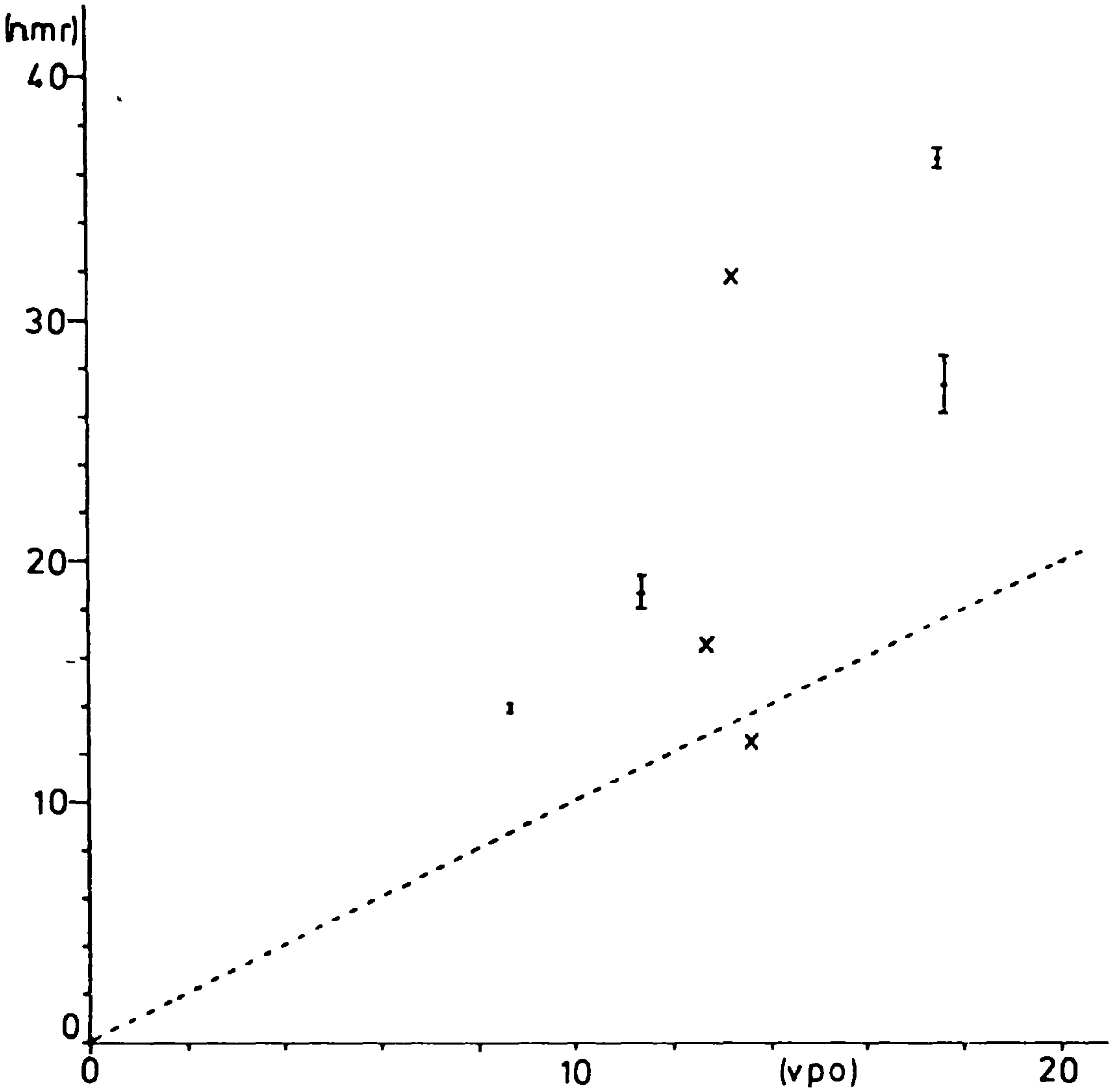


Figure 6. The correlation of DPs as determined by n.m.r. and v.p.o.

uncertainties over the DPs actually being attained cast doubt on whether or not real progress was being made in the development of experimental techniques and procedure, it seemed appropriate to seek alternative methods of determining DP's or extent of reaction. One possible method utilised a relatively new technique, which is the research interest of another group in this department, and will be discussed in the next section.

3.2 (iv) Electron Spectroscopy for Chemical Analysis (ESCA), and it's Application to Determining Molecular Weights.

The application of ESCA to structure and bonding in polymers has largely been pioneered by Dr. D.T. Clarke's research group at Durham, and has been recently and comprehensively reviewed.[108-110] The ESCA experiment involves measuring the kinetic energies of electrons ejected by the interaction of a monoenergetic beam of soft X-rays with the sample under investigation, measurement of the kinetic energies of the ejected electrons together with the known energy of the incident X-ray photons allows the computation of the binding energies of the electrons in the sample. The details of the experimental procedure by which this is accomplished need not concern us here, this infomation is discussed in detail in the references quoted above. In principle all electrons, from the core to valence levels can be studied, however the fact that the cross sections for photoionisation of core levels is generally considerably higher than for valence levels together with the fact that core orbitals are essentially localised on atoms, and therefore have binding energies characteristic of a given element, means that in ESCA predominant emphasis is on the study of core levels

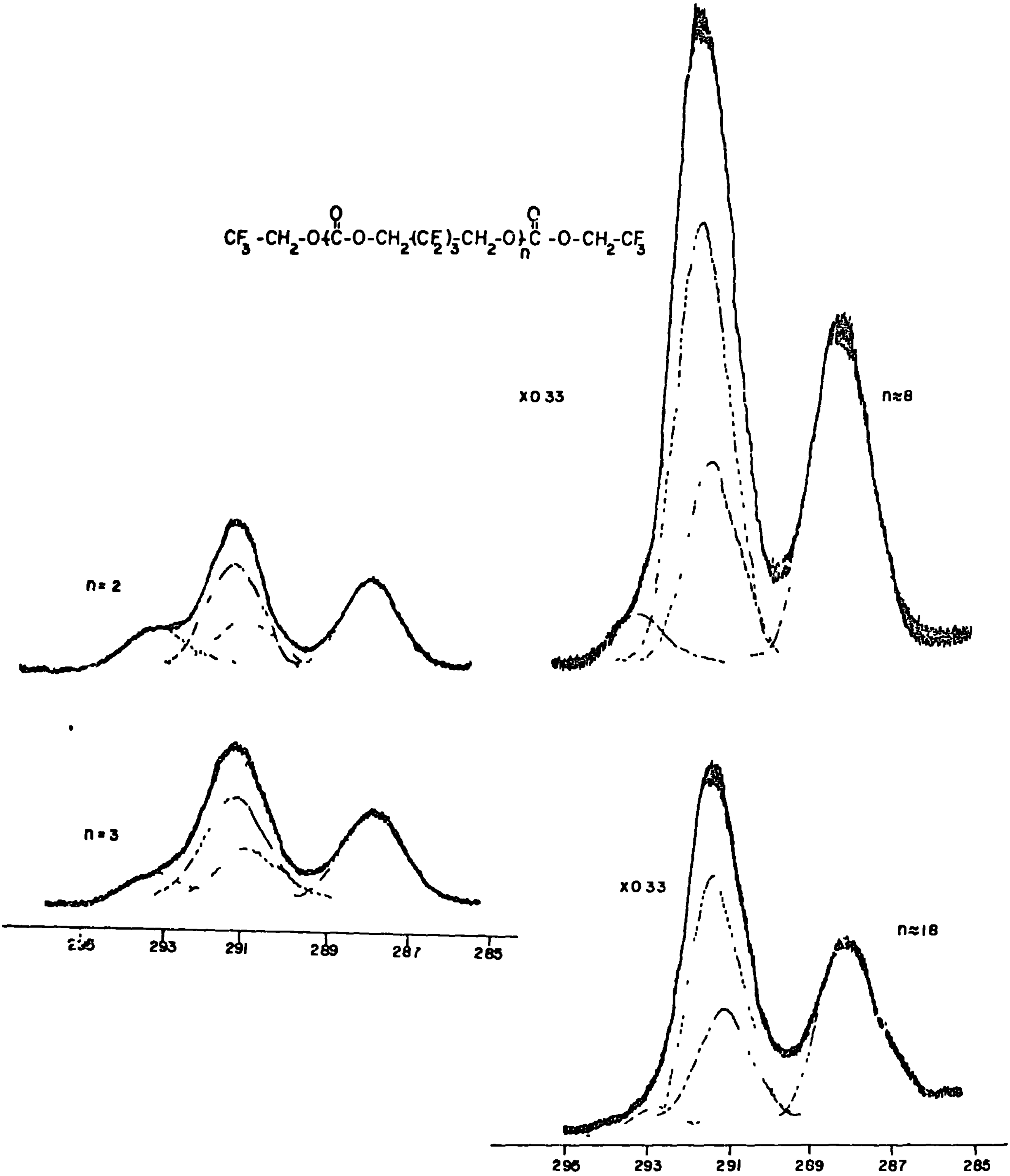
The detailed interpretation of ESCA spectra provides information at a variety of levels, and examination of large numbers of well characterised compounds has placed the analytical technique on a secure basis. Elemental analysis can be accomplished by examination of the observed binding energies and their relative intensities, providing the sensitivity factors for the instrumental arrangement used have been established by prior calibration.

Shifts of binding energies within the range characteristic for a particular core level provide information on the structural features present in a sample, and the relative intensities of the different peaks provide the data from which molecular structures may be worked out. The homogeneity of the sample as a function of depth can be established, for example by varying the angle of incidence of the X-ray beam, and with a knowledge of escape depth dependencies the variation of molecular structure as a function of depth into the sample may be calculated in favourable cases. The photoionisation process is often accompanied by electronic reorganisation at the ionisation site which gives rise to satallite peaks in the ESCA spectrum, the detailed analysis of these low intensity peaks provides another level of information which can be used to elaborate the details of molecular structure and in favourable cases information concerning the details of surface conformation maybe worked out. The application of ESCA to the elaboration of chemical composition is particularly well established in the case of fluorocarbon based systems for which the span in shift range for the carbon core level is (C_{1s}) is particularly favourable consequent upon the large electronic effect of replacing hydrogen by fluorine.[111-113]

It is often the case that particular structural features may be characteristic of the end groups of a given polymer system. The direct detection of such end groups by means of their characteristic binding energies should, in principle, provide a convenient means of establishing DPs in relatively low molecular weight samples, this end group counting approach is analogous to the ^{19}F n.m.r. method described earlier and as in that method the reliability of the approach will rest on the accuracy with which the relative abundance of the end group can be determined. A particularly favourable situation arises for systems with terminal groups that involve $-CF_3$ residues, such as the series of fluorinated aliphatic polycarbonates of interest in this work. If due care is taken to ensure that ESCA statistically samples the repeat unit (by for example considering the relative intensities of the same element with differing escape depth dependencies) then the comparison of area ratios for chemically shifted components of a given core level maybe used to estimate DPs.

The C_{1s} levels for a set of condensation products previously characterised by v.p.o. and/or ^{19}F n.m.r. are shown in Figure 7, the ordinate axis represents binding energy in eV and the abscissa counts per second. The observed peaks fall into three fairly distinct regions, which can be most easily distinguished in the lowest molecular weight sample. The peak at lowest binding energy (~288 eV) is assigned to the methylene $\left(CH_2\right)$ carbon, the broad peak at (~291 eV) encompasses both the carbonate carbon $\left(O-\overset{O}{\overset{\|}{C}}-O\right)$ and difluoromethylene carbons $\left(CF_2\right)$, with the highest binding energy peak (~293.5 eV) being ascribed to the terminal trifluoromethyl (CF_3) carbon. These assignments, and in particular the fact that the C_{1s} level appropriate to the carbonate and difluoromethylene environments occur at approximately the same binding energy, were independently corroborated by the study of appropriate model systems.

To proceed from these assignments to DPs it is clearly essential to know the relative abundancies of the various structural features as accurately as possible, and this quite clearly involves deconvolution of the experimental spectra. Although this appears at first sight to be a formidable task, particularly for the higher molecular weight samples where resolving the trifluoromethyl peak from the combined carbonate and difluoromethylene peaks looks particularly difficult, there are a number of factors which alleviate the apparent difficulties. Thus, prior calibration with model compounds allows the peak shape and binding energy to be very rigorously defined. Using a Dupont 310 curve resolver it is possible to use one channel for each environment in the sample, a peak of the correct shape is then set at the appropriate binding energy for each environment, matching of the total envelope of the experimental spectrum with that of the deconvoluted peaks



<u>Figure 7.</u> The C_{1s} ESCA spectra of the various samples of poly(hexafluoropentamethylene carbonate).

is achieved by adjustment of the peak areas only, in practise it is found that one unique fit is obtained and very small changes in relative peak areas make easily detectable differences in the overall envelope shape. The reliability of this procedure and the details of deconvolution techniques in general have been discussed in detail elsewhere.[114] Having deconvoluted the spectra and determined the relative abundancies of the four different C_{1s} enviroments, it was possible to calculate the DPS of the various samples from both the ratio of difluoromethylene to trifluoromethyl abundancies, and the carbonate to trifluoromethyl ratio. This enables a check on the internal consistency of the ESCA method to be made, the results of these analyses are summerised in Figure 8.

The two methods of computing DPs give slightly different results which may indicate specific orientation effects at the polymer surface, however the two are within 10% and show an excellent correlation with DPs determined by v.p.o., as is shown in Figure 9. By contrast DPs determined by ^{19}F n.m.r. for the same set of samples shows an apparently random scatter which is also shown in Figure 10. Clearly the problems of reliable integration of the ^{19}F n.m.r. discussed earlier relegates this method to that of an easy way of obtaining an approximate idea of the extent of reaction in these experiments. On the other hand the good correlation between the completely independent v.p.o. and ESCA methods means that either method can be used to obtain reasonably accurate measures of the DPs obtained.

3.2 (v)Experimental Procedure Modifications Designed to Increase Product DP.

The work described in the previous two sections established that the products of the condensation reactions described earlier had, at best, DPs of the order of 20 corresponding to an extent of reaction of 95%. In view of the simple nature of the experimental apparatus and procedures adopted this could be regarded as a fairly satisfactory achievement, however from the point of view of the original aims of the project a significant

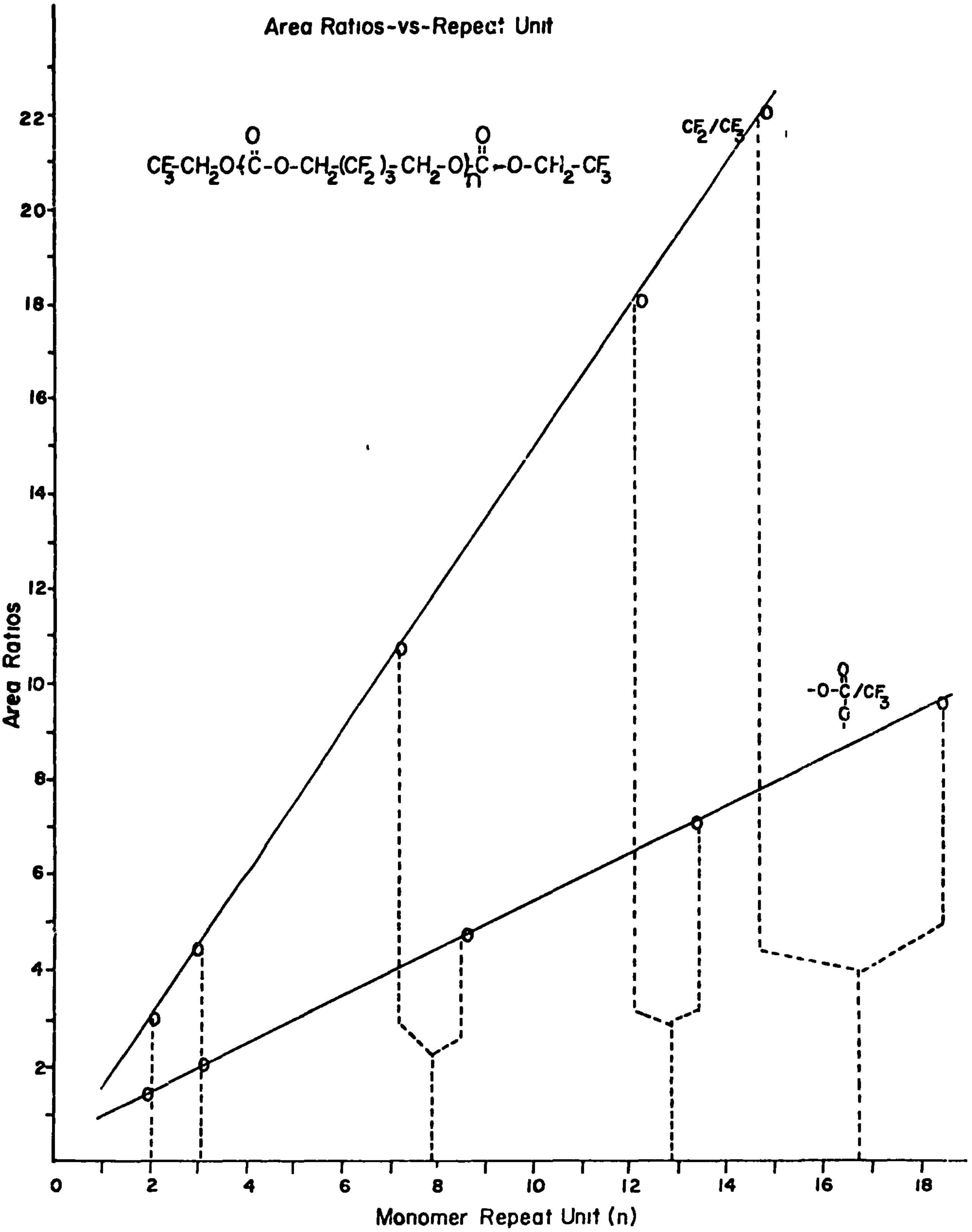


Figure 8. The computation of the DP of the various samples of poly(hexafluoropentamethylene carbonate).

