SYNTHESIS AND PROPERTIES OF FLUORINE-CONTAINING POLY α-ESTERS

by

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To my Father and Mother

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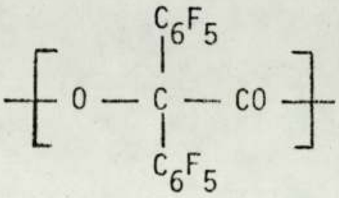
SYNOPSIS

The synthesis and polymerisation of the anhydrocarboxylate of 2-hydroxy-2-pentafluorophenyl propanoic acid (5-methyl-5-pentafluorophenyl-1,3-dioxolan-2,4-dione) has been examined and compared with anhydrocarboxylates of other α-hydroxy acids in order to assess the effect of fluoroaromatic substituents on the polymerisation reaction and the properties of the polymers (poly α-esters) produced. It has been shown that the relatively low molecular weights obtained by the tertiary base initiated polymerisation of this monomer are not a function of monomer purity nor of the fluoroaromatic substituent but are common to tertiary base initiated polymerisations of this series of monomers in general. Kinetic studies coupled with analysis of the polymers produced have been carried out using various combinations of monomer, initiator and solvent (reaction medium). The results have been tentatively interpreted in terms of a polymer mechanism including a termination step which produces a carboxyl excess over the 1:1 hydroxyl:carboxyl ratio encountered with poly α-esters produced by related ring-opening reaction. Good structure-reactivity correlations for both monomers and initiators were obtained using the Taft equation.

The synthesis of other fluorine-containing α-hydroxy acids has been examined, in particular that of decafluorobenzilic acid since this provides a potential route to the perfluoroaromatic poly α-ester:



$$\left[O - \underset{C_6F_5}{\overset{C_6F_5}{C}} - CO \right]$$

The low yields encountered in the synthesis of the parent acid from the Grignard reaction between pentafluorophenyl magnesium bromide and various derivatives of oxalic acid are explained in terms of competitive reactions producing unwanted by-products such as perfluorobenzilide. An improved procedure is suggested involving the 'in situ' formation of an insoluble salt of the desired product concurrently with hydrolysis of the Grignard complex.

Selected properties of the poly α-esters prepared in the course of the work were examined with the particular purpose of determining the difference in behaviour conferred by phenyl and pentafluorophenyl substituents. X-ray diffraction, differential scanning calorimetry, thermal and uv stability and surface properties were studied. As expected the differences were relatively small, the most significant being associated with glass transition temperature and surface properties.

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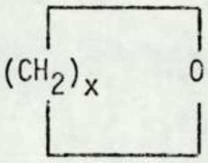
CHAPTER 1

1.1 Introduction

Ring-opening, together with addition and condensation, represent the three major classes of polymerisation reaction. Of the three types, ring-opening is peculiar in that it possesses some features of the other two classes. In several cases it provides the best, and sometimes the only, route to polymers of a particular structure. Aliphatic polyethers for example, have been prepared by ring-opening polymerisation of cyclic ethers of the general formula (I) and their derivatives.



(I)

In the context of this thesis, ring-opening polymerisation is taken to refer to the polymerisation of heterocyclic monomers. Although some cyclic olefins, such as cyclopentene, undergo polymerisation in the presence of appropriate initiators, the mechanism involved is a metathesis process(1) and not of general applicability. In its more general sense, ring-opening polymerisation produces heterochain polymers. Thus, polymerisation of the cyclic ether (I) will produce the polyether (II).

$$\left[O - (CH_2)_x \right]_n$$

(II)

The polymerisation of a ring compound is described in an earlier textbook(2) as proceeding by an interchange reaction, induced either catalytically or by the presence of small amounts of end-group-producing substances. In recent years, however, research has shown the position to be considerably more complex than this generalisation implies.

Ring-opening polymerisation can, in some ways, be classed as both condensation and addition, since although the polymer formed has the structural features of a condensation polymer, in a large number of cases it has the same composition as the monomer. The polymerisation mechanism of this class of compounds has some aspects of both conventional addition and condensation polymerisation (or more correctly chain and stepwise polymerisation). It resembles chain polymerisation in that it proceeds by the addition of monomer, but never of larger units, to growing chain molecules. As in stepwise polymerisation, the polymer molecules continue to increase in molecular weight throughout the reaction.

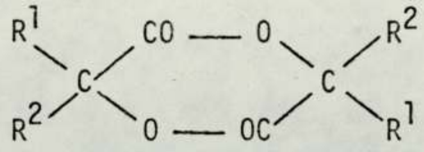
The polymerisability of a cyclic monomer depends upon the following factors:-

1. The reactivity of the particular functional group or hetero-atom present in the ring.
2. Ring size and the extent of ring strain.
3. The nature and number of ring substituents.
4. The initiator and polymerisation conditions being used.

Ring strain has been considered