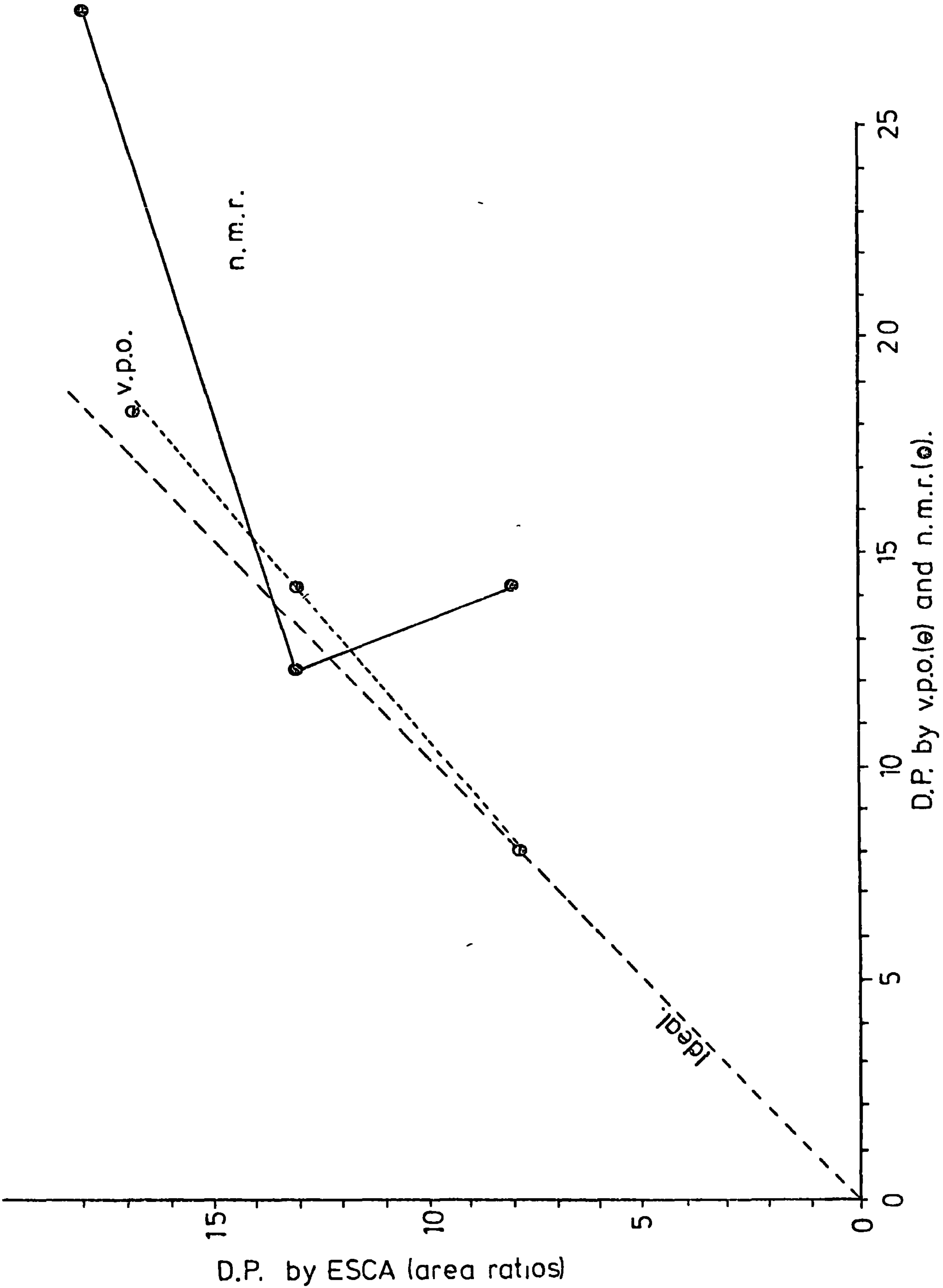


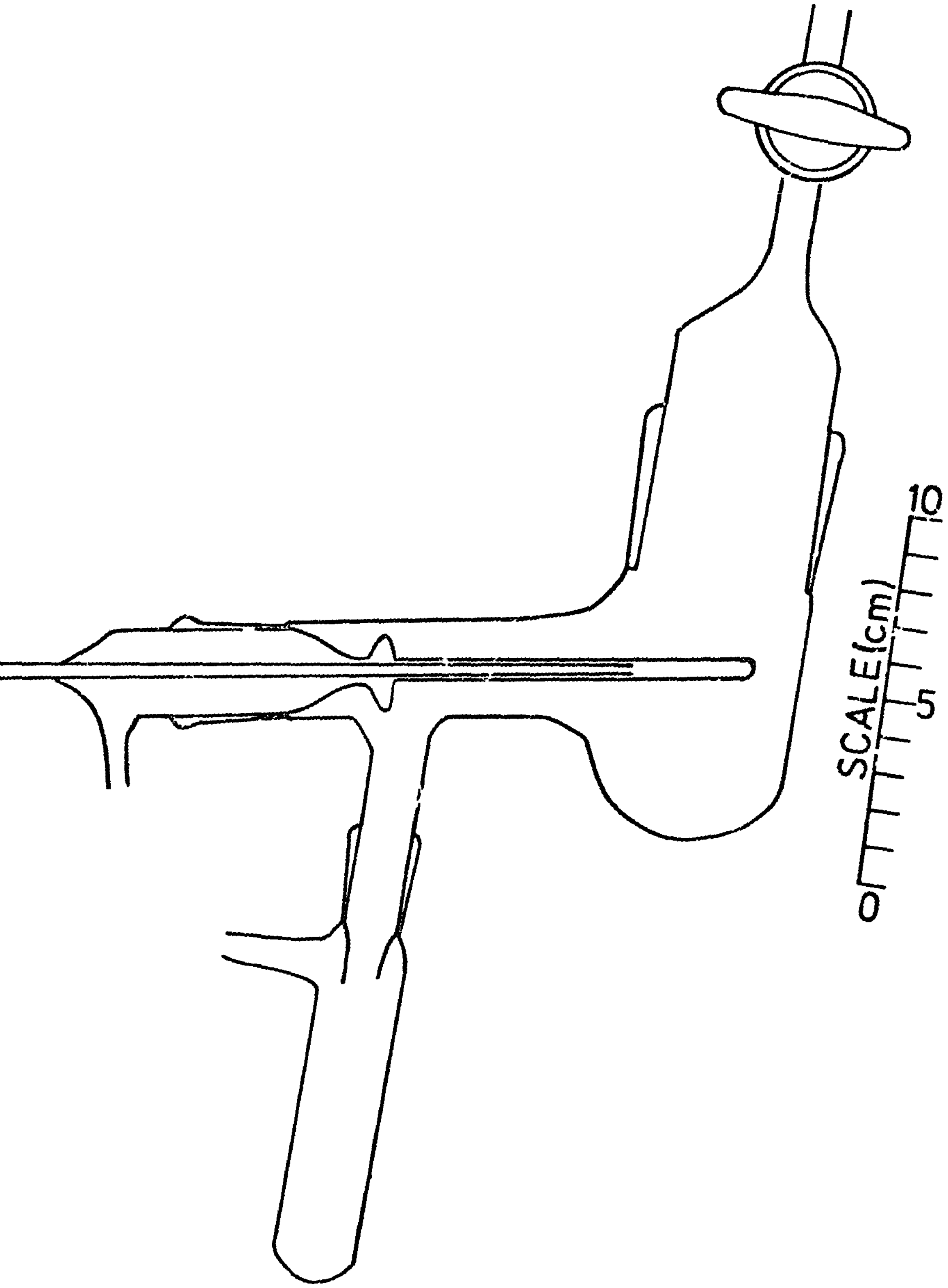
Figure 9. The correlation of DP as determined by ESCA with v.p.o. and n.m.r.

improvement in the extent of reaction and consequently DP was required. It is well known that many of the physical properties and parameters associated with polymeric materials increase with increasing molecular weight, until a limiting plateau value is reached. The glass transition temperature is such a parameter and since the objective of this research was to obtain reliable data for the correlation of molecular structure and Tg it was of considerable importance to improve the DP attained to a level where the measured Tg could confidently be taken as the true value for a genuine high polymer. This required improving the DP by a factor of two or more if possible, which according to Carothers equation would require improving the reaction conversion to a least 97.5%. An alternative approach to the determination of the plateau value for Tg would have been to carefully fractionate the materials obtained so far and then to plot Tg against DP to either establish that the plateau value had been reached or allow extrapolation of the curve to the plateau value, this approach has appeal only as a last resort since the reliable fractionation of polymers requires considerable care in selection of solvents and relatively large amounts of material and time; further, if the plateau value cannot be shown to have been reached the procedure of extrapolating the Tg versus DP curve is somewhat uncertain. All in all the most desirable outcome would be to synthesise higher DP materials.

It has long been known in polycondensation reactions that the successful synthesis of high polymers may be accomplished by technological improvements of existing reaction procedure, to enable a high degree of conversion during the reaction as possible.[115] Attention is required to maximise the surface area to allow the removal of the eliminated product, to provide efficient mechanical stirring for intimate mixing of the reactants, and adequate facility for the condensation and removal of the eliminated product from the reaction mixture, together with an effective vacuum system to assist in the removal of the eliminated product in the latter stages of the reaction. With these factors in mind a polymerisation apparatus was designed based upon a molecular distillation apparatus in use in the laboratory at the time, this is shown in Figure 10, it was constructed in glass initially to allow any further modifications to be made with relative ease.

Polymerisation carried out in this apparatus, using the liquid catalyst previously proved and a technique similar to that of previous experiments, resulted in successful elimination of 85% of the theoretical amount of the di(2,2,2-trifluoroethyl) carbonate. Analysis of the crude reaction product using ^{19}F n.m.r. gave the extent of reaction as ~96% (DP ~ 25), comparable to the results obtained in the earlier apparatus. Modification of this apparatus to include a makeshift system of mechanical stirring via a glass rod and stirrer as shown in Figure 11 was undertaken. Polymerisation carried out in this second glass apparatus resulted in 90% of the eliminated product being collected and ~97% extent of reaction as mentioned by ^{19}F n.m.r. (DP ~ 33), an improvement over the original results, although problems were encountered sealing around the apparatus/stirrer seal. These problems were not unexpected since the wear rate on this type of seal is high and increases as the viscosity of the stirred medium increases.

In the third and final variant of the apparatus an Edwards Vacuum Ltd. rotary shaft seal was obtained and mounted on a specially constructed metal flange bolted to another flange which in turn was welded to a metal to graded glass joint attached to a larger polymerisation apparatus as shown in Figure 12. A custom built stirrer with a very fine clearence between the blades and the sides of the reaction vessel and very effective stirring action was used with the apparatus. Polymerisation in this apparatus with 20g of the bis(2,2,2-trifluoroethyl) carbonate of HFPD and ~1 mole % of liquid catalyst at 150° resulted in 91% collection of the eliminated product and 98.5% extent of reaction as monitored by ^{19}F n.m.r. (DP ~ 66), to give a light brown-green clear polymer initially, which turned opaque subsequently



gure 10. The first technological modification of the polymerisation apparatus.

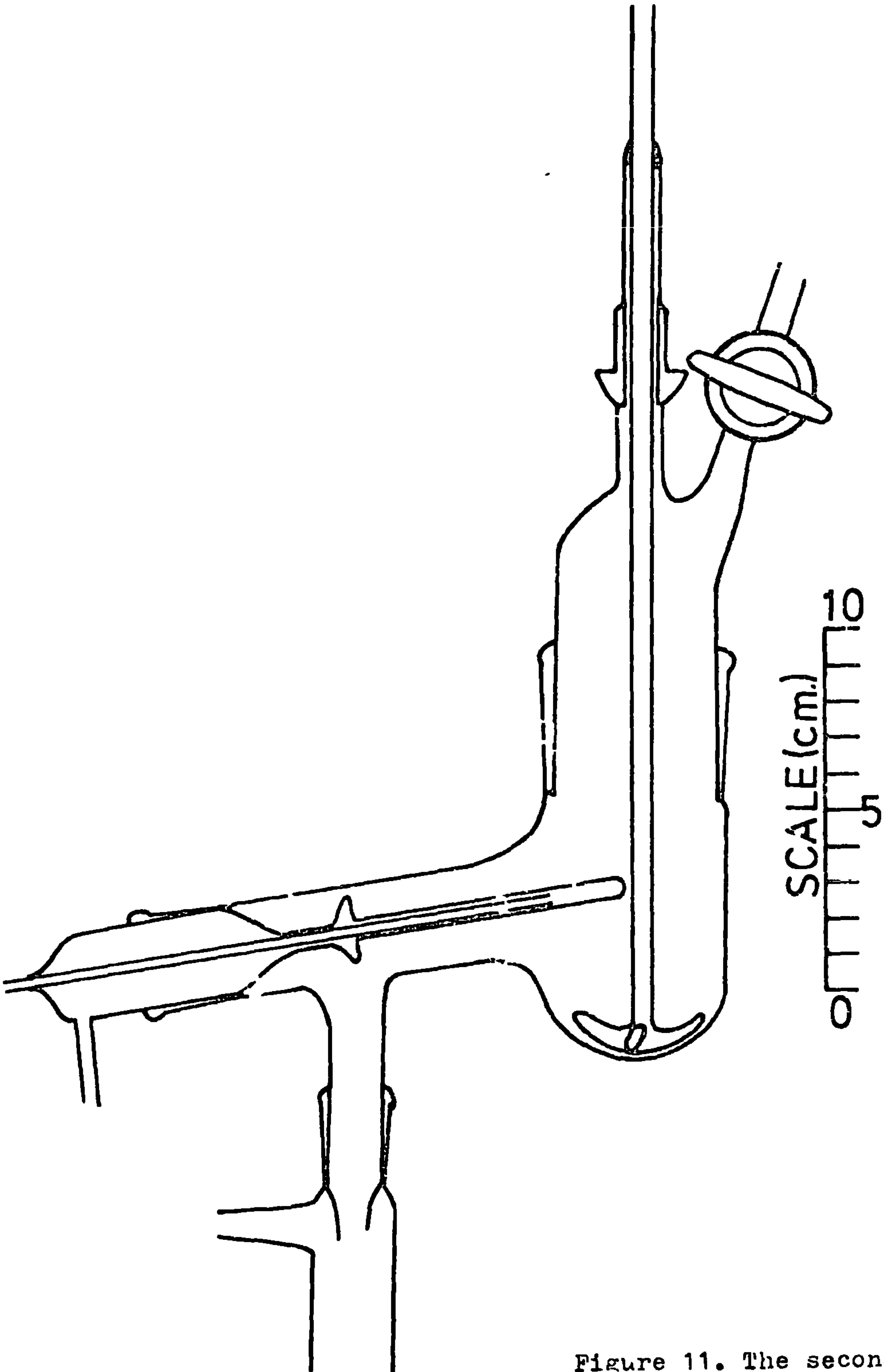


Figure 11. The second modification of the polymerisation apparatus.

on crystallisation. Determination of the intrinsic viscosity of this polymer in 1,4-dioxane solution at 25° gave a value of 0.29. This compares almost exactly with that quoted in the patent literature for poly(hexafluoropentamethylene carbonate) derived by the phosgenation route, further characterisation of this polymer will be described in the following section of this thesis.

3.2 (vi) Preparation of Some Other Polycarbonates.

The development of this experimental procedure and construction of the apparatus to allow the synthesis of high polymers of poly(hexafluoropentamethylene carbonate) could now be extended to include the synthesis of other polycarbonates. This involved the synthesis of tetrafluorobutane-1,4-diol and octafluorohexane-1,6-diol from readily available starting materials as shown in Figure 13, to complete the series of fluorinated aliphatic polycarbonates originally encompassed by the project. The synthesis of the bis(2,2,2-trifluoroethyl) carbonates of these diols in a manner analogous to that used for the bis(2,2,2-trifluoroethyl) carbonate of HFPD was undertaken concurrently with the synthesis of some hydrocarbon biscarbonates. The synthesis of the hydrocarbon monomers, and hence polymers, was undertaken since only one glass transition temperature of an aliphatic polycarbonate, poly(hexamethylene carbonate), was available in the literature. The synthesis and determination of the glass transition temperature of a range of these polymers would therefore add relevent and useful data to that presently available, and hopefully allow extension of the correlation between molecular structure and Tg and a refinement of the aTP values used in the prediction of Tg (see section 1). Readily available diols were used with an experimental procedure similar to that leading to the bisethyl carbonate of hexamethylene-1,6-diol described previously (section 2.6) to give the bisethyl carbonates of: ethane-1,2-diol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, decamethylene-1,10-diol, diethylene glycol,

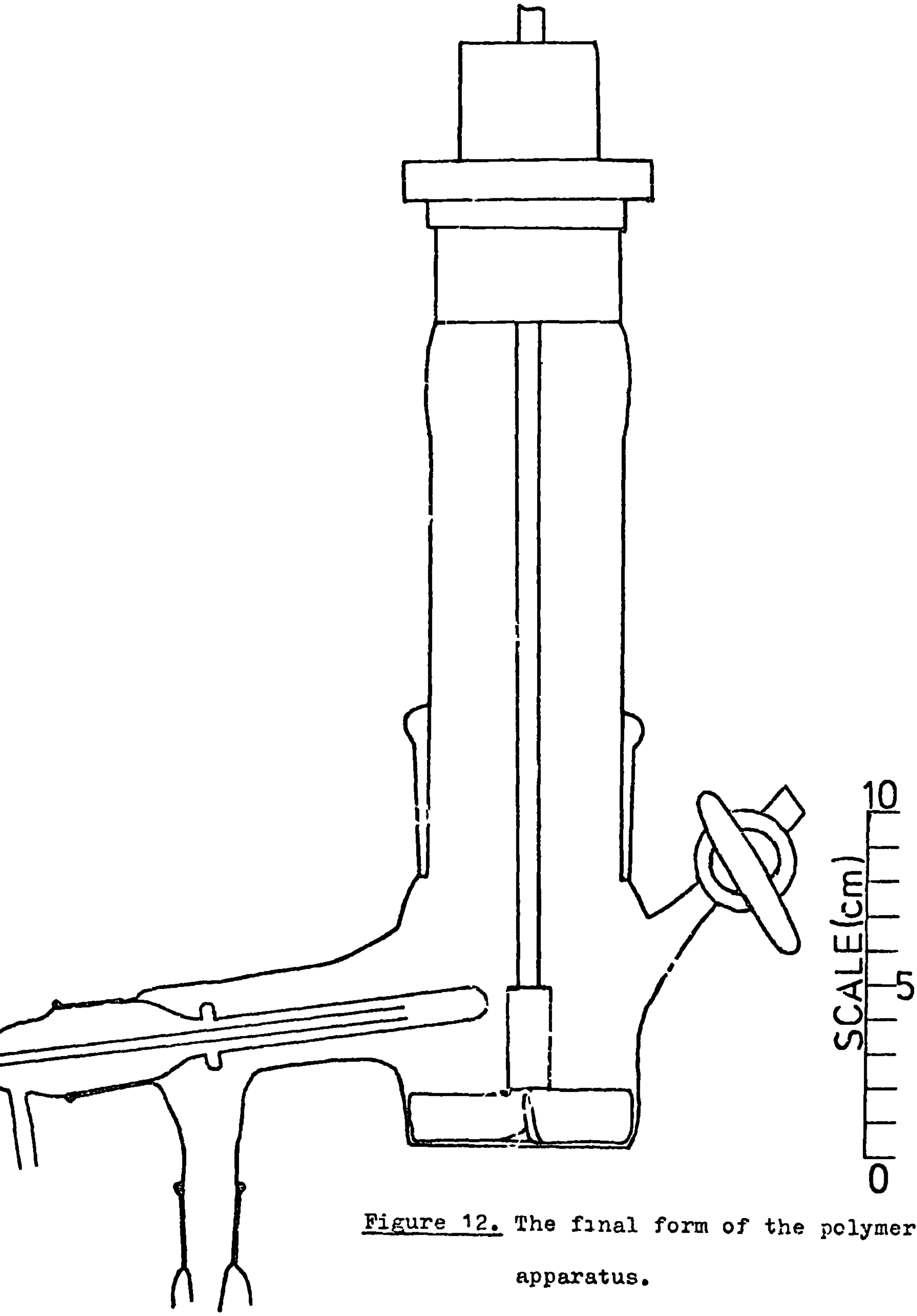


Figure 12. The final form of the polymerisation apparatus.

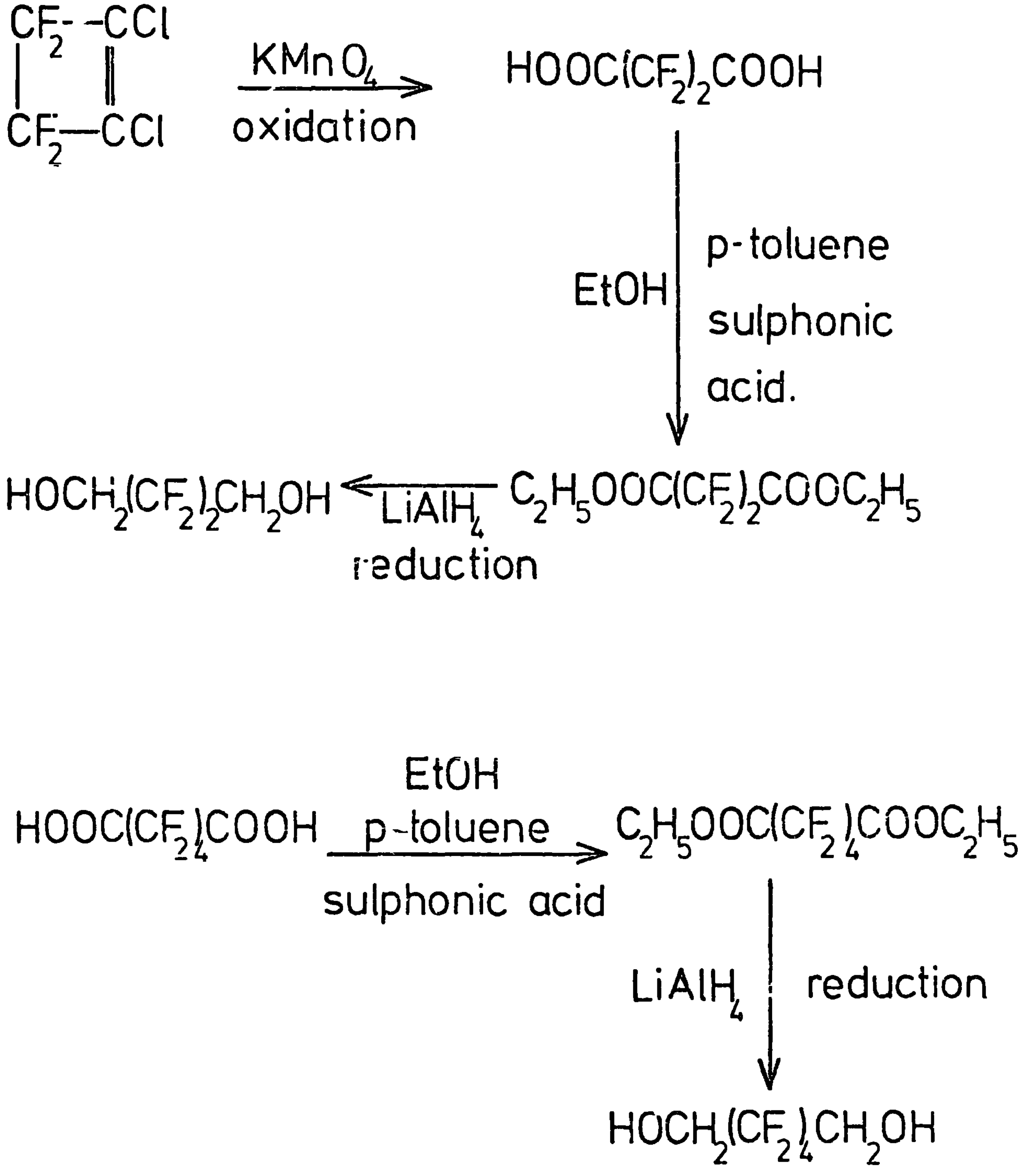


Figure 13. The synthetic routes to 2,2,3,3-tetrafluorotetramethylene-1,4-diol(upper) and 2,2,3,3,4,4,5,5-octafluorohexamethylene-1,6-diol(lower).

triethylene glycol and tetraethylene glycol.

After rigorous purification and characterisation these monomers were reacted using the technique established above, this was successful in the cases of the fluorocarbon monomers and all the hydrocarbon monomers except those derived from ethane-1,2-diol, propane-1,2-diol and propane-1,3-diol where the expected tendency to form cyclic products consequent upon the inherent stability of the five and six membered rings formed, resulted in cyclic carbonates as well as diethyl carbonates being obtained. During the polymerisation of the hydrocarbon monomers the rate of reaction was noted to be qualitatively somewhat slower than that of the fluorocarbon monomers, an observation in agreement with the mechanistic rationalisation of the course of this reaction discussed in Section 2; this led to a slight lengthening of the reaction duration to two and a half hours. The characterisation and some physical properties of the polymers produced will be reported at length in the next section of this thesis.

EXPERIMENTAL

3.3 Preparation of 2,2,2-Trifluoroethyl Chloroformate.

Phosgene (110g,1.1 moles) was condensed, at an external acetone/solid carbon dioxide bath temperature of -20°, into dry (Na) ether (1 litre) using the phosgenation apparatus shown in Figure 5 in a 3 litre round bottom 3 necked flask equipped with gas inlet, mechanical stirrer, thermometer well, dropping funnel and gas outlet. On completion of the condensation, after approximately 2hrs, dry ($CaCl_2$) pyridine (80.5ml, 0.998 moles) dissolved in dry (Na) ether (160ml) was added to the phosgene solution via the dropping funnel over a period of 10 mins. The yellow precipitate of pyridinium chloroformate formed was then stirred for 15 mins at -20° to ensure completion of reaction, and a solution of 2,2,2-trifluoroethanol (70ml, 0.97 moles) in dry (Na) ether (250ml) was added, using the dropping funnel, over the next 30 mins and at such a rate that the reaction temperature was maintained at -20°. A white precipitate of pyridine hydrochloride formed, and stirring was continued for a further 2hrs after removal of the acetone/solid carbon dioxide bath, to allow the reaction product to warm up to room temperature. Pyridinium hydrochloride was then filtered off using a Buchner funnel, the solvent ether removed by distillation, and the residue purified by distillation on an automatically controlled concentric tube distillation column (~ 90 plates) under reduced pressure, to give 2,2,2-trifluoroethoxycarbonyl chloride (2,2,2-trifluoroethyl chloroformate) (120g, 75%) b.p. 39° at 160mm Hg (Litt[106] : b.p. 40° at 165mm Hg) (Found: C,21.85; H, 0.97; Cl, 21.9; F, 34.8: $C_3H_2ClF_3O$ requires: C, 22.17; H, 1.24; Cl, 21.82; F, 35.07; M, 162.5). The ^1H n.m.r. showed a quartet at 5.77τ (J = 8 Hz) ($-CH_2-$) and the ^{19}F n.m.r. a triplet at 75.9p.p.m. (J = 8 Hz) ($-CF_3$). Vmax 1735 (>C = O), 1310 ($-CF_3$), 1285 ($-CH_2-$), 1180, 1130 cm^{-1}.

3.4 Preparation of the bis(2,2,2-trifluoroethyl)carbonate of hexafluoropentane-1,5-diol.

A mixture of hexafluoropentane-1,5-diol (64g, 0.302 moles), dry ($CaCl_2$) pyridine (58.6ml, 0.725 moles) and dry (Na) ether (500ml) contained in a three necked round bottom flask, equipped with a thermometer, dropping funnel, dry nitrogen inlet, gas outlet to bubbler, and mechanical stirrer, was stirred vigorously and cooled to 0-5° by the use of an external ice/salt bath. A solution of 2,2,2-trifluoroethyl chloroformate (117.8g, 0.725 moles) in dry (Na) ether (100ml) was then added over 40 mins. and at such a rate that the reaction temperature did not exceed 5°. A precipitate of pyridine hydrochloride formed during the reaction, on completion of which stirring was continued for a further 3hrs. with the cooling bath removed. The pyridine hydrochloride was then filtered off using a Buchner funnel, and the ether solvent removed with a rotary evaporator. The reaction product was then distilled under reduced pressure on an automatically controlled concentric tube distillation column (90 theoretical plates) to give bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene (bis(2,2,2-trifluoroethyl) carbonate of hexafluoropentane-1,5-diol) (108g, 77%) b.p. 84° at 0.1mm Hg (Found: C, 28.74; H, 2.09; F, 49.66, M(m.s.), 464; required for $C_{11}H_8F_{12}O_6$: C, 28.46; H, 1.74; F, 49.12; M, 464). The ^1H n.m.r. spectrum showed a complex peak centred on 5.65τ consisting of a triplet, 5.6τ (J = 12 Hz) assigned to the methylene groups ajacent to difluoromethylene groups, and a quartet, 5.75τ (J = 8 Hz) assigned to the methylene groups ajacent to the trifluoromethyl groups. ^{19}F n.m.r. showed to sets of triplets at 77.1 p.p.m. (J = 12 Hz) (CF_2 groups at C_2 and C_4), and a broad singlet at 127.9 p.p.m. (CF_2 group at C_3) from external $CFCl_3$ reference, in the relative group intensity ratios 3:2:1. Vmax, 1780 ($>C=O$), 1320 ($-CF_3$), 1250 ($-CH_2-$), 1165 ($-CF_2-$) cm^{-1}.

3.5 Polymerisation of the bis(2,2,2-trifluoroethyl) carbonate of hexafluoropentane-1,5-diol.

a) The bis(2,2,2-trifluoroethyl) carbonate of HFPD (10g, 0.021 moles) in a pear shaped flask was degassed and let down to a dry nitrogen atmosphere three times on a vacuum line, and then transferred to a dry box where the catalyst, sodium 2,2,2-trifluoroethoxide (0.05g), was added. The catalyst was prepared by adding sodium metal (0.23g, 0.1 mole) to 2,2,2-trifluoroethanol (0.72ml, 0.1 mole) in dry (Na) ether (20ml) under a dry nitrogen atmosphere, and removing the ether solvent by distillation and evaporation under reduced pressure (vacuum line). After the addition of a teflon coated stirrer bar, the flask was attached to the polymerisation apparatus shown in Figure 4, and heated to 150° in a Wood's metal bath for 2hrs. This resulted in the distillation of 2,2,2-trifluoroethoxycarbonyloxy-2,2,2-trifluoroethane (di(2,2,-trifluoroethyl) carbonate) a clear liquid (3.8g) b.p. 114° at 760mm Hg (Litt[116]: 62.5° at 75mm Hg) (Found: C, 26.55; H, 1.45; F, 50.9; M(m.s.), 226; required for $C_5H_4F_6O_3$: C, 26.56; H, 1.78; F, 50.42; M, 226,). The ^{1}H n.m.r. showed a quartet at 5.75τ (J = 8Hz) ($-CH_2-$) and the ^{19}F n.m.r. a triplet at 75.9 p.p.m. (J = 8Hz) ($-CF_3$). Vmax, 1780 (>C=O), 1425,1330,1280,1240, 1170cm^{-1}.

Reduction of the system pressure to 0.01mm Hg over the next 30 mins. resulted in a gradual increase in the viscosity of the reaction mixture until the reaction was terminated after 5hrs. Analysis of the reaction residue by ^{19}F n.m.r. in $(CD_3)_2CO$ solution, established the relative intensity ratio of the CF_3 triplet at 77.1 p.p.m. to the CF_2 triplet at 122.3 p.p.m. as 0.09:1, corresponding to a degree of polymerisation ∼17 and an extent of reaction of 94%. The ^{1}H n.m.r. showed a broad triplet at 5.6τ (J = 12Hz) and the ^{19}F n.m.r. a triplet at 77.1 p.p.m. ($-CF_3$) a triplet at 122.3 p.p.m. (J = 12Hz) (CF_2 groups at C_2 and C_4) and a broad singlet at 127.9 p.p.m. (CF_2 group at C_3) in the relative group intensities

0.18:2:1. Vmax, 1780 (>C=O), 1280 (broad), 1170 ($-CF_2-$), 995, 900, 790cm^{-1}.

b) Using the experimental procedure outlined in section 3.5.a. the monomer (10g, 0.021 moles) was heated at atmospheric pressure and 120° for 2hrs, reduction of the system pressure after this time resulted in quantitative distillation of monomer (b.p. 86° at 0.1mm Hg), which was identified by it's i.r. spectrum. Analysis of the distillate by g.l.c. (Column '$O_{2\frac{1}{2}}$', 150°) showed it to be pure monomer with no detectable contamination.

c) Again using the procedure described in section 3.5.a, the reaction was repeated by heating the monomer (10g, 0.021 moles) at atmospheric pressure and 190° for 2 hrs, monomer distillation followed system pressure reduction, this was shown to be uncontaminated by g.l.c. (Column '$O_{2\frac{1}{2}}$', 150°).

d) The reaction method described in section 3.5.a was repeated with a reduction in the amount of catalyst used (0.025g, 0.8 mole-%), the duration of the heating period prior to system pressure reduction was halved to 1hr. and the period of heating at reduced pressure was reduced to 1hr, the reaction proceeded successfully with the elimination of di(2,2,2-trifluoroethyl) carbonate (4.24g, 87% reaction). Analysis of the crude reaction residue as a solution in $(CD_3)_2CO$ by ^{19}F n.m.r. indicated a degree of polymerisation of ~11 (91% overall reaction).

e) A solution of (1ml, 2 mole-%), prepared by dissolving sodium (0.5g, 0.022 moles) in 2,2,2-trifluoroethanol (36ml, 0.5 moles), was added to the bis(2,2,2-trifluoroethyl) carbonate of HFPD (10g, 0.021 moles) in a pear shaped flask using a syringe. The experimental procedure described in 3.5.d was followed, reaction occured resulting in the elimination of di(2,2,-2-trifluoroethyl) carbonate (4.24g, 87% overall reaction), and a degree of polymerisation of ~14 (93% overall reaction) as monitored by ^{19}F n.m.r. on a solution of the crude reaction product in $(CD_3)_2CO$.

f) Injection of 0.4ml (0.8 mole %) of the catalyst solution prepared in

3.5.e, into heated (150°) bis(2,2,2-trifluoroethyl) carbonate of HFPD (10g, 0.021 moles), resulted in immediate reaction with the evolution of di(2,2,2-trifluoroethyl) carbonate (4.14g, 85% overall reaction). On completion of the reaction procedure described in 3.5.d, analysis of reaction product by ^{19}F n.m.r. indicated an overall extent of reaction of 94% (degree of polymerisation ~ 17).

3.6 Molecular Weight Determinations of Reprecipitated Reaction Products.

A rough fractionation of polymer samples was achieved by dissolving up the reaction products in dimethyl formamide (~ 5ml) using a teflon coated stirrer bar, and then precipitating this into an excess of chloroform (~ 50ml) vigorously stirred by a large teflon coated stirrer bar. Collection of the insoluble portion was achieved by decanting after 15mins, the solution of solvent and nonsolvent were evaporated and the soluble fraction of polymer collected, the last traces of solvent were removed by heating (100°) each fraction under reduced pressure. Each fraction was then subjected to analysis by ^{19}F n.m.r., as outlined in section 3.5.a, and v.p.o. using dimethyl formamide as solvent in a Perkin Elmer 115 vapour phase osmometer. A full discussion of this technique together with experimental details will be found in the next section of this thesis.

Some of these polymer fractions were analysed by ESCA using methods that have been described by Clark and co-workers.

3.7 Preparation of Poly(hexafluoropentamethylene carbonate) Using Improved Apparatus.

a) Using the modified molecular distillation apparatus shown in Figure 10, the bis(2,2,2-trifluoroethyl) carbonate of HFPD (10g, 0.021 moles) was degassed and let down to dry nitrogen atmosphere three times using a vacuum line. The reaction vessel was heated in a Wood's metal bath maintained at 150°, addition of the catalyst (0.4ml), prepared as described in section 3.5.e was carried out by means of a syringe inserted through the gas inlet of the apparatus. This initiated the elimination of di(2,2,2-trifluoroethyl) carbonate (4.14g, 85%) over the next hour, the system pressure was reduced to 1mm Hg for a further hour before the reaction was terminated. The ^{19}F n.m.r. of the crude reaction in solution ($(CD_3)_2CO$) showed the relative intensity ratio of the CF_3 triplet as 0.06: 1 corresponding to a degree of polymerisation of ~ 25, and an extent of reaction of 96%.

b) The apparatus was modified to include mechanical stirring transmitted via a glass rod and stirrer, as shown in Figure 11. On repeating the experimental procedure given in section 3.7.a. successful reaction was observed with the elimination of di(2.2,2-trifluoroethyl) carbonate (4.38g, 90%), and a degree of polymerisation of 33 (97.5% overall reaction) as determined by the CF_3; CF_2 relative intensity ratio in the ^{19}F n.m.r. of the crude reaction product in $(CD_3)_2CO$ solution.

c) Bis(2,2,2-trifluoroethyl) carbonate of HFPD (20g, 0.043 moles) was transferred to the custom built polymerisation apparatus shown in Figure 12. Here a proprietary (Edwards Vacuum) rotary vacuum seal with attached stirrer was mounted via flanges to a graded glass to metal joint to the apparatus. After degassing and letting down to a dry nitrogen atmosphere three times using the vacuum line, the polymerisation was initiated by injecting the catalyst (0.4ml, 1 mole-%) into the hot stirred monomer. immediate evolution and distillation of di(2,2,2-trifluoroethyl) carbonate was noted, collecting 8.85g (91%) of this product before reduction in the system pressure after 1hr reaction time. Further reaction for 1hr, under reduced pressure (~ 0.1mm Hg) produced notable increase in viscosity of the material remaining in the reaction vessel, the involatile product recovered after cooling was poly(hexafluoropentamethylene carbonate) (10.15g, 99%) (Found: C, 30.15; H, 2.00; F, 47.70; required for $C_6H_4F_6O_3$: C, 30.27; H, 1.69; F, 47.88). The ^{19}F n.m.r. analysis of this reaction product showed the relative intensity ratio CF_3: CF_2: to be 0.023 : 1, corresponding to a degree of polymerisation of ~ 66 and an extent of reaction 98.5% Vmax, 1780

($>C=O$), 1280 ($-CH_2-$), 1170 ($-CF_2-$)cm^{-1}. Further characterisation of this polymer will be described in section 4 of this thesis.

3.8 Preparation of Tetrafluorosuccinic Acid.

Dry ($MgSO_4$) acetone (1.5 l) and potassium permanganate (82.95g, 0.525 moles) were put into a three necked round bottom flask equipped with a thermometer, dropping funnel, mechanical stirrer and 2 double surface reflux condensers topped by an acetone/solid carbon dioxide trap. The flask was cooled to -20° using an external acetone/solid carbon dioxide bath, and 1,2-dichloroperfluorocyclobuteneadded drop wise via the dropping funnel, care being taken to keep the reaction temperature at -20° by manipulation of the rate of addition. On completion of the addition, approximately 30mins, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature with vigorous stirring over the next 3hrs. The mixture was then heated to 50° (refluxing) for 30mins using a water bath, before being poured into water (2 l) contained in a large round bottom flask. Sulphur dioxide was then bubbled into the aqueous solution until decolourisation to a light brown colour occured signifying the reduction of any excess potassium permanganate present. The solution was reduced in volume to ~ 0.75 l, using a rotary evaporator to remove the acetone and water, and then sulphuric acid (50% w/w solution) was carefully added until the solution pH reached one. Acidification is particularly important since continuous ether extraction maybe inefficient if the solution is not acidic enough. The solution was continuously extracted with diethyl ether over a 48hr. period and the resulting ether layer dried over $MgSO_4$, the solution was decanted from the dessicant and the solvent ether evaporated under reduced pressure and heating (80°) to give a white solid (62g, 65%) of tetrafluorosuccinic acid, characterised by correct i.r. and m.p..

2,2,3,3,4,4,5,5-octafluoroadipic acid was obtained by a similar route from perfluorocyclohexene by technicians within this department and this was used without further characterisation for the following esterification and reduction reactions to obtain the respective diols, 2,2,3,3-tetrafluorobutane-1,4-diol and 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol. In sections 3.9 and 3.10 the experimental procedure will be described for the synthesis of octafluorohexane-1,6-diol, quantities used for the tetrafluorobutane-1,4-diol will appear in brackets, [ ], immediately afterwards.

3.9 Esterification of 2,2,3,3,4,4,5,5-octafluoroadipic Acid, [2,2,3,3-tetrafluorosuccinic Acid].

2,2,3,3,4,4,5,5-octafluoroadipic acid (80g, 0.275 moles) [2,2,3,3-tetrafluorosuccinic acid (62g, 0.33 moles)] , absolute ethanol (100ml, 1.7 moles), toluene (50ml, 0.5 moles), p-toluene sulphonic acid (1g, 0.005 moles) and a teflon coated stirrer bar were placed in a round bottom flask, fitted with a Vigreux column (1cm diameter, 14cm length), still head, thermometer, water condenser, vacuum reciever adaptor and collection vessel containing 50g of anhydrous potassium carbonate. The reaction mixture was heated using an oil bath (100°), refluxing and distillation of an azeotropic mixture of ethanol, toluene and water taking place at 75-6° , this was continued until the still head temperature rose to 78°. The distillation was then stopped the distillate thoroughly shaken with the potassium carbonate, to remove the water, filtered through a Buchner funnel, and returned to the reaction flask. The distillation was recommenced, until the still head temperature reached 81° ; subsequent resumption of the distillation under reduced pressure lead to distillation of diethyl perfluoroadipate, a colourless transparent liquid (92g, 95%) b.p. 90-95° at 0.1mm Hg (Litt^{117} : 156-9° at 27mm Hg). [diethyl perfluorosuccinate (74.5g, 93%), b.p. 71° at 0.1mm Hg (Litt^{118} : 89° at 15mm Hg)] .

3.10 Preparation of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol, [2,2,3,3,-tetrafluorobutane-1,4-diol] .

The following apparatus was thoroughly dried in an oven before being assembled under a purge of dry nitrogen gas: a three necked flask equipped with a gas inlet, dropping funnel, mechanical stirrer and a double surface reflux condenser with concentrated sulphuric acid bubbler as an outlet. Into this was placed lithium aluminium hydride (20g, 0.74 moles) [30g, 1.1 moles] with dry (Na) ether (500ml), addition of diethyl octafluoroadipate (86g, 0.25 moles) [diethyl tetrafluorosuccinate (53g, 0.28 moles)] was then carried out carefully so as to maintain as even a rate of ether refluxing as possible over 30mins. The reaction mixture was then left to stir vigorously for 1hr, after which sulphuric acid (150ml, 50% w/w) was added to destroy the excess lithium aluminium hydride present and hydrolyse any organometallic complexes. an ice/water bath being used to control the vigorous reaction. The semisolid reaction product was then poured into sulphuric acid (1 l, 50% w/w), the ether layer seperated, the aqueous layer was extracted three times with ether and the ether extracts were combined. The ether was removed by distillation, benzene (200ml) added to the residual liquid and using a Dean-Stark distillation apparatus, the remaining water in the sample was removed by azeotropic distillation. Crystallisation from the benzene solution gave a white solid 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol, (53g, 81%) [2,2,3,3-tetrafluorobutane-1,4-diol (38.5g, 85%)], with correct i.r. and m.p..

3.11 Preparation of the bis(2,2,2-trifluoroethyl) carbonate of octafluorohexane-1,6-diol and tetrafluorobutane-1,4-diol.

Using the experimental method described in section 3.4 octafluorohexane-1,6-diol (43.25g, 0.165 moles) [tetrafluorobutane-1,4-diol (24.3g, 0.15 moles)] dry ($CaCl_2$) pyridine (32.6ml, 0.36 moles) [28.8ml, 0.33 moles] and dry (Na) ether (500ml) were reacted with a solution of 2,2,2-trifluoroethyl chloroformate (58.5g, 0.36 moles) [53.6g, 0.33 moles] in dry (Na) ether (100ml) to give bis(2,2,2-trifluoroethyoxycarbonyloxy) 2,2,3,3,4,4,5,5-octafluorohexamethylene,(bis(2,2,2-trifluoroethyl) carbonate of octafluorohexane-1,6-diol), (80.5g, 95%), b.p. 102° at 0.1mm Hg, (Found: C, 27.98; H, 1.45; F, 52.11; M (m.s.) 514; required for $C_{12}H_8F_{14}O_6$: C, 28.03; H, 1.57; F, 51.73; M, 514). The ^{1}H n.m.r. showed a complex peak centred on 5.2τ consisting of a triplet, 5.14τ (J = 12Hz) (-CH_2 adjacent to -CF_2) and a quartet, 5.27τ (J = 8Hz) (-CH_2 adjacent to-CF_3). The ^{19}F n.m.r. showed a triplet at 76.9 p.p.m. (J = 8Hz) (-CF_3) and two broad absorptions centred at 121.9 p.p.m. (-CF_2 at C_2 and C_5) and 125.32 p.p.m. (-CF_2 at C_3 and C_4) from $CFCl_3$ external reference, in the relative group intensity ratios 3:2:2. Vmax, 1785 (>C=O), 1325 (-CF_3), 1260 (-CH_2-), 1180 (-CF_2-)cm^{-1}.

[bis(2,2,2-trifluoroethoxycarbonoxy)-2,2,3,3-tetrafluoromethylene, (bis(2,2,2-trifluoroethyl) carbonate of tetrafluorobutane-1,4-diol), b.p. 64° at 0.1mm Hg, (Found: C, 29.01; H, 1.75; F, 45.9; M(m.s.) 414; required for $C_{10}H_4F_{10}O_6$: C, 29.00; H, 1.95; F, 45.87; M, 414). The ^{1}H showed a complex peak centred on 5.05τ consisting of a quartet 5.12τ (J = 8Hz) (-CH_2 adjacent to-CF_3) and a complex triplet 5.02τ (J = 12Hz) (-CH_2 adjacent to-CF_2) the fine structure on this peak not being resolvable. The ^{19}F n.m.r. showed a triplet at 73.9 p.p.m. (J= 8Hz) (-CF_3) and a triplet of doublets at 120.87 p.p.m. (J = 12Hz, 4Hz) (-CF_2) from external $CFCl_3$ reference in the relative group intensity ratio 3:2; Vmax, 1780 (>C=O), 1320 (-CF_3), 1250 (-CH_2-), 1175 (-CF_2-)cm^{-1}.]

3.12 Preparation of the bisethyl carbonates of aliphatic diols.

The experimental procedure was similar to that used in section 2.3, and that outlined in a patent.[87] Generally a mixture of the diol (1 molar proportion) and dry ($CaCl_2$) pyridine (3.6 molar proportions) in a round bottom flask equipped with a dropping funnel, thermometer, mechanical stirrer, gas inlet and outlet to a sulphuric acid bubbler, was stirred vigorously and cooled to 0-5° by the use of an external ice/salt bath. Ethylchloroformate (2.4 molar proportions) was added at a rate so as to maintain the temperature at 0-5°, the occurence of reaction is shown by the

	Amounts of Reactants used			PRODUCT					
	Diol (moles)	Chloroformate (moles)	Pyridine (moles)	Yield (%)	B.p. (Pressure) Lit.	Molecular Formula	Elemental Analysis		IUPAC systematic name Common name
							C	H	
$HO(CH_2)_2OH$	29.9 (0.482)	129.9 (1.203)	147.3 (1 841)	90	66° (0.01) 116-7° (2)[119]	$C_8H_{18}O_6$	48 21 (48 01)	6.97 (7.05)	bis(ethoxycarbonyloxy)-ethylene bis(ethyl) carbonate of ethane-1,2-diol
$HO(CH_2\overset{Me}{C}H)OH$	50 00 (0.658)	169.5 (1.569)	189.5 (2 369)	53	80° (0.1) -	$C_9H_{20}O_6$	50 87 (50.47)	7.80 (7.53)	bis(ethoxycarbonyloxy)-methyl-1,2-ethylene bis(ethyl) carbonate of propane-1,2-diol
$HO(CH_2)_3OH$	50.00 (0.658)	169.5 (1.569)	189.5 (2.369)	75	88° (0.02) -	$C_9H_{20}O_6$	50.82 (50.47)	7.80 (7.53)	bis(ethoxycarbonyloxy)-trimethylene bis(ethyl) carbonate of propane-1,3-diol
$HO(CH_2)_4OH$	45.45 (0.505)	129.9 (1.203)	147.3 (1.841)	60	86° (0.1) 118-121° (1:5)[87]	$C_{10}H_{22}O_6$	52.76 (52.63)	7.93 (7 95)	bis(ethoxycarbonyloxy)-tetramethylene bis(ethyl) carbonate of butane-1,4-diol
$HO(CH_2)_5OH$	44.55 (0.428)	111.8 (1.036)	123.7 (1.546)	75	102° (0.05) 138° (2.5)[87]	$C_{11}H_{24}O_6$	54.70 (54 54)	8.26 (8.32)	bis(ethoxycarbonyloxy)-pentamethylene bis(ethyl) carbonate of pentane 1,5-diol
$HO(CH_2)_{10}OH$	80.00 (0 459)	118.6 (1.099)	132.6 (1.657)	60	160° (1) 168-170° (0.5)[87]	$C_{16}H_{30}O_6$	59.96 (60.35)	9.74 (9.50)	bis(ethoxycarbonyloxy) decamethylene bis(ethyl) carbonate of decamethylene-1,10-diol
$H(OCH_2CH_2)_2OH$	53.10 (0.507)	129.9 (1.203)	143.4 (1.792)	78	134° (1) 138-148° (2)[119]	$C_{10}H_{18}O_7$	48.06 (47.99)	7.20 (7.25)	bis(ethoxycarbonyl) di-(oxyethylene) bis(ethyl) carbonate of diethylene glycol
$H(OCH_2CH_2)_3OH$	74.94 (0.499)	129.9 (1.203)	143.4 (1.792)	78	170° (1) -	$C_{12}H_{22}O_8$	48.88 (48.97)	7.82 (7.53)	bis(ethoxycarbonyl) tri-(oxyethylene) bis(ethyl) carbonate of triethylene glycol
$H(OCH_2CH_2)_4OH$	96.90 (0.500)	129.9 (1.203)	143.4 (1.792)	68	210° (1) -	$C_{14}H_{26}O_9$	49.64 (49.76)	7.84 (7.74)	bis(ethoxycarbonyl)tetra-(oxyethylene) bis(ethyl) carbonate of tetramethylene glycol

formation of a white precipitate of pyridine hydrochloride. On completion of the ethyl chloroformate addition the cooling bath was removed and the mixture left to stir overnight to ensure completion of reaction. Dry (Na) toluene (? 1) was then added to the reaction mixture and the pyridine hydrochloride filtered off using a Buchner funnel, the solution was then washed five times with water to remove residual pyridine and dried over $MgSO_4$. After filtering off the $MgSO_4$ the toluene was removed by distillation, and the residue distilled under reduced pressure on an automatically controlled concentric tubes distillation column (90 theoretical plates) apparatus. Exact experimental quantities used in each particular case as well as elemental analysis are included in Table 5.

3.13 Polymerisation of the bis(2,2,2-trifluoroethyl) carbonates of octafluorohexane-1,6-diol and tetrafluorobutane-1,4-diol.

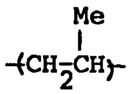
Using the experimental procedure described in section 3.7.c, the bis (2,2,2-trifluoroethyl) carbonates of octafluorohexane-1,6-diol (20g, 0.039 moles) [tetrafluorobutane-1,4-diol (20g, 0.048 moles)] were polymerised using a catalyst prepared as described in section 3.5 (0.8ml, 1 mole-%) to give di(2,2,2-trifluoroethyl) carbonate (9.743g, 94%) [7.892g, 90%] and the required poly(oxycarbonyloxy-2,2,3,3,4,4,5,5-octafluorohexamethylene). (poly(octafluorohexamethylene carbonate)), (11g, 98%), (Found: C, 29.18; H, 1.63; F, 52.36; required for $C_7H_4F_8O_3$: C, 29.18; H, 1.40; F, 52.76;). Vmax, 1780 ($>C=O$), 1270 ($-CH_2-$), 1180 ($-CF_2-$) cm^{-1}. [poly(oxycarbonyloxy-2,2,3,3,-tetrafluorotetramethylene), (poly(tetrafluorotetramethylene carbonate)), (8.6g, 95%), (Found: C, 32.27; H, 2.40; F, 40.15; required for $C_5H_4F_4O_3$: C, 31.93; H, 2.14; F, 40.41. Vmax, 1780 ($>C=O$), 1260 ($-CH_2-$), 1190 ($-CF_2-$) cm^{-1}.]

3.14 Polymerisation of the bisethyl carbonates of aliphatic diols.

An experimental method analogous to that given in section 3.7.c, was used to react the bisethyl carbonates of aliphatic diols using a catalyst solution

(0.2ml, 1 mole-%) made up by dissolving sodium metal (0.92g, 0.04 moles) in methanol (10g, 0.312 moles), which had been dried (Mg) distilled and stored over 3A molecular sieve. The reaction vessel was heated in a Wood's metal bath maintained at 30° below boiling point of the starting material at atmospheric pressure, or 240° whichever was the lower. In every case immediate reaction took place upon the addition of the catalyst solution, to give diethyl carbonate as the eliminated product. In the cases where polymerisation had taken place, reduction of the system pressure after 45mins to ~1mm Hg lead to a gradual increase in viscosity of the reaction mixture until the reaction was terminated 1.5hr later; where cyclisation took place then the reduction in system pressure lead to the distillation of the cyclic product formed. After cooling the polymeric residues were removed from the reaction vessel by dissolving them in chloroform, and reprecipitating them into ether, solvent removal by heating under reduced pressure then followed. Characterisation of these polymers will be reported in the next section of this thesis. Specific experimental details of reaction are contained in Table 6, as well as the elemental analysis of the polymers obtained; the cyclic products were well known compounds identified from their i.r. spectra and melting points.

TABLE 6. Reaction of bis ethyl carbonates of aliphatic diols.

Reactant HO( )OH	Quantity g (moles)	Product $(Et_2O)_2O$	Product Cyclamer	Product Polymer	Formula of Polymer	C	H
		g (%)	g (%)	g (%)		Found (calc.)	Found (calc.)
$-(CH_2)_2-$	20.2 (0.098)	10.59 (92)	8.20 (95)	-	m.p. 39° (39-40°)[120]	-	-
 $-(CH_2-\overset{Me}{CH})-$	20.0 (0.093)	10.03 (91)	9.25 (97)	-	b.p. 240° (242°)[120]	-	-
$-(CH_2)_3-$	19.9 (0.093)	9.87 (90)	9.29 (98)	-	m.p. 27° (28-9°)[120]	-	-
$-(CH_2)_4-$	18.0 (0.079)	8.35 (92)	-	8.80 (98)	$C_5H_8O_3$	51.45 (51.72)	6.97 (6.94)
$-(CH_2)_5-$	20.2 (0.083)	9.05 (92)	-	10.52 (97)	$C_6H_{10}O_3$	55.64 (55.77)	8.14 (7.74)
$-(CH_2)_{10}-$	20.4 (0.064)	6.74 (89)	-	12.20 (95)	$C_{11}H_{20}O_3$	65.68 (65.97)	10.48 (10.09)
$-(OCH_2CH_2)_2-$	20.4 (0.082)	8.18 (85)	-	10.34 (96)	$C_5H_8O_4$	45.17 (45.45)	6.11 (6.10)
$-(OCH_2CH_2)_3-$	21.6 (0.073)	7.80 (90)	-	12.54 (97)	$C_7H_{12}O_5$	47.85 (47.72)	7.22 (6.86)
$-(OCH_2CH_2)_4-$	20.1 (0.059)	6.53 (93)	-	12.82 (98)	$C_9H_{16}O_6$	48.78 (49.08)	6.98 (7.32)

Section 4.

The characterisation and some physical properties of some fluorinated aliphatic and aliphatic polycarbonates.

Section 4. The Characterisation and Properties of the Polycarbonates Produced in this Study.

4.1 Introduction.

This section contains a discussion of the methods used to characterise the polymers obtained previously. The possible methods of characterisation are briefly reviewed, then the actual methods used and results obtained are discussed in more detail.

The unique properties of polymers are derived chiefly from their long chain nature, high molecular weights and molecular weight distributions and their characterisation may be said to have begun with the recognition of their macromolecular nature by Staudinger in the 1920's and 1930's. The earliest workers in this area used methods based upon the well established laws governing the colligative properties of dilute solutions as well as chemical methods of endgroup analysis for the determination of number average molecular weight ($\bar{M}n$). Later developments, during the late 1930's and early 1940's, of light scattering and ultracentrifugation techniques lead primarily to the determination of weight average molecular weight ($\bar{M}w$). Detailed analysis of molecular weight distribution was laborious involving careful fractionation and determinations of $\bar{M}n$ and $\bar{M}w$ for individual fractions, this situation changed with the advent of gel permeation chromotography (GPC) in the 1960's. In general all of these characterisation methods work well when applied to relatively simple cases, such as linear homopolymers readily soluble in relatively non polar solvents at room temperature and not displaying extreme values of molecular weight or molecular weight distribution. A short review of widely used methods of molecular weight determinations and characterisation of the thermal behaviour of polymers is presented before turning to the actual characterisation of of the materials of interest in this work.

4.1. (i) Molecular Weight Determination

Endgroup Analysis

Both chemical and physical methods can be used to measure number average molecular weight, $\bar{M}n$, in linear polymers having identifiable endgroups. The sensitivity of chemical methods usually limits their application to samples with $\bar{M}n < 25,000$; whilst physical methods, using spectroscopic or isotopic labelling techniques usually afford higher sensitivity. The method is not universally applicable, since for many polymers there maybe several different kinds of end groups and the distribution may vary from sample to sample.

Membrane Osmometry

This technique is widely used and requires that equilibrium conditions be established for the thermodynamic analysis of the results to be valid. One of the oldest methods of polymer characterisation, modern applications utilise high speed automatic osmometers, but uncertainty in the characteristics and behaviour of the semipermeable membranes used in this method still persists, requiring the osmometer to be carefully tested with well behaved polymer samples of known $\bar{M}n$ before using it for unknowns. Diffusion of low molecular weight species through the membrane limits the applicability of the method to rather high $\bar{M}n$ i.e. $> 50,000$.

Vapour Phase Osmometry.

This method would appear to be the most popular colligative properties procedure for samples with $\bar{M}n$ 50,000. Two matched thermistors are suspended in a thermostated cell saturated with solvent vapour, placing a drop of polymer solution on one thermistor and a drop of pure solvent on the other results in a temperature drop across the thermistors. This is a result of the lowering of the vapour pressure of the solvent in the solution drop by the solute, causing condensation of solvent from the vapour in the chamber onto this drop, the resulting release of the latent heat of vapourisation raises the temperature of this drop slightly. The temperature change can be accurately monitored by the bridge circuitry of which the thermistors form a part. The calibration of this equipment with solutions of known molality thus enables the determination of the number average molecular weight, $\overline{M}n$.

Light Scattering.

The instrumentation for this technique is expensive and its application is consequently less widespread. It allows the determination of weight average molecular weight, $\overline{M}w$, and additionally gives the mean-square radius of gyration, a measure of the size of a polymer molecule in solution. The major difficulty in applying this technique resides in clarifying the polymer solutions to remove extraneous scattering material, so that the difference in scattered light intensity between a polymer solution and its solvent maybe measured accurately.

Gel Permeation Chromatography.

This method was developed during the mid 1960's and has largely displaced the more laborious fractionation techniques based on solubility as an approach to separating polymer molecules by weight, and thus determining the distribution of molecular weights. For simple systems, such as linear homopolymers of moderate molecular weight and distribution breadth, soluble in relatively non polar solvents at room temperature, GPC works well. However it must be remembered that separation is based on molecular size rather than mass and for simple case just described, there is a one-one relation between these variables, which may not be the case in more complicated systems.

Dilute Solution Viscometry.

Viscometry in one form or another, is perhaps the method most commonly used to give an indication of the molecular weight of a polymer. The particular case of dilute solution viscometry of interest here can be used to give a quick and cheap estimate of molecular weight. The relative viscosity, η_r, (viscosity ratio) is the ratio of the time taken for a known volume of polymer solution to flow through a capilliary, to that taken by the same volume of pure solvent. The reciprocal of this gives the specific viscosity η_{sp}, which when divided by the polymer solution concentration gives the reduced viscosity, η_{red}, (viscosity number). The logarithm of the relative viscosity divided by the polymer solution concentration gives the inherent viscosity, η_{inh}, (logarithmic viscosity number). -Extrapolating both the inherent and reduced viscosities to infinite dilution should result in their convergence to give the intrinsic viscosity, $[\eta]$, (limiting viscosity number).

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} = \lim_{C \to 0} \frac{\ln \eta_r}{C}$$

In suitably precalibrated systems the intrinsic viscosity can be related to the molecular weight via the Mark-Houwink equation:-

$$[\eta] = kM^x$$

where k and x are constants depending on the system.

The foregoing summary gives some indication of the amount of effort which has been expended over the years in developing methods for the determination of molecular weight. This is a direct consequence of the importance of this characterising parameter in the gradual development of models relating the bulk properties of polymeric materials to their detailed chemical and physical structures. Thus it was realised early on that the properties of linear polymers were a function of molecular weight, and that strength, toughness and low sensitivity to chemical attack, characteristic of polymers as a class of materials are not well developed until a molecular weight of the order of 10^4 is reached. In the context of this investigation it was particularly important to establish that genuine high molecular weight samples had been prepared, the more so since it was suspected that some of the data reported in the literature for relatively poorly characterised materials might be unreliable, and this clearly causes problems for the attempts to construct a usefully predictive Tg/structure correlation discussed in Section 1.

4.1 (ii) Thermal Characterisation

The physical properties of a linear or lightly branched polymers are a function of the temperature at which the property is measured. Particular types of behaviour are separated by transition temperatures such as the glass transition temperature (Tg), the melting point (Tm) and the decomposition temperature (Tdec). Since, for example, elastomeric properties are not evident until a temperature of 20-30° above Tg, a knowledge of this parameter provides a lower limit to the useful working range of a potential elastomer; similarly the upper temperature limit for a potential structural material has to be well below Tm or Tdec whichever is the lower. The obvious importance of these characterising transition temperatures has stimulated investigation into methods of determining them in a rapid and reliable manner on small quantities of material. Thermal analysis has been progressively developed to the stage where it is now possible to have a reliable estimate of all the parameters on samples of only a few tens of milligrams. As discussed at length in Section 1 of this thesis the parameters of interest to the sponsors of this project are primarily Tg and Tdec.

A technique that has been used to determine the glass transition temperature of a polymer is differential scanning calorimetry (DSC), used more generally to investigate the thermal properties of polymers. In this analysis technique a sample of the polymer and a reference are heated at a programmed rate by individually controlled elements, governed by sensors built into the heating block. The power supplied to these heaters is adjusted continuously in response to any thermal effects in the sample, in order that the sample and reference are maintained at the same temperature. The differential power required to achieve this is recorded on an output recorder together with the programmed temperature of the system. By keeping the thermal mass of the sample, reference holders and all other thermal resistances to a minimum, together with high gain amplification the response time of the instrument can be made so short that the output from the system is a nearly instantaneous measure of the energy transferred to or from the sample. Therefore any change that involves heat exchange in the solid state (for example: glass transition, crystallisation, melting, reaction) is noted by a change in the recorded output.

Although DSC measurements can be used to indicate the onset of thermal degradation the more usual technique applied in this area is thermogravimetry (TG). As the name suggests this technique involves measuring the weight of a sample as a function of its temperature, the major problem of accurately monitoring the sample temperature is overcome either by precalibrating the furnace, or by using a null deflection balance which enables the sample to be maintained in a constant position relative to the temperature sensing device. The atmosphere (i.e. gas and pressure) and rate of temperature change can be varied over a considerable range. In practise the technique is generally used in one of two modes:

a) Most commonly as a dynamic technique, in which the weight loss of a sample is measured continuously as a function of a constant rate of heating.

b) The weight loss of a sample is measured as a function of time at a constant temperature, this allows in favourable cases the study of thermal degradation mechanisms and determination of the kinetic parameters involved.

The two methods of thermal analysis described above are of fairly universal application in polymer laboratories througnout the world and in particular in the laboratory where this work was carried out. Other thermal analysis techniques of a more specialist nature are available, such as thermomechanical analysis, flammability testing and thermal conductivity measurements.

4.2 Discussion.

In Section 3 of this thesis it was stated that all polymers arising from bulk polymerisation consist of a mixture of varying molecular weights when first prepared, and that the properties of the bulk material can be adversely affected by the presence of a relatively small amount of low molecular weight material. In an attempt to remove any possible low molecular weight residues the raw products were subjected to reprecipitation from a solvent into a non-solvent, and volatile impurities were removed from the recovered polymer by heating under reduced pressure (10^{-3}mm Hg). The poly(hexafluoropentamethylene carbonate) whose synthesis was described in Section 3 was initially characterised by determining its intrinsic viscosity in 1,4 dioxane. In order to determine whether simple reprecipitation process adopted was yielding samples of high polymer, the molecular weight of this product was determined (after some difficulties see Section 3) by vapour phase osmometry using a Perkin Elmer 115 molecular weight apparatus, with methylethylketone as the solvent. The value of $\overline{M}n$ obtained was 31,800 indicating a degree of polymerisation of 137. The instrument manufacturers specify that the range of determinable molecular weights is "upto 50,000 with a standard deviation of ± 2% and to 100,000 in ideal solution". The molecular weights are obtained by first establishing a calibration curve correlating the observed out of balance potential (Δ R) for standard solutions with their molalities; the out of balance potential caused by solutions of solutes of unknown molecular weight but of known concentration by weight are measured and from the calibration curve the molalities and hence molecular weights can be calculated, and then extrapolated to infinite dilution. Ideally the calibration curve and the extrapolation of molecular weight to infinite dilution should be straight lines, in practice lines were fitted by a standard least squares procedure and the correlation coefficient, a measure of the accuracy of the fit, for the methylethylketone calibration was 0.997 and for the extrapolation to infinite dilution 0.949. Thus it was confidently concluded that the preparative and purification techniques, the development of which formed the subject of Section 3, gave a genuine high polymer; hence, any physical property measured on this sample should be truely characteristic of this particular polymer.

In consequence as each polymer was prepared, a general procedure of dissolving the reaction product in a solvent (acetone in the case of fluorocarbon polymers and chloroform in the case of hydrocarbon polymers), reprecipitation into non-solvent (chloroform for the fluorocarbon polymers and diethyl ether for the hydrocarbon polymers), and removal of volatile residues from the recovered polymer by heating under reduced pressure was adopted. The intrinsic viscosity of the polymer was then measured followed by molecular weight determinations by v.p.o. to show that a true high polymer had been produced. The results obtained are shown in Table 7 together with the measured glass transition temperatures (Tg) (see later) and the elemental analysis obtained for the polymer samples.

Generally the values obtained for inherent viscosities and molecular weights indicate genuine high polymers and where the materials have been reported previously the agreement with the literature is satisfactory. The three fluorinated aliphatic polycarbonates had similar intrinsic viscosities and respectably high molecular weights. Two of these materials have been reported previously; the preparation of poly(hexafluoropentamethylene carbonate) by the direct phosgenation route from the diol was described in a patent[95] and although no molecular weight was recorded the intrinsic viscosity was identical with the value obtained in this work; poly(octafluorohexamethylene carbonate) has been reported by Russian workers,[98] also

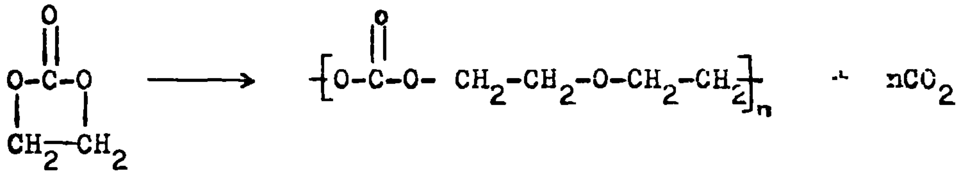
TABLE 7. Results of the experimentally determined properties for the prepared polycarbonates

Polymer $-O\overset{\overset{O}{\|}}{C}OCH_2-(\;)-CH_2-$	Intrinsic Viscosity[a]	$\bar{M}_n$[b]	DP	Tg	Elemental Analysis		
					C	H	F
$-(CF_2)_2$	0.24	14800(0.992)	78	257	32.27 (31.93)	2.40 (2.14)	40.15 (40.41)
$-(CF_2)_3$	0.29	31800(0.949)	134	241	30.51 (30.27)	2.09 (1.69)	47.70 (47.88)
$-(CF_2)_4$	0.25	29800(0.996)	103	236	29.18 (29.18)	1.63 (1.40)	52.36 (52.76)
$-(CH_2)_2$	0.68	8500 (0.950)	71	238	51.45 (51.72)	6.97 (6.94)	-
$-(CH_2)_3$	1.15	9300 (0.998)	70	232	55.64 (55.37)	8.14 (7.74)	-
$-(CH_2)_4$	1.05	11200(0.977)	77	223	57.90 (58.32)	8.99 (8.39)	-
$-(CH_2)_8$	-	3500 (0.998)	42	-	65.68 (65.97)	10.48 (10.06)	-
$-(CH_2OCH_2)_1$	0.49	6300 (0.999)	51	261	45.17 (45.45)	6.11 (6.10)	-
$-(CH_2OCH_2)_2$	0.56	5800 (0.999)	32	244	47.85 (47.72)	7.22 (6.86)	-
$-(CH_2OCH_2)_3$	-	10500(0.999)	47	236	48.78 (49.08)	6.98 (7.32)	-

[a] Fluorocarbon polymers in 1,4-dioxane, hydrocarbon polymers in chloroform all at 25.00° ± 0.01°.

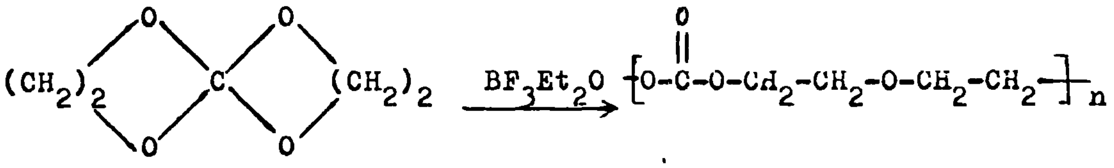
[b] Correlation coefficients for methyl ethyl ketone calibration 0.897 used for fluorocarbon polymers, and for chloroform 0.995 used for hydrocarbon polymers; in parenthesis for the extrapolations to infinite dilution for the particular polymer.

via the direct phosgenation route, and in this case the highest values of intrinsic viscosity and molecular weight recorded (0.14 and 5230) were considerably lower than those obtained here. No physical data have been presented previously for poly(tetrafluorotetramethylene carbonate) although it has formed the subject of a patent claim. The synthesis of the four aliphatic polycarbonates has been descibed previously,[87] and indeed formed the basis for the preparative technique adopted in this work. The intrinsic viscosities obtained are very similar to those reported previously although the earlier work did not include molecular weight values. Poly(decamethylene carbonate) did not dissolve homogeneously in the solvent at the concentrations required for the determination of the intrinsic viscosity, but did so at the concentration required for the determination of molecular weight. Of the aliphatic ether polycarbonates, only poly(diethylene glycol carbonate) has been previously reported. One group of Japanese workers described a novel synthesis of this polymer via the ring opening polymerisation of ethylene carbonate using a range of catalysts, reaction (27), to give a



(27)

material with an intrinsic viscosity of 0.31.[121] Another Japanese group have described an equally novel ring opening polymerisation of a spiro ortho carbonate by Lewis acid catalysts, reaction (28) and section 1.6 (vii),



(28)

to give a product with $\bar{M}n \sim 6{,}000$.[91] Poly(triethylene glycol carbonate) and poly(tetraethylene glycol carbonate) have not been previously reported and the former did not give an homogeneous solution at the concentrations required for intrinsic viscosity measurements, but did so at the concentrations required for molecular weight determinations.

The last four products recorded in Table 7 have significantly lower DPs than the other prepared materials. The reasons for this are not immediately obvious but it maybe that the markedly higher melt viscosity of the poly(decamethylene carbonate) inhibited the attainable DP in that case, and possibly the marginally lower thermal stability of the aliphatic ether polycarbonates (see later) results in competitive chain terminating reactions.

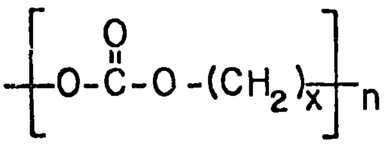
The foregoing discussion establishes that the materials produced in this work are high polymers, before turning attention to their physical properties it is necessary to confirm that the structures of the products are as expected. The first point to be made in this connection is that the elemental analysis (Table 7) are in good agreement with the assigned structures for all the samples. Considering the method of preparation it seems reasonable to speculate that the only plausible side reactions would be of the pyrolytic decomposition type, eliminating small stable molecules, for example CO, CO_2, H_2O etc, such occurences would have made significant differences to the elemental analysis results.

The n.m.r. spectra of the polymers were also in good agreement with the assigned structures, in particular in the absence of signals attributable to end groups and the observed chemical shifts of the signals associated with the constituent groups. Thus, for the fluorinated aliphatic polycarbonates, the ^{1}H n.m.r. spectra showed a broad triplet (J ~ 8Hz) at 5.2 τ $\left(-O\overset{O}{\overset{\|}{C}}O\underline{CH_2}(CF_2)_n\underline{CH_2}-\right)$ and no detectable quartet signal due to $CF_3\underline{CH_2}-$ end groups. The ^{19}F n.m.r. spectra showed bands in the appropriate intensity ratios at 121 p.p.m. and 125 p.p.m. the lower field band showing a triplet splitting of ~ 8Hz as expected for these systems; there was no detectable trifluoromethyl resonance at ~ 77 p.p.m.. In a similar manner the ^{1}H n.m.r. spectra of the aliphatic polycarbonates showed resonances at ~ 5.8 τ

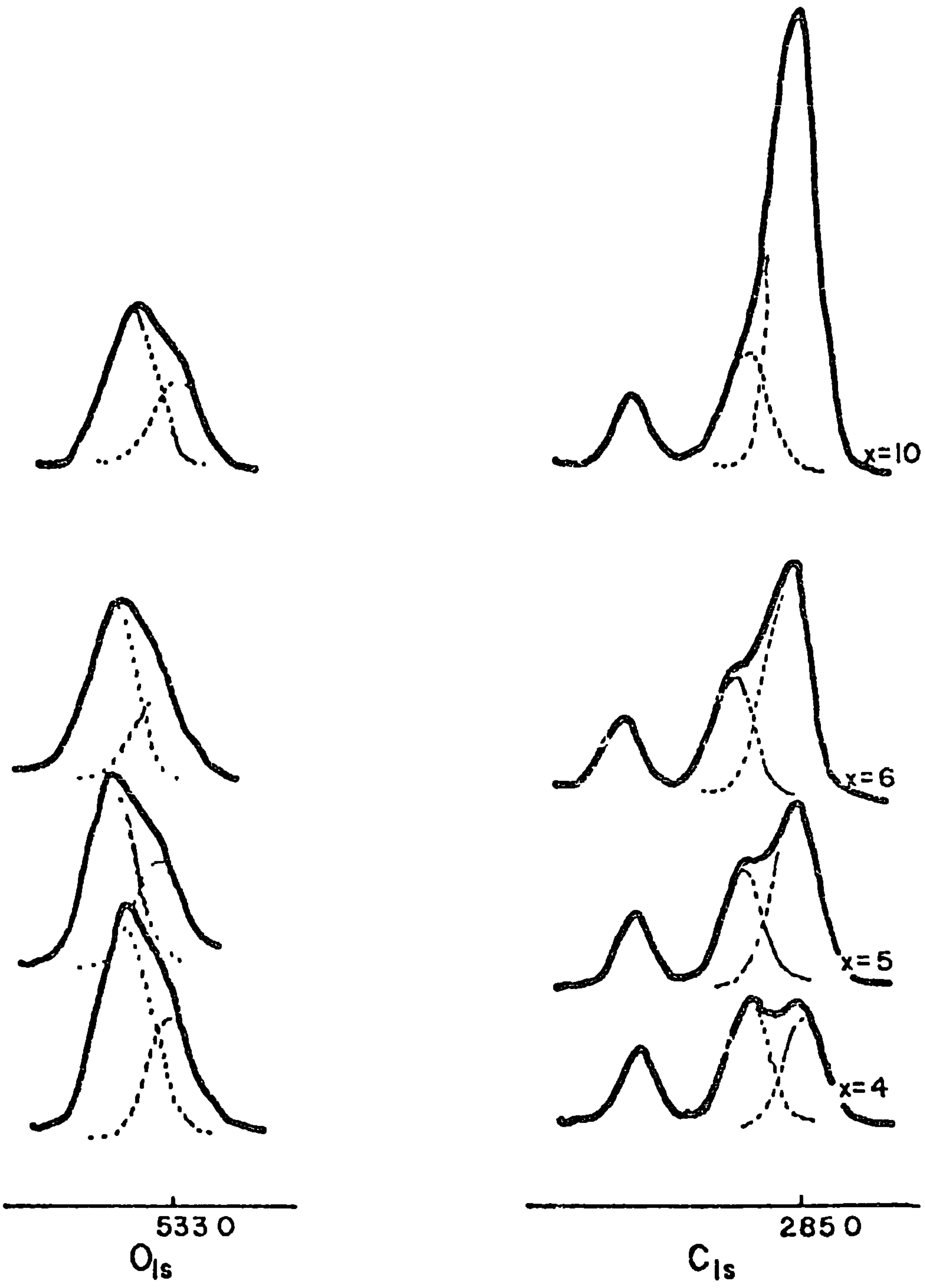
$\left(O\overset{\overset{O}{\|}}{C}O\underline{CH_2}\left(CH_2\right)_n\underline{CH_2}\right)$ and ~ 8.4τ $\left(O\overset{\overset{O}{\|}}{C}OCH_2\left(\underline{CH_2}\right)_nCH_2\right)$, and the aliphatic ether polycarbonates displayed two bands at ~5.7τ $\left(O\overset{\overset{O}{\|}}{C}O\underline{CH_2}\left(CH_2OCH_2\right)_n\underline{CH_2}\right)$ and ~5.3τ $\left(O\overset{\overset{O}{\|}}{C}OCH_2\left(\underline{CH_2}O\underline{CH_2}\right)_nCH_2\right)$, in both systems integrated intensities were appropriate to the assigned structures and no evidence for the presence of ethyl end groups could be detected.

The ESCA spectra of the aliphatic polycarbonates and aliphatic ether polycarbonates, shown in Figures 14 and 15 respectively, provided further confirmation of the assigned structures in that the intensity ratios of the various carbon-1s and oxygen-1s levels in the deconvoluted spectra indicate the expected stoichiometry and the observed shifts are in agreement with those measured in related model systems.[115] This technique also failed to detect any evidence of end groups or possible structural anomolies. The infra-red spectra of these materials are recorded in Appendix C and are in complete agreement with the assigned structures showing no unexpected features.

Having established that the products obtained were high polymers with the anticipated structures, the physical properties of interest of these polymers were examined, the characterising parameter of greatest interest was described in Section 1 of this thesis and the technique used to determine it was differential scanning calorimetry, DSC. Recapping, Tg is a property of an amorphous polymer, marking the transition from glass-like to rubber-like behaviour, which is usually connected with the onset of main chain segmental motion. Amorphous regions of partially crystalline polymers also exhibit characteristic changes associated with a polymer at Tg, the magnitude of the change decreasing with decreasing amorphous content, i.e. Tg is difficult to detect in highly crystalline polymers. The lack of a clear definition of Tg resides in the lack of a clear definition and understanding of glass-like and rubber-like behaviour; however, readily detectable changes do occur at Tg, and the transition does have a close analogy with a



$$-\!\!\left[\mathrm{O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}(CH_2)_x}\right]\!\!-_n$$



<u>Figure 14.</u> The C_{1s} and O_{1s} ESCA spectra of the poly(methylene carbonates).

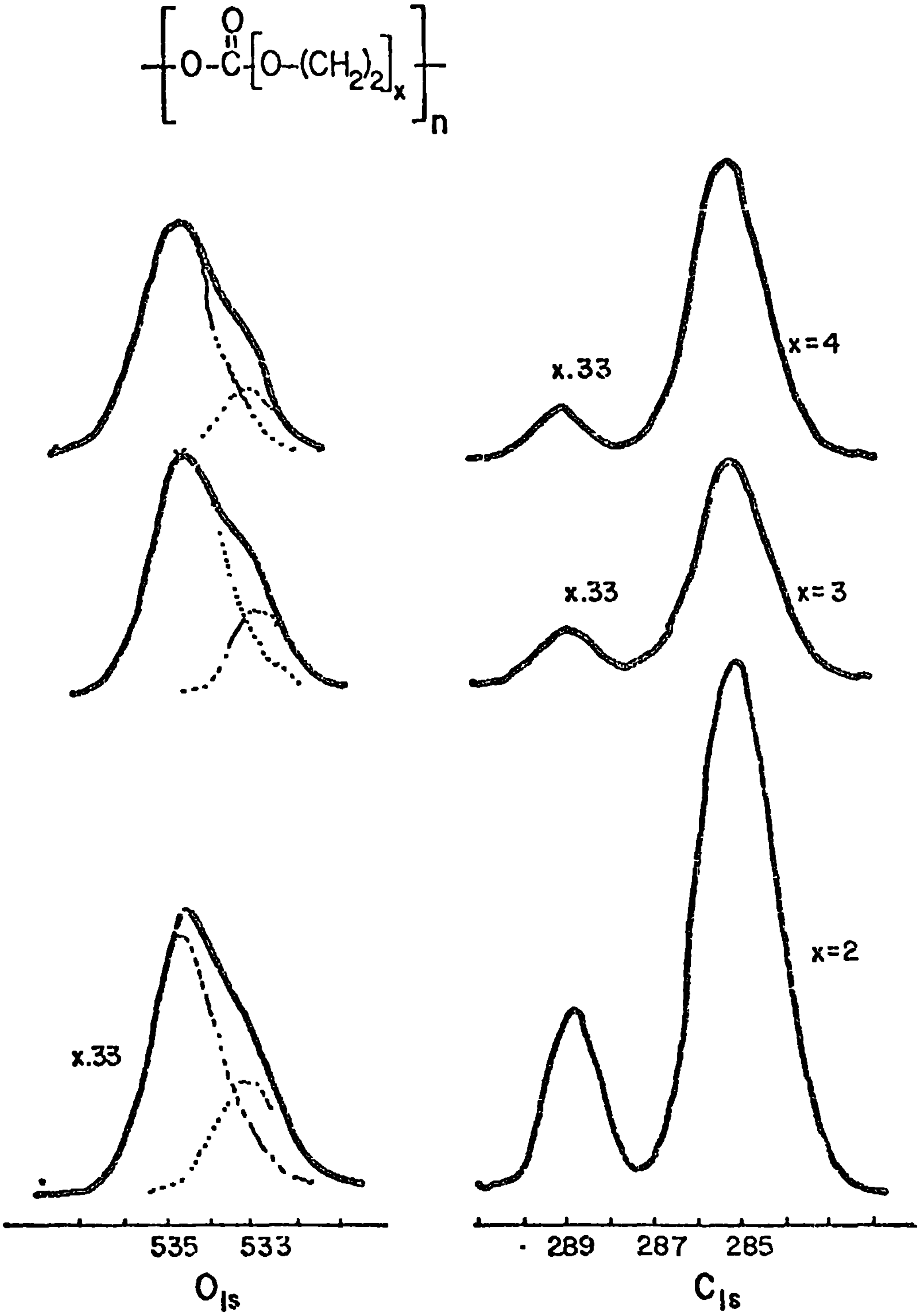


Figure 15. The C_{1s} and O_{1s} ESCA spectra of the poly(ethylene glycol carbonates).

classical thermodynamic second order transition, i.e. a discontinuity in a secondary thermodynamic quantity, for example, the expansion coefficient, heat capacity; and is therefore often referred to as a second order transition.

The specific heat of a polymer, Cp, changes abruptly at Tg, and since the signal from a DSC is proportional to Cp, this form of calorimetry has found ready application in the determination of Tg. Unfortunately differential scanning calorimetry is a dynamic technique and because of the nature of the glass transition it is a strongly rate dependent phenomenon, kinetic effects making the experimental interpretation of DSC curves difficult. The simple consistent but arbitrary treatments, shown in Figure 16, allows the definition of a dynamic glass transition temperature, Tgd, but ignores the dynamic dependence of Tg, Attempts to eliminate heating rate effects have recommended the extrapolation of measured values of Tgd to zero heating rates.[122] More elaborate analysis[123] have shown that the determination of Tg is possible by DSC to a degree of great accuracy independent of tho heating rate used, utilising relatively sophisticated data handling techniques. Very great precision is not required in the context of this work and the method used is a modified approach based on the first of the simple methods shown in Figure 16. The detailed procedure adopted was, ineffect, defined by the sponsors of this work and is used in an attempt to build up a set of Tg data obtained in an experimentally consistent manner and so minimise uncertainties in the values used to construct the Tg/structure correlation discussed in Section 1. A rapid scan of the sample as prepared was first carried out to identify the Tg approximately. The sample was then annealed at ~30-40° above the transition temperature for 10-15mins and then cooled as rapidly as possible (at 320°/min) to 150°K; the object of this procedure being to obtain as large a proportion of the material as possible in the amorphous state. The sample was then heated at 40°/min through the transition

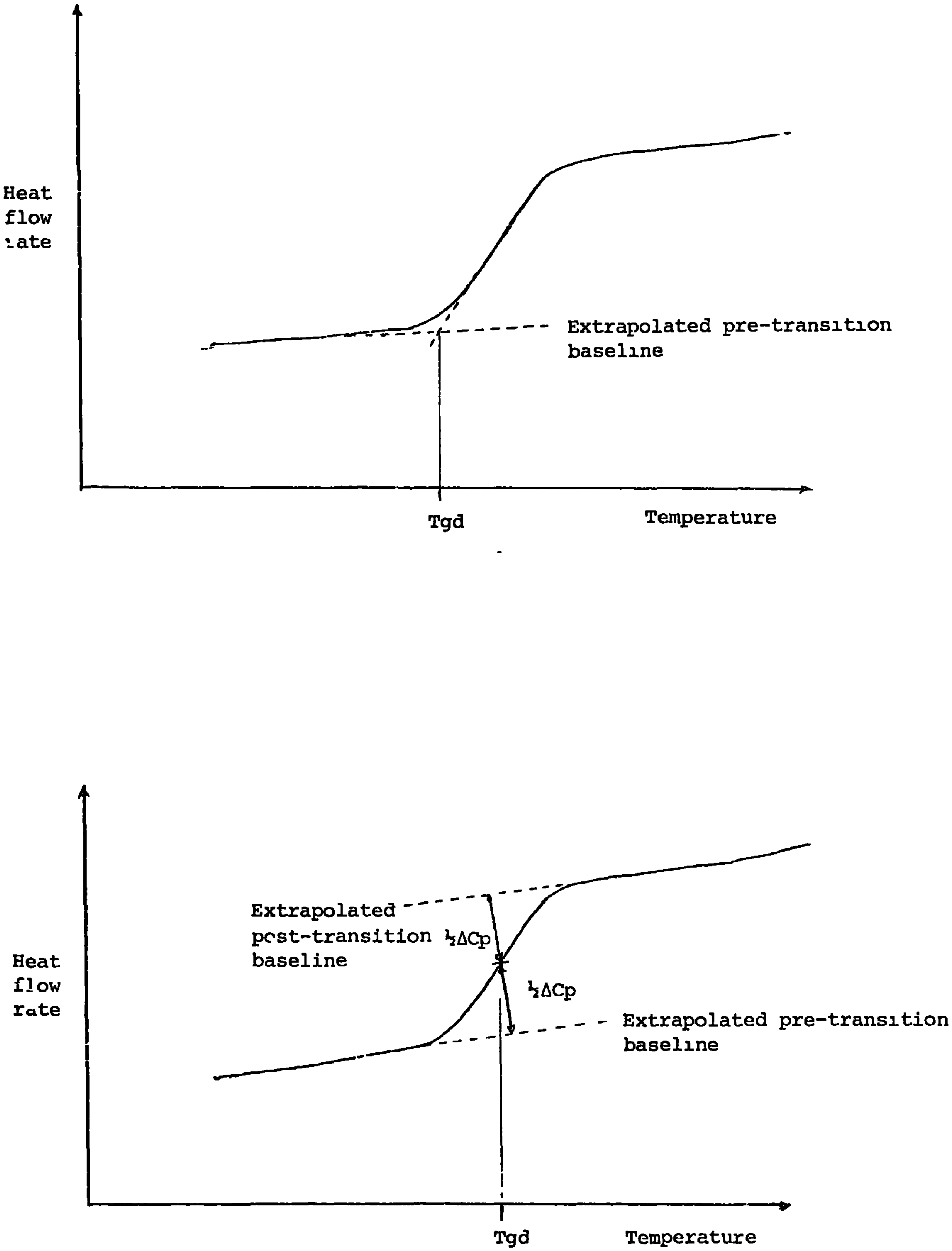


Figure 16. Two simple methods of determining Tg from the experimental DSC data.

region and the whole procedure repeated until a consistent value of Tg was obtained. The results are listed in Table 7 and the values were consistent within the range of ± 1°.

The Tg values for the fluorinated aliphatic polycarbonates were of particular interest because the Tg/structure correlation has lead to theoretical predictions of Tgs of 214°K for poly(hexafluoropentamethylene carbonate) and 233°K for poly(tetrafluorotetramethylene carbonate), if these very low values were realised and if the materials displayed favourable characteristics in other respects they would have been of considerable technological interest. The measured (Table 7) and predicted values are in some disagreement and the differences are outside the expected margins of error for the theory (see Section 1). However, it should be borne in mind that the number of data points used to construct the additive temperature parameters was very limited, the most closely related structure for which a Tg value was available prior to this work being that reported by the Russian workers for poly(octafluorohexamethylene carbonate), namely 232°K on a sample of $\bar{M}n \sim 5000$. Since this was the only data point its accuracy is of considerable importance and the relatively low DP sample may have given an artificially low value. It is therefore of interest to note that the Tg value reported by the Russian group is only a little lower than the value obtained here for a sample with a molecular weight six times greater.

At the time of writing recomputation of the additive temperature parameters in the light of the results reported here has not been undertaken, but clearly the data provided on this set of fluorinated aliphatic polycarbonates must increase the reliability of the derived parameters. Further the inclusion of the six aliphatic and aliphatic ether polycarbonates increases the reliable data base for such computations.

Some general qualitative trends appear to be discernable in the Tg values recorded in Table 7. Thus, for all three sets of polycarbonates increasing separation between carbonate functions is accompanied by lowering of Tg. Another comparison which can be drawn is between polymers which have the carbonate group separated by the same number of atoms in the main chain, i.e. poly(hexafluoropentamethylene carbonate), poly(pentamethylene carbonate) and poly(diethylene glycol carbonate), where the separating moieties are respectively $-CH_2CF_2CF_2CF_2CH_2-$, $-(CH_2)_5-$, and $-CH_2CH_2OCH_2CH_2-$. For this set it is perhaps suprising to find that the highest Tg (261°K) occurs for the polymer with what might intuitatively be expected to be the most flexible sequence of atoms (i.e. the ether), whilst the observation of a higher Tg (241°K) for the fluorinated aliphatic polymer as compared to the hydrocarbon sequence (237°K) is in line with expectations. It should be noted that the majority of the polymers prepared in this work displayed crystalline melting points, and indeed it proved impossible to detect a glass transition for poly(decamethylene carbonate) presumably because of a very high rate of crystallisation for this polymer and a consequently limited proportion of amorphous material.

The above discussion of the results obtained in this work serves to underline the difficulties involved in predicting Tg on the basis of structural repeat unit for regular homopolymers, these difficulties apply to both quantitative and even qualitative estimations, and clearly theory in this difficult area has a long way to go.

The second physical property of interest in this study was the thermal stability of the polymers produced, this data was obtained using thermogravimetry (TG), and was carried out by heating a sample of the prepared polymer in a Stanton Reacroft TG 750 thermobalance at a fixed heating rate of 1°/min from room temperature to 500° in an atmosphere of nitrogen. The data obtained for the three different groups the fluorinated aliphatic, aliphatic and aliphatic ether polycarbonates are shown in Figures 17,18 and

19 respectively.

A report[124] on the nonoxidative degradation of several polyesters, observed that the stability of the polyesters increases if either the acid or diol chain length is increased. This generalisation is clearly reflected in the thermal stabilities of all the polycarbonates prepared, with the exception of poly(tetraethylene glycol carbonate). Another thorough investigation of the overall degradations of some aliphatic polyesters using themogravimetry,[125] has established that all the degradation starts at about 275° by random scissions at the ester linkages, and that differences in degradation behaviour were best explained in terms of secondary reactions which were found to be dependent on the nature of the end groups formed by the initial scission and on the chain length of the acid and diol used to prepare the polymer. This generalisation also appears to hold for the majority of samples in all three classes of polycarbonates prepared in this work, with two exceptions. Figure 17 shows that the TG curve for poly(tetrafluorotetramethylene carbonate) is significantly different in shape and position to those of the other two fluorinated aliphatic polycarbonates, this difference is reproducible and must indicate a different degradative process. Although time has not allowed a detailed study of these degradation processes, it appears that in this case the polymer initially looses $\sim$ 10% of its weight before large scale degradation occurs, with a repeat unit mass of 188 a.m.u. this loss might be either H_2O (18) or HF (20), but why this polymer should differ from the closely related members of this group is difficult to see. The other amomolous TG curve is shown in Figure 19 for poly(tetraethylene glycol carbonate), in discussing this result it should be noted that the onset of weight loss for all three aliphatic ether polycarbonates occurs more gradually but at a significantly lower temperature than for any of the other polymers and that this slightly lower thermal stability may account for the lower DPs obtained in the preparation of this

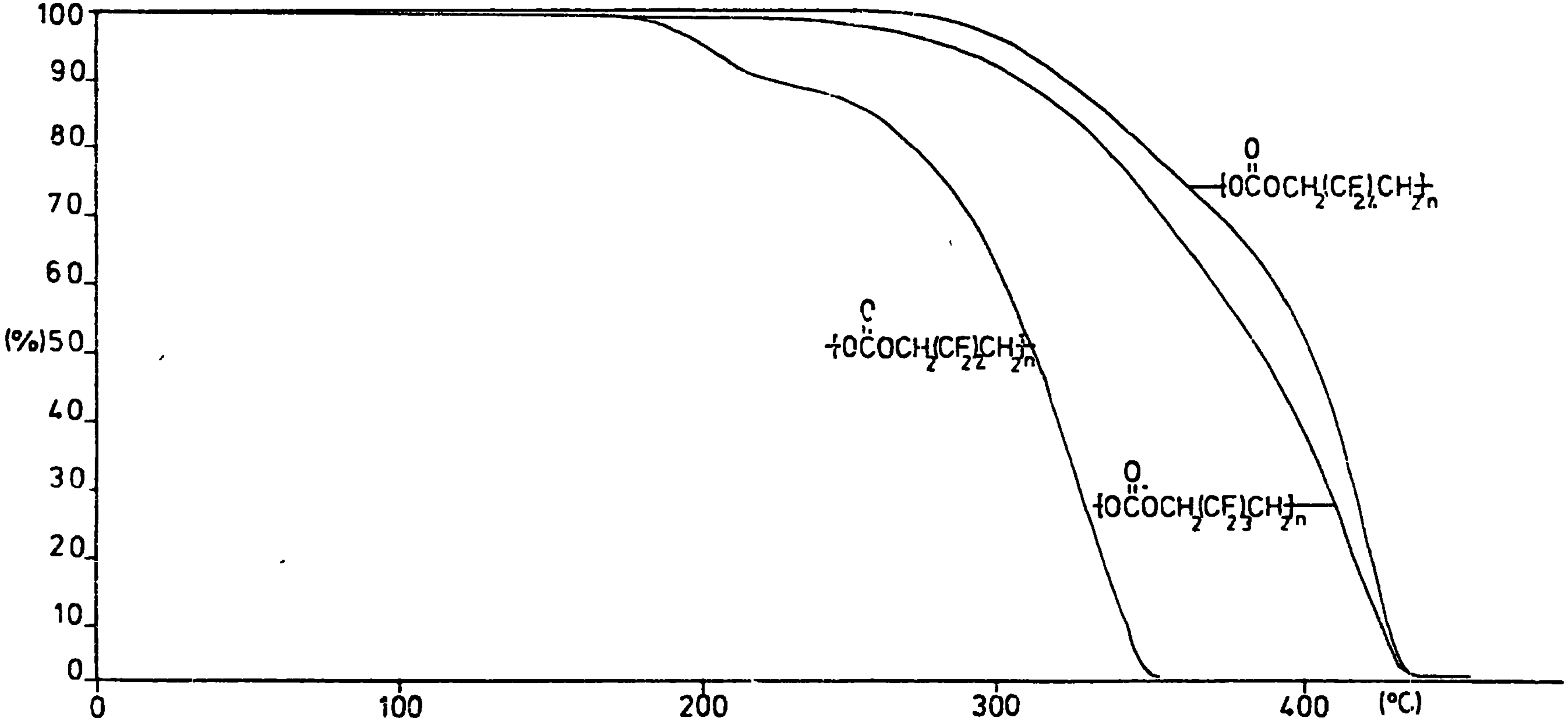


Figure 17. Thermograms of the fluorinated aliphatic polycarbonates.

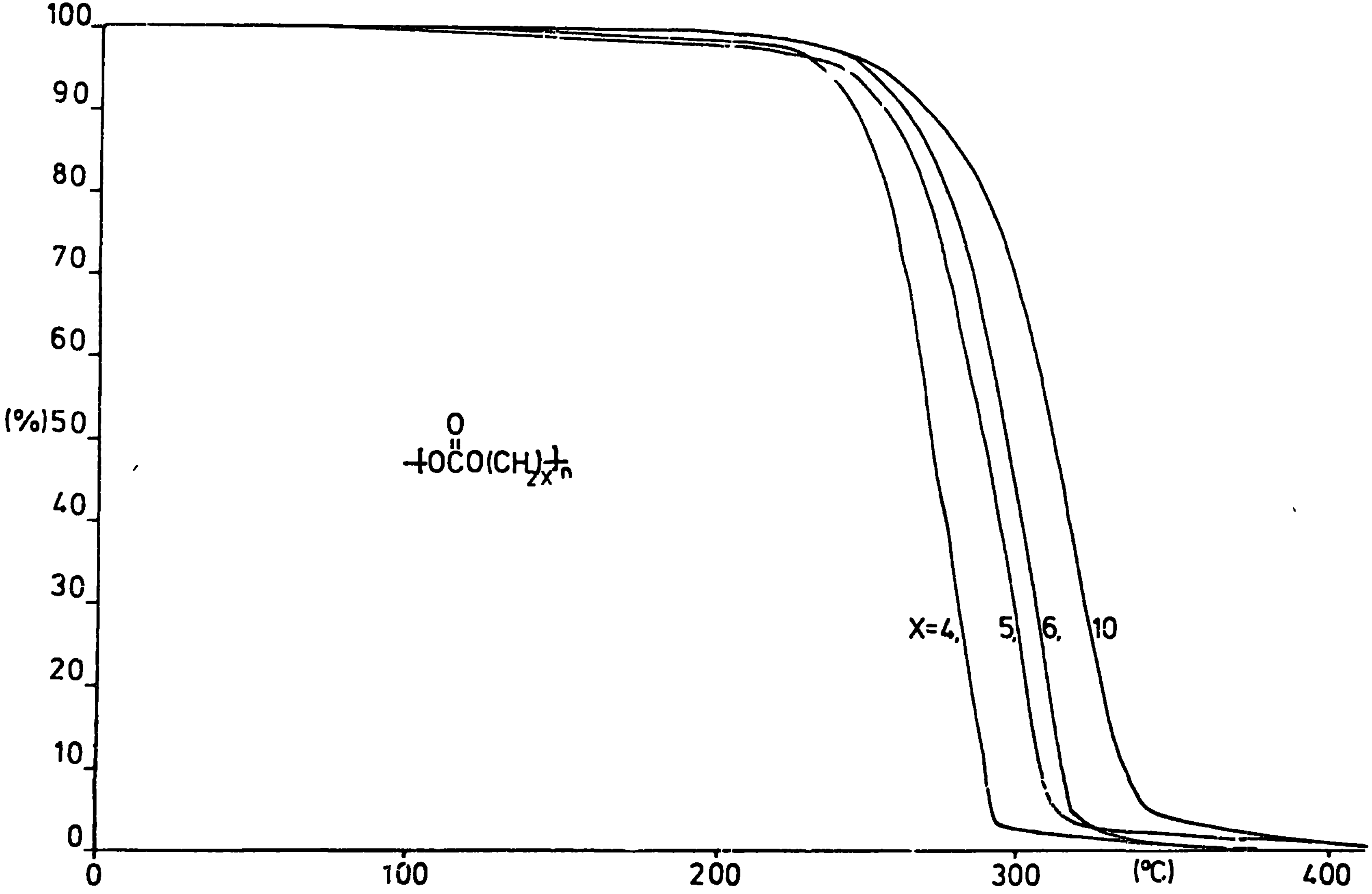


Figure 18. Thermograms of the aliphatic polycarbonates.

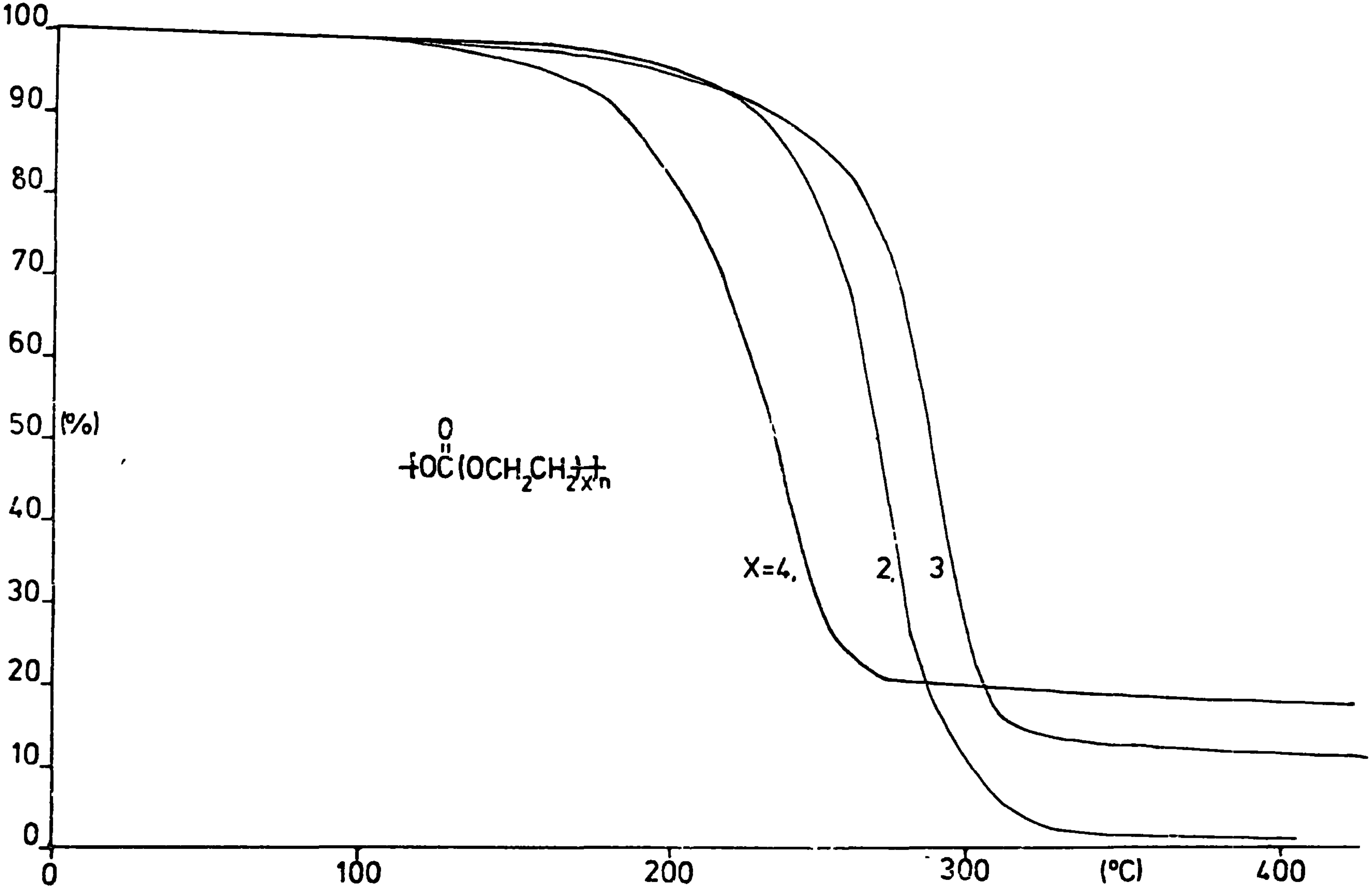


Figure 19. Thermograms of the aliphatic ether polycarbonates.

group of polymers. The significant and reproducible differences between the TG curves for this set of polymers reported in Figure 19 are not easily explained in this area is one which clearly merits further careful study.

Finally, the actual physical appearance and qualitative properties of the polymers prepared merits brief comment. The fluorinated aliphatic polycarbonates were translucent very pale green-brown materials and were fairly tough in-elastic thermoplastics, the aliphatic polycarbonates were tough leathery buff coloured materials, whilst the aliphatic ether polycarbonates were clear light brown gums.

EXPERIMENTAL

4.3 Experimental

All the prepared polymers were dissolved in a solvent, acetone for the fluorocarbon polymers and chloroform for the hydrocarbon polymers, in the polymerisation apparatus from which it was then removed and reprecipitated into excess vigorously stirred non-solvent, chloroform for the fluorocarbon polymers and diethyl ether for the hydrocarbon polymers. The immediately reprecipitated residue was then collected by decanting off the solvent/non-solvent mixture, and heated under reduced pressure (0.1mm Hg, 24hrs) in order to remove any volatile impurities. The residue was then analysed by elemental analysis before viscometric determinations were made in an Ubbelohde viscometer immersed in a water bath thermostated at 25.00° (± 0.01°). Accurately known solutions (~ 1% concentration) of the polymer samples were made up in a solvent, 1,4-dioxane for the fluorocarbon polymers and chloroform for the hydrocarbon polymers, and the time of flow through the viscometer determined repeatedly until four identical consecutive values were obtained (± 0.1 secs, stopwatch accuracy), the solution was then diluted successively three times by a half, to allow time of flow determinations at four different concentrations, enabling the intrinsic viscosity at infinite dilution to be obtained by extrapolation.

Molecular weight determinations were performed on a Perkin Elmer 115 vapour phase osmometer, operating at 40° with methylethylketone as the solvent for the fluorocarbon polymers and at 36° with chloroform as the solvent for the hydrocarbon polymers. Benzil was used as the calibrant for the technique, all molecular weight determinations being extrapolated to infinite dilution for the reported results (Table 7, discussion).

Differential scanning calorimetry measurements were made using a Perkin Elmer DSC2 equipped with the sub-ambient facility enabling scans to be made generally from 150°K to 400°K at a heating rate of 40°/min, cooling being performed at 320°/min (see discussion). Calibration of the instrument in the temperature range of interest was carried out using pure cyclohexane melt (186°K) and crystallisation (279°K) transitions. All polymer samples were heated to ~ 30-40° above the transition of interest and annealed there for 10-15 mins, cooling to 150°K then followed at 320°/min.

Thermogravimetry (TG) was performed on a Stanton Redcroft TG 750 apparatus at a heating rate of 1°/min in an atmosphere of nitrogen.

Appendices.

Appendix A:

Apparatus, instruments and techniques.

Vacuum system.

This consisted of a conventional vacuum system incorporating a rotary oil pump and mercury diffusion pump, and was used for degassing samples and 'vacuum distillations' requiring pressures of the order of 10^{-3}mm.Hg.

Mass spectra: - see Appendix B.

Infra-red spectra: - see Appendix C.

Nuclear magnetic resonance spectra.

These were recorded either with a Bruker Spectrospin HX 90E high resolution n.m.r. spectrometer (operating at 84.67 MHz for ^{19}F and 90.00 MHz for ^{1}H spectra), or a Varian A56/60 spectrometer (operating at 56.4 MHz for ^{19}F and 60.0 MHz for ^{1}H spectra at an operation temperature of 40°); unless otherwise stated ^{19}F chemical shifts are in p.p.m. from external fluorotrichloromethane (positive upfield) and ^{1}H chemical shifts are measured on the τ scale relative to external tetramethylsilane.

Carbon and hydrogen analyses, were carried out using a Perkin Elmer 240 CHN analyser.

Combined g.l.c./mass spectra, were run on a V.G. Micromass 12B coupled to a Pye 104 gas chromatograph, using a column as specified in the analytical g.l.c. section later.

Analytical gas-liquid chromatography (g.l.c.), were carried out using a Pye 104 gas chromatograph with nitrogen as the carrier gas and a flame ionisation detector, the stationary phase column 'O' consisted of silicone gum rubber on crushed firebrick (1.52m. x 6mm diam.).

Molecular weights, were obtained with a Perkin Elmer Model 115 molecular weight apparatus utilizing the vapour pressure (isopiestic) method of determining the number average molecular weight ($\bar{M}_n$) of a solute in a solution. Measurements were made in dimethylformamide, chloroform or methylethylketone, operating at 57°, 36° and 40° respectively, solutions of benzil were used as calibrants.

Differential scanning calorimetry, was performed using a Perkin Elmer DSC 2 differential scanning calorimeter with the liquid nitrogen cooled sub-ambient temperature accessory fitted, to enable scans from 140°K to 400°K at a heating rate of 40°/min to be made on samples sealed in aluminium volatile sample pans, the output being recorded on a X-Y recorder.

Viscometry determinations were made using a Ubbelohde viscometer immersed in a Thomson and Mercer thermostated water bath at 25.00 ± 0.01 . The time of flow of an accurately known concentration of polymer solution (~1% solution) through the viscometer was determined until 4 consecutive results were obtained (± 0.1 secs, stopwatch accuracy). Successive dilutions of the polymer solution (x 0.5) were carried out in the viscometer.

ESCA spectra, were recorded on an A.E.I. ES100 spectrometer using Mg $K_{\alpha 1,2}$ radiation. Samples were deposited as thin films on gold, care being taken to prevent contamination of the surface. Electrons expelled from the sample enter the analyser region consisting of a two element retarding lens and a 10 in. mean diameter hemispherical analyser. A Mullard Channeltron electron multiplier is used as a detector, the output being fed to Nuclear Enterprises counting electronics and the spectra being plotted on a X-Y recorder. Overlapping peaks were deconvoluted by using a Du Pont 310 curve resolver, and line shapes derived from previous studies of monomeric systems.

Appendix B.

Mass Spectra.

Mass spectra were recorded with an A. E. I. MS9 spectrometer at an ionising beam energy of 70eV. The important and typical ions are tabulated in the form:

mass number (intensity as % of base peak, assignment, possible origin of the ion). e.g. 69(60%,CF_3).

charges on ions are omitted and the base peak is designated B.

2,2,3,3-Tetrafluoropropxycarbonyloxyethane.

204(<1%,P), 177(40%,$C_4H_5F_4O_3$, P-C_2H_3), 159(15%,$C_4H_3F_4O_2$, P-C_2H_5O or $C_5H_7F_4O$), 145(7%,$C_4H_5F_4O$), 115(25%,$C_3H_3F_4$), 112(17%), 95(10%,$C_3H_5F_2O$), 93(9%), 91(7%,$C_3H_7O_3$), 82(25%,$C_2H_4F_2O$), 65(15%), 64(12%,$C_2H_2F_2$), 63(7%, CH_3O_3), 59(17%,C_3H_7O), 51(67%,CHF_2), 45(62%,CHO_2,C_2H_5O), 44(40%,CO_2), 31(100%,CH_3O,B), 29(40%), 28(25%), 27(30%),

Bis(methoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.

328(<1%,P), 298(10%,$C_7H_4F_6O_6$,P-C_2H_6), 254(80%,$C_6H_4F_6O_4$), 174(15%), 153(5%), 125(5%), 113(10%), 100(11%,C_2F_4), 95(15%), 91(12%,$C_3H_7O_3$), 89(7%,$C_3H_5O_3$), 77(5%,$C_2H_5O_3$), 76(7%,$C_2H_4O_3$), 69(7%), 64(15%,$C_2H_2F_2$), 59(100%,$C_2H_3O_2$,B), 45(95%,C_2H_5O or CHO_2). 44(40%,CO_2), 36(12%), 31(10%), 29(17%,C_2H_5), 28(20%), 18(17%,H_2O), 15(17%,CH_3).

Bis(ethoxycarbonyloxy)-2,2,3,3,4,4 hexafluoropentamethylene.

356(<1%,P), 329(32%,$C_9H_{11}F_6O_6$,P-C_2H_3), 268(8%,$C_8H_{10}F_6O_3$,P-$C_3H_4O_3$), 254(20%,$C_7H_8F_6O_3$,P-$C_4H_6O_3$), 239(27%,$C_6H_4F_6O_3$,P-$C_5H_9O_3$), 207(20%), 196 (27%,$C_5H_5F_6O$), 176(15%,$C_5H_2F_6$), 156(7%), 143(24%), 100(8%,C_2F_4), 95(17%, $C_2H_4FO_3$), 64(20%,$C_2H_2F_2$), 63(17%,CH_3O_3), 61(75%), 59(73%,$C_2H_3O_2$), 45(75%, C_2H_5O), 44(27%,CO_2), 31(49%,CH_3O or CF), 30(5%,CH_2O), 29(100%,C_2H_5,B), 28(29%,C_2H_4), 27(15%,C_2H_3).

Bis(phenoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.

452(<1%), 315(8%,$C_{12}H_9F_6O_3$,P-$C_7H_5O_3$), 271(4%,$C_{11}H_9F_6O$), 210(1%), 176(20%,$C_5H_2F_6$), 169(55%), 142(3%), 121(10%,$C_7H_5O_2$), 107(7%,C_7H_7O), 95(10%,C_6H_8O), 94(47%,C_6H_7O), 93(12%,C_6H_6O), 78(10%,C_6H_6), 77(100%,C_6H_5,B), 66(7%), 65(18%), 64(7%), 51(8%,CHF), 44(19%,CO_2), 39(13%), 31(10%), 28(65%,C_2H_4).

2,2,2-Trifluoroethoxycarbonyl chloride.

162(1%,P), 127(57%,$C_3H_2F_3O_2$,P-Cl), 101(4%), 99(10%,$C_2H_2F_3O$,P-CClO), 95(4%,$C_2H_2{}^{37}ClO_2$,P-CF_3), 93(14%,$C_2H_2ClO_2$,P-CF_3), 83(100%,$C_2H_2F_3$,B), 81(1%,$C^{37}ClO_2$,P-$C_2H_2F_3$), 79(6%,$CClO_2$,P-$C_2H_2F_3$), 69(14%,CF_3), 65(28%, $C^{37}ClO$), 63(83%,CClO), 51(4%,CHF_2), 44(16%,CO_2), 35(3%,Cl), 33(41%,CH_2F), 32(3%,CHF), 31(10%,CF), 30(9%,CH_2O), 29(14%,CHO), 28(16%,CO).

Bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.

464(<1%,P), 462(2%,$C_{11}H_6F_{12}O_6$,P-2H), 444(2%,$C_{11}H_7F_{11}O_6$,P-HF), 433(6%, $C_{10}H_8F_{11}O_6$), 390(11%,$C_9H_6F_{12}O_3$), 321(9%,$C_8H_6F_9O_3$), 302(1%,$C_7H_4F_6O_6$), 257(2%,$C_6H_4F_7O_3$,P-$C_5H_4F_5O_3$), 239(1%,$C_6H_5F_6O_3$), 227(3%,$C_5H_5F_6O_3$), 207(6%, $C_5H_4F_5O_3$), 193(6%,$C_4H_2F_5O_3$), 157(10%,$C_4H_4F_3O_3$), 127(62%,$C_3H_2F_3O_2$), 123(25%), 100(7%,C_2F_4), 95(9%,$C_2H_4FO_3$), 83(100%,$C_2H_2F_3$,B), 69(6%,CF_3), 64(12%, $C_2H_2F_2$), 63(5%,CH_3O_3), 61(6%), 51(5%,CHF_2), 44(2%,CO_2), 33(16%,CH_2F), 31(24%,CF), 30(2%,CH_2O), 29(9%,CHO), 28(5%,CO).

2,2,2-Trifluoroethoxycarbonyloxy-2,2,2-trifluoroethane.

226(<1%,P), 207(17%,$C_5H_4F_5O_3$,P-F), 206(4%,$C_5H_3F_5O_3$,P-HF), 162(25%, $C_3H_2F_4O_3$,P-$C_2H_2F_2$), 157(33%,$C_4H_4F_3O_3$,P-CF_3), 128(4%,$C_3H_3F_3O_2$,P-$C_2H_1F_3O$), 127(86%,$C_3H_2F_3O_2$,P-$C_2H_2F_3O$), 125(11%), 113(46%,$C_3H_4F_3O$), 80(13%), 84(12%, $C_2H_3F_3$), 83(100%,$C_2H_2F_3$,B), 81(7%), 69(30%,CF_3), 64(22%,$C_2H_2F_2$), 63(14%, CH_3O_3), 61(16%), 58(12%), 57(7%), 55(4%), 51(31%,CHF_2), 50(6%,CF_2), 45(13%,CHO_2), 44(100%,CO_2,B), 43(8%), 41(9%), 39(5%), 36(7%), 33(93%, CH_2F), 32(11%,CHF), 31(38%,CF), 29(40%), 28(95%), 27(13%), 26(8%).

Bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3-tetrafluorotetramethylene.

414(<1%,P), 412(1%,$C_{10}H_6F_{10}O_6$,P-2H), 394(0.5%,$C_{10}H_7F_9O_6$,P-HF), 383(3%,$C_9H_8F_9O_6$,P-CF), 340(3%,$C_8H_6F_{10}O_3$), 270(5%,$C_7H_5F_7O_3$,P-$C_3H_2F_3O_3$), 227(4%,$C_5H_5F_6O_3$), 207(5%,$C_5H_4F_5O_3$), 193(3%,$C_4H_2F_5O_3$), 157(4%,$C_4H_4F_3O_3$), 143(2%,$C_3H_2F_3O_3$), 127(38%,$C_3H_2F_3O_2$), 113(26%,C_3HF_4), 95(6%,$C_2H_4FO_3$), 83(100%,$C_2H_2F_3$,B), 77(6%), 69(8%,CF_3), 65(21%,$C_2H_3F_3$), 64(4%,$C_2H_2F_2$), 62(5%), 51(6%,CHF_2), 45(4%,CHO_2), 44(3%,CO_2), 33(17%,CH_2F), 31(8%,CF), 30(4%,CH_2O), 29(12%,CHO), 28(4%,CO).

Bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3,4,4,5,5-octafluorohexamethylene.

514(<1%,P), 512(0.2%,$C_{12}H_6F_{14}O_6$,P-2H), 494(5%,$C_{12}H_7F_{13}O_6$,P-HF), 483(2%,$C_{11}H_8F_{13}O_6$,P-CF), 440(5%,$C_{10}H_6F_{14}O_3$), 370(5%,$C_9H_5F_{11}O_3$), 289(1%, $C_7H_5F_8O_3$), 227(2%,$C_5H_5F_6O_3$), 207(3%,$C_5H_4F_5O_3$), 193(1.5%,$C_4H_2F_5O_3$), 163(1%), 157(4%,$C_4H_4F_3O_3$), 143(1.5%,$C_3H_2F_3O_3$), 131(7%), 127(39%,$C_3H_2F_3O_2$), 114(2.5%, $C_3H_2F_4$), 113(35%,C_3HF_4), 100(4%,$C_2H_3F_3O$), 95(10%,$C_2H_4FO_3$), 84(3%,$C_2H_3F_3$), 83(100%,$C_2H_2F_3$,B), 69(9%,CF_3), 65(14%,$C_2H_2F_2$), 51(5%,CHF_2), 45(3%,CHO_2), 44(2%,CO_2), 33(13%,CH_2F), 31(6%,CF), 30(4%,CH_2O), 29(11%,CHO), 28(2%,CO).

Bis(ethoxycarbonyloxy)-ethylene.

206(<1%,P), 179(<1%,$C_6H_9O_6$,P-C_2H_5), 119(1%,$C_5H_{11}O_3$,P-$C_3H_3O_3$), 118(1%, $C_5H_{10}O_3$), 117(1%,$C_5H_9O_3$), 104(1%,$C_4H_8O_3$,P-$C_4H_6O_3$), 91(52%,$C_3H_7O_3$), 89(5%, $C_3H_5O_3$), 88(8%), 76(5%), 72(5%,$C_3H_5O_2$), 64(5%), 63(7%), 59(10%,C_3H_7O), 58(2%), 49(2%), 47(2%), 46(5%), 45(36%,C_2H_4O or CO_2), 43(100%,C_2H_3O), 42(6%), 31(45%,CH_3O), 30(9%,CH_2O), 29(45%,C_2H_5), 28(18%,C_2H_4), 27(30%, C_2H_3), 26(11%,C_2H_2).

Bis(ethoxycarbonyloxy)-1-methyl-ethylene.

220(<1%,P), 207(<1%,$C_8H_{15}O_6$,P-CH), 191(<1%,$C_7H_{11}O_6$,P-C_2H_5), 130(<1%, $C_6H_{10}O_3$,P-$C_3H_5O_3$), 118(<1%,$C_5H_{10}O_3$,P-$C_4H_7O_3$), 110(2%), 108(2%), 102(2%, $C_4H_6O_3$,P-$C_5H_{10}O_3$), 91(7%,$C_3H_7O_3$), 87(3%), 74(4%,$C_3H_6O_2$), 73(1%, $C_3H_5O_2$), 64(10%,CH_4O_3), 63(4%,CH_3O_3), 59(7%,C_3H_7O or $C_2H_3O_2$), 58(11%,C_3H_6O or $C_2H_2O_2$), 57(11%), 45(27%,CHO_2 or C_2H_5O), 44(100%, CO_2,B), 43(25%,C_2H_3O), 31(38%,

CH_3O), 29(40%, C_2H_5), 28(35%, C_2H_4), 27(31%, C_2H_3), 26(12%, C_2H_2).

Bis(ethoxycarbonyloxy)-trimethylene.

220(<1%, P), 193(0.5%, $C_7H_{13}O_6$, $P-C_2H_3$), 181(1%), 169(1%, $C_5H_9O_6$, $P-C_4H_7$), 139(1%), 131(14%, $C_6H_{11}O_3$, $P-C_3H_5O_3$), 130(17%, $C_6H_{10}O_3$), 119(5%, $C_5H_{11}O_3$), 110(2%), 108(2%), 103(30%, $C_4H_7O_3$), 91(50%, $C_3H_7O_3$), 86(14%), 75(4%, C_4H_9O or $C_3H_7O_2$), 71(5%, C_3H_5O), 63(40%, CH_3O_3), 59(53%, C_3H_7O), 58(75%, $C_2H_2O_2$ or C_3H_6O), 57(30%, C_3H_5O), 45(50%, CHO_2 or C_2H_5O), 44(80%, CO_2), 41(25%, C_3H_5), 31(80%, CH_3O), 29(100%, C_2H_5, B).

Bis(ethoxycarbonyloxy)-tetramethylene.

234(<1%, P), 219(1%, $C_9H_{15}O_6$, $P-C\ H_3$), 181(1%), 155(6%, $C_7H_{13}O_3$, $P-C_3H_5O_3$), 131(<1%, $C_6H_{11}O_3$, $P-C_4H_7O_3$), 117(1%, $C_5H_9O_3$), 110(2%), 108(2%), 94(6%), 91(4%, $C_3H_7O_3$), 72(17%, C_4H_8O), 71(15%, C_4H_7O), 64(10%, CH_4O_3), 45(13%, CHO_2 or C_2H_5O), 44(100%, CO_2, B), 42(42%, C_3H_6), 41(21%, C_3H_5), 31(24%, CH_3O), 29(25%, C_2H_5), 28(20%, C_2H_4), 27(22%, C_2H_3).

Bis(ethoxycarbonyloxy)-pentamethylene.

248(<1%, P), 221(1%, $C_9H_{17}O_6$, $P-C_2H_3$), 158(6%, $C_8H_{15}O_3$, $P-C_3H_5O_3$), 146(2%, $C_7H_{14}O_3$, $P-C_4H_7O_3$), 131(4%, $C_6H_{11}O_3$, $P-C_5H_9O_3$), 119(4%, $C_5H_{11}O_3$, $P-C_6H_9O_3$), 100(5%, $C_6H_{12}O$), 91(41%, $C_3H_7O_3$), 85(40%, C_5H_9O), 69(95%, C_3H_7O or C_5H_9), 68(100%, C_5H_8, B), 67(37%, C_5H_7), 63(40%, CH_3O_3), 58(25%, $C_2H_2O_2$), 57(17%, C_4H_9), 56(27%, C_4H_8), 45(30%, C_2H_5O or CHO_2), 44(75%, CO_2), 41(52%, C_3H_5).

Bis(ethoxycarbonyloxy)-hexamethylene.

262(<1%, P), 186(2%), 128(1%, $C_7H_{12}O_2$), 110(2%), 100(2%, $C_6H_{12}O$), 91(13%, $C_3H_7O_3$), 88(5%, $C_3H_4O_3$), 85(4%), 82(16%, C_6H_{10}), 81(0.5%, C_6H_9), 67(24%, C_5H_7), 59(18%, C_3H_7O), 55(14%, C_4H_7), 54(16%, C_4H_6), 46(10%), 45(34%, CHO_2 or C_2H_5O), 44(100%, CO_2, B), 43(17%, C_3H_7), 42(12%, C_3H_6), 41(21%, C_3H_5), 39(12%), 38(12%), 36(34%), 35(6%), 31(65%, CH_3O), 29(43%, C_2H_5 or CHO), 28(34%, C_2H_4), 27(35%, C_2H_3), 26(13%, C_2H_2).

Bis(ethoxycarbonyloxy)-decamethylene.

318(<1%, P), 201(<1%, $C_{11}H_{21}O_3$, $P-C_5H_9O_3$), 184(<1%, $C_{11}H_{20}O_2$), 156(<1%, $C_{10}H_{20}O$), 138(3%, $C_{10}H_{18}$), 124(<1%, C_9H_{16}), 117(1%, $C_5H_9O_3$), 110(3%, C_8H_{14}), 109(5%,C_8H_{13}), 96(8%,C_7H_{12}), 95(7%,C_7H_{11}), 91(8%,C_3H_7O), 83(5%,C_6H_{11}), 82(10%,C_6H_{10}), 81(8%), 69(8%,C_3H_6O or C_5H_9), 68(15%,C_5H_8), 67(12%,C_5H_7), 66(5%), 64(8%), 63(7%,CH_3O_3), 59(8%,C_3H_7O), 55(20%,C_4H_7), 54(12%,C_4H_6), 45(25%, CHO_2 or C_2H_5O), 44(100%,CO_2,B), 31(40%,CH_3O), 29(30%,C_2H_5).

Bis(ethoxycarbonyloxy)-di(oxyethylene).

250(<1%,P), 207(<1%,$C_8H_{15}O_6$,P-C_2H_3), 160(1%,$C_7H_{13}O_4$ or $C_6H_8O_5$), 147(2%,$C_6H_{11}O_4$,P-$C_3H_5O_3$), 132(1%,$C_5H_8O_4$,P-$C_5H_{10}O_3$), 117(30%,$C_5H_9O_3$,P-$C_5H_9O_4$), 110(3%), 108(3%,$C_4H_{12}O_3$), 91(7%,$C_3H_7O_3$), 89(40%,$C_4H_9O_2$), 88(12%,$C_4H_8O_2$), 73(8%,C_4H_9O), 72(8%,C_4H_8O), 70(5%,C_4H_6O), 64(17%,CH_4O_3), 59(12%,C_3H_7O or $C_2H_3O_2$), 58(8%,C_3H_6O or $C_2H_2O_2$), 46(9%,C_2H_6O), 45(63%,CHO_2 or C_2H_5O), 44(100%,CO_2,B), 43(20%,C_2H_3O), 40(13%), 31(53%,CH_3O), 29(60%,C_2H_5), 28(47%, C_2H_4), 27(35%,C_2H_3), 26(15%,C_2H_2).

Bis(ethoxycarbonyloxy)-tri(oxyethylene).

294(<1%,P), 266(<1%, $C_{10}H_{18}O_8$,P-C_2H_4), 221(<1%,$C_9H_{17}O_6$,P-$C_3H_3O_3$), 207(<1%,$C_9H_{19}O_5$), 191(<1%,$C_8H_{15}O_5$), 150(1%,$C_6H_{14}O_4$), 131(2%,$C_5H_9O_4$), 118(2%, $C_5H_{10}O_3$), 100(3%), 91(47%,$C_3H_7O_3$), 75(3%,C_4H_9O or $C_3H_7O_2$), 68(8%), 63(20%, CH_3O_3), 59(7%,C_3H_7O), 45(100%,CHO_2 or C_2H_5O,B), 44(35%,CO_2), 31(75%,CH_3O), 29(100%,C_2H_5,B), 28(23%,C_2H_4), 27(33%,C_2H_3), 26(8%,C_2H_2).

Bis(ethoxycarbonyloxy)-tetra(oxyethylene).

338(<1%,P), 210(3%), 195(<1%,$C_8H_{19}O_5$), 149(3%,$C_6H_{13}O_4$), 119(10%, $C_5H_{11}O_3$), 91(40%,$C_3H_7O_3$, 63(20%,CH_3O_3), 59(7%,C_3H_7O), 56(10%), 45(100%, CHO_2 or C_2H_5O,B), 44(30%,CO_2), 41(13%), 31(70%,CH_3O), 29(90%,C_2H_5), 28(30%,C_2H_4), 27(32%,C_2H_3).

Appendix C.

Infra-red spectra.

Infra-red spectra were recorded on a Perkin Elmer 457 grating infra-red spectrophotometer using KBr cells as a thin contact film, except for spectrum number 21 which was recorded as a KBr disc.

Infra-red spectrum No.	Compound (IUPAC systematic name).
1	2,2,3,3-Tetrafluoropropoxycarbonyloxyethane.
2	Bis(methoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.
3	Bis(ethoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.
4	Bis(phenoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.
5	Polymerisation residue from bis(phenoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.
6	2,2,2-Trifluoroethoxycarbonyl chloride.
7	Bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentamethylene.
8	2,2,2-Trifluoroethoxycarbonyloxy-2,2,2-trifluoroethane.
9	Bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3-tetrafluorotetramethylene.
10	Bis(2,2,2-trifluoroethoxycarbonyloxy)-2,2,3,3,4,4,5,5-octafluorohexamethylene.
11	Bis(ethoxycarbonyloxy)-ethylene.
12	Bis(ethoxycarbonyloxy)-1-methyl-ethylene.
13	Bis(ethoxycarbonyloxy)-trimethylene.
14	Bis(ethoxycarbonyloxy)-tetramethylene.
15	Bis(ethoxycarbonyloxy)-pentamethylene.
16	Bis(ethoxycarbonyloxy)-hexamethylene.
17	Bis(ethoxycarbonyloxy)-decamethylene.
18	Bis(ethoxycarbonyloxy)-di(oxyethylene).
19	Bis(ethoxycarbonyloxy)-tri(oxyethylene).

20 Bis(ethoxycarbonyloxy)-tetra(oxyethylene).

21 Poly(oxycarbonyloxy-2,2,3,3,4,4-hexafluoropentamethylene).

22 Poly(oxycarbonyloxy-2,2,3,3-tetrafluorotetramethylene).

23 Poly(oxycarbonyloxy-2,2,3,3,4,4,5,5-octafluorohexamethylene).

24 Poly(oxycarbonyloxytetramethylene).

25 Poly(oxycarbonyloxypentamethylene).

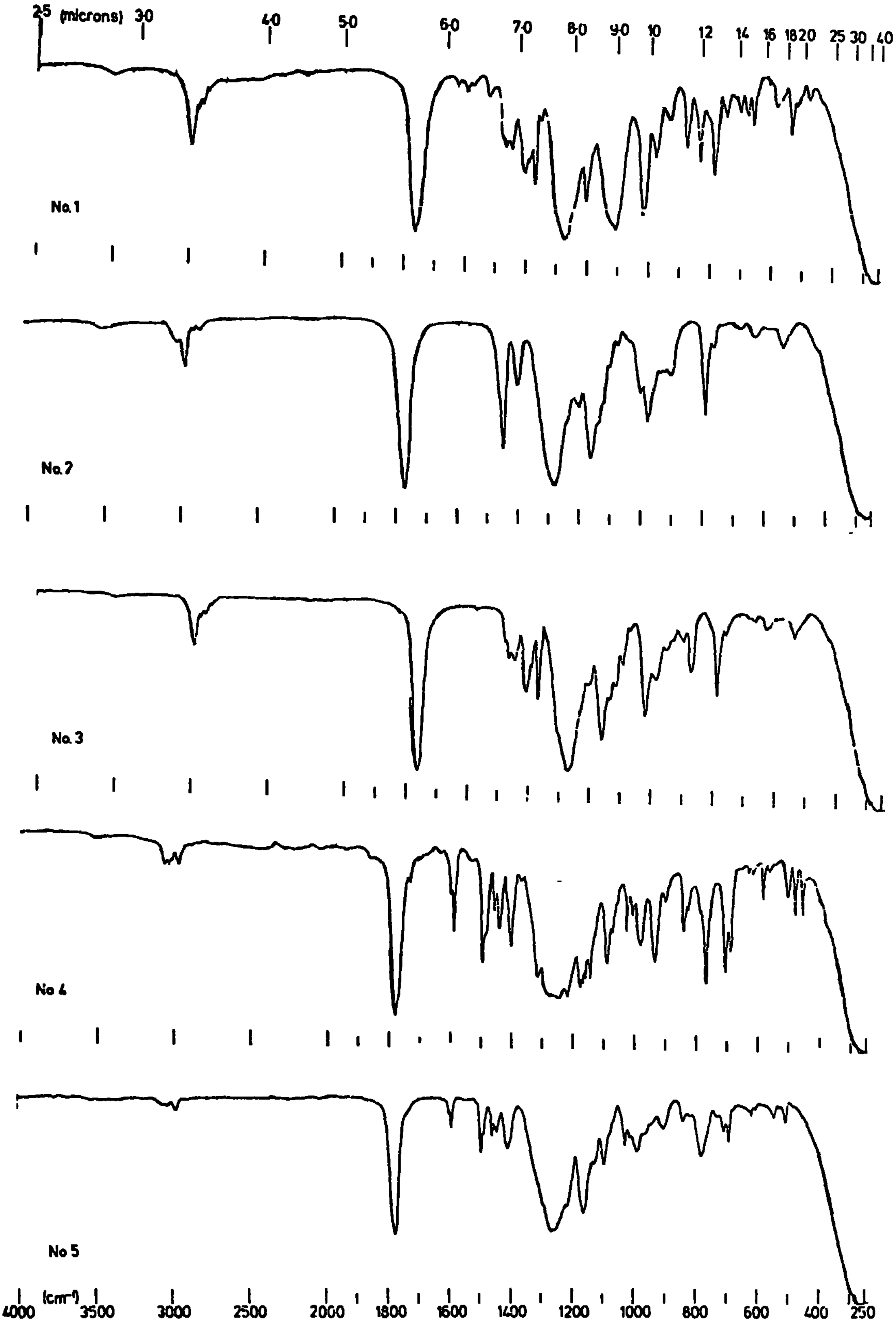
26 Poly(oxycarbonyloxyhexamethylene).

27 Poly(oxycarbonyloxydecamethylene).

28 Poly(di(oxyethylene)oxycarbonyl).

29 Poly(tri(oxyethylene)oxycarbonyl).

30 Poly(tetra(oxyethylene)oxycarbonyl).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No. 2
No. 3
No 4
No 5
(cm⁻¹)
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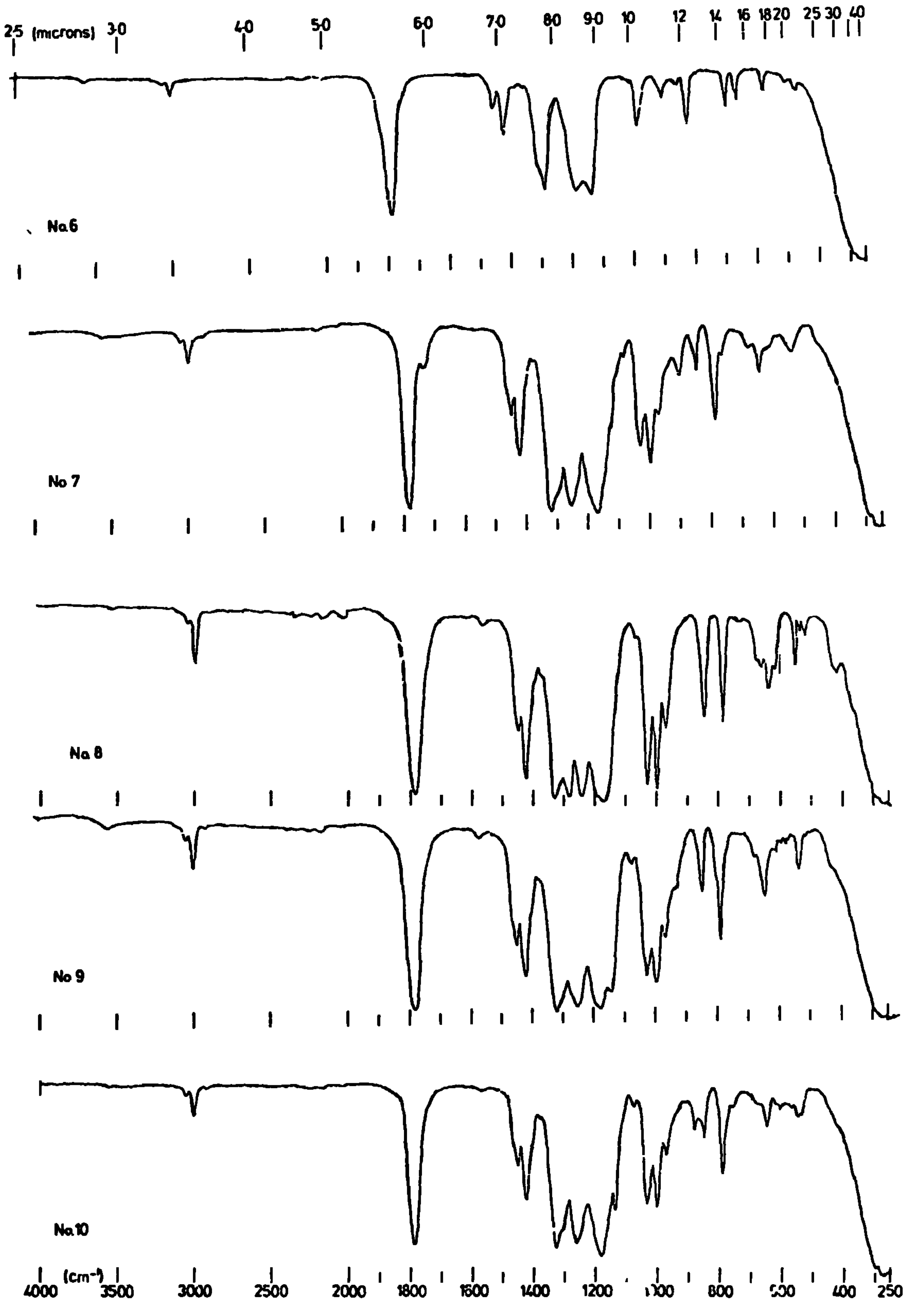
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No 9
No 10
(cm⁻¹)
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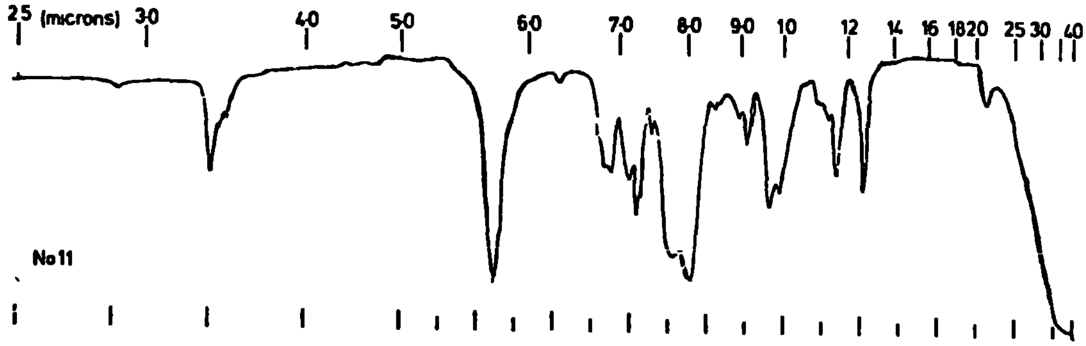

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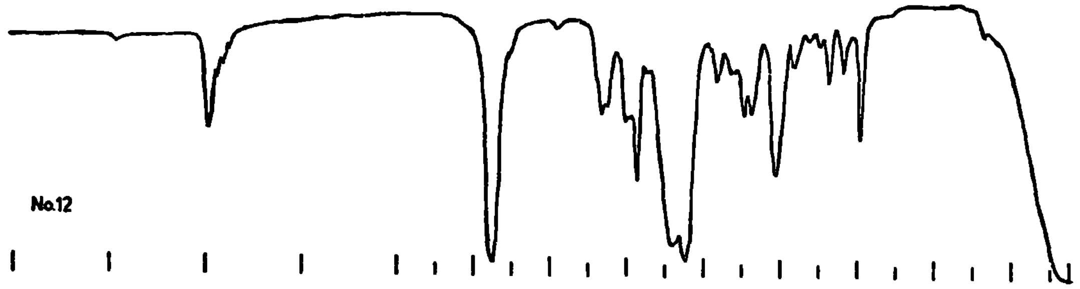
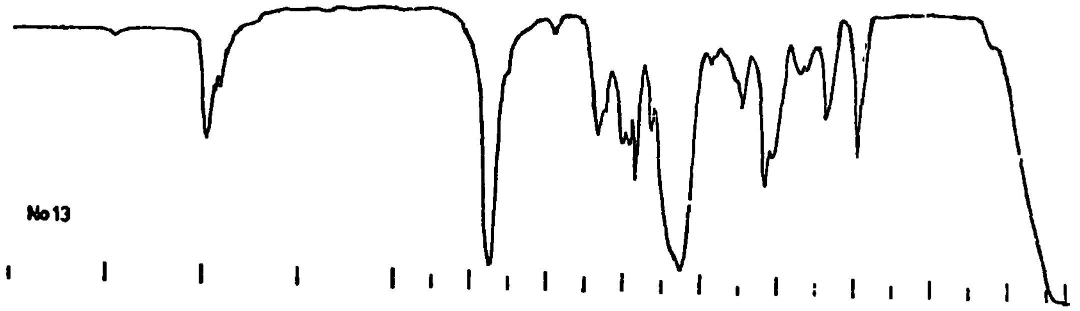


No.12



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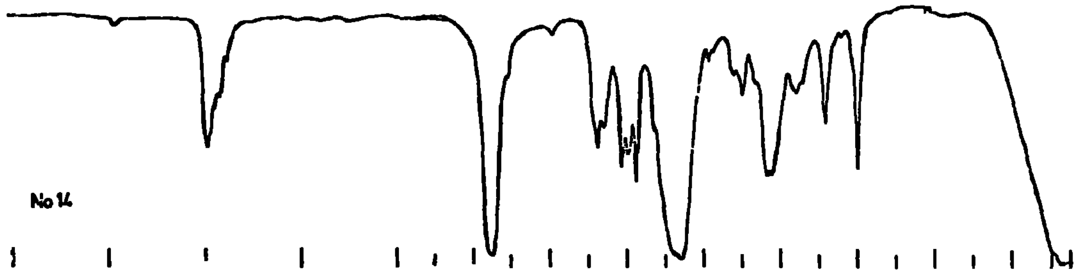

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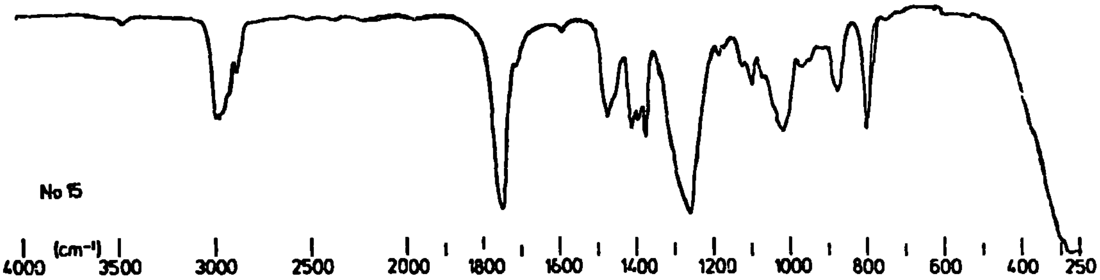

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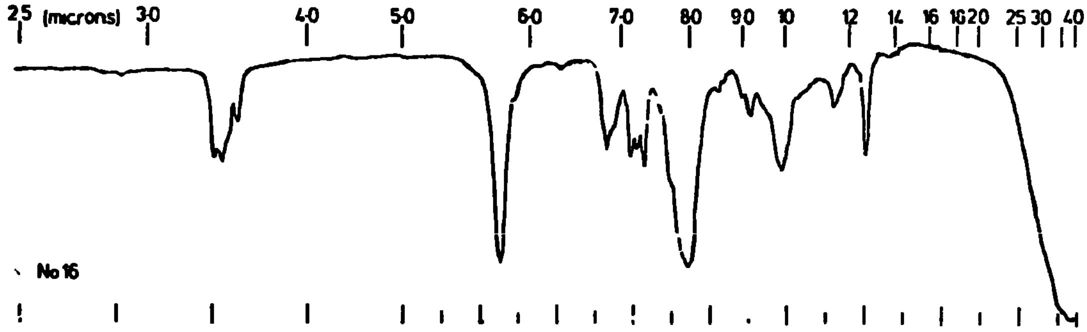

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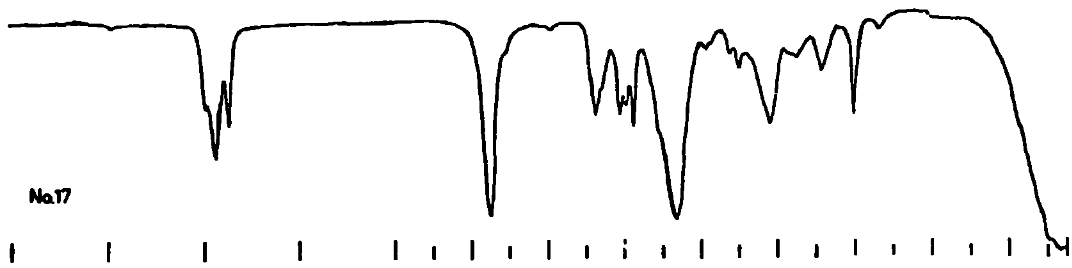

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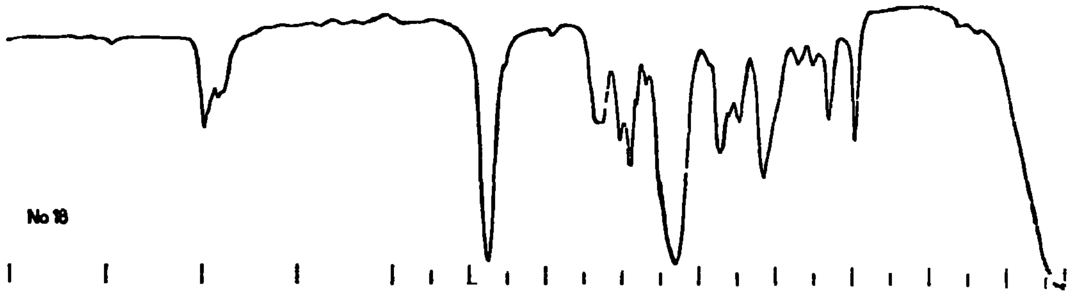

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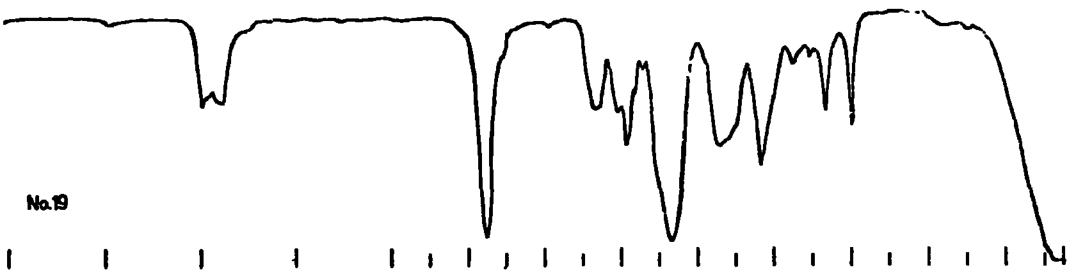

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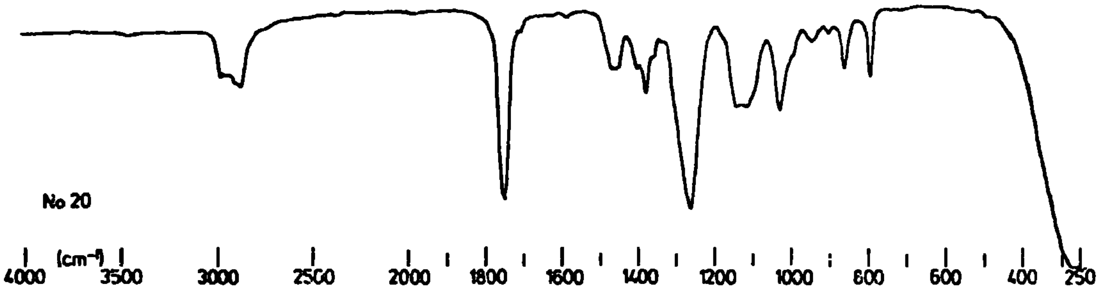

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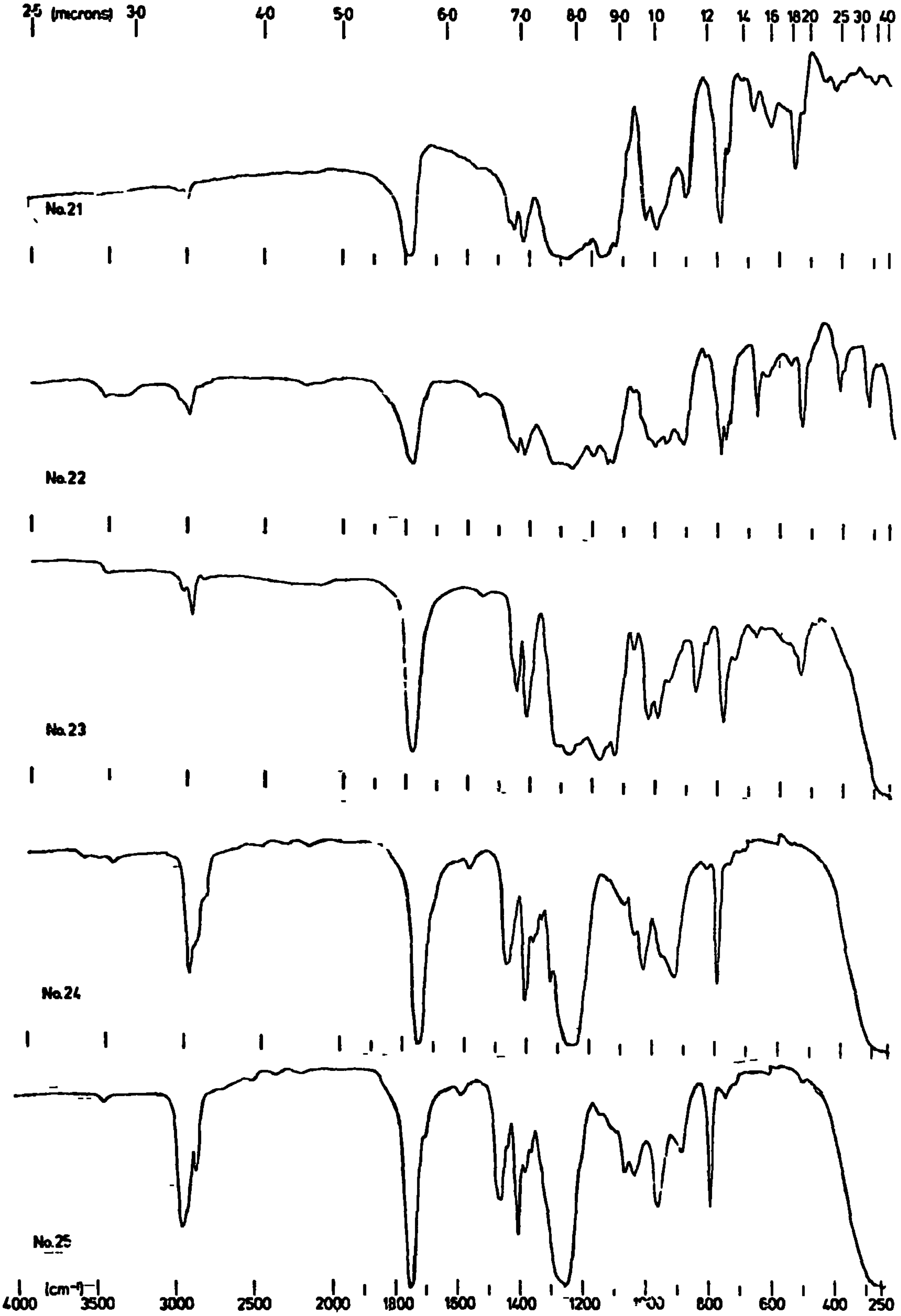
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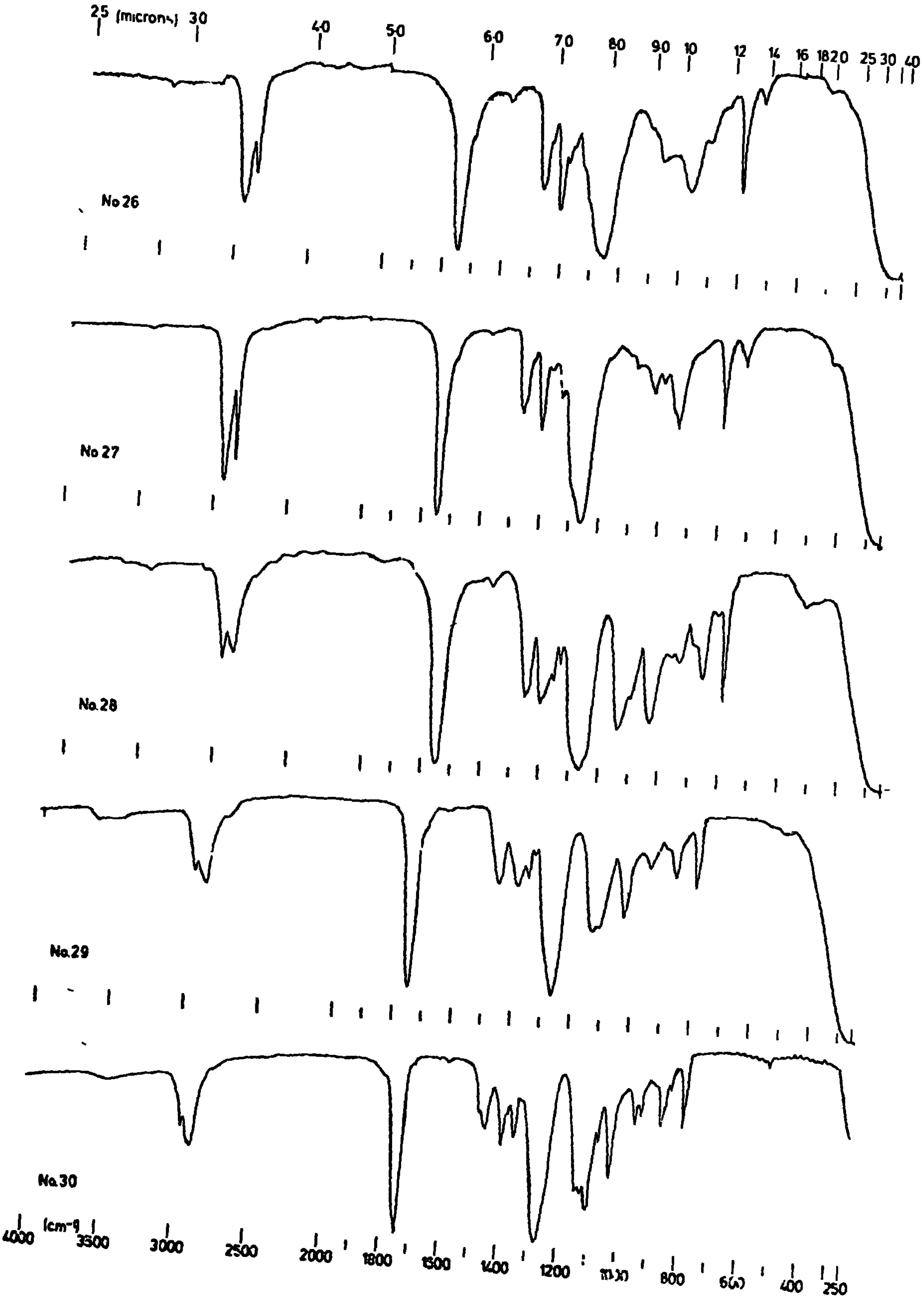
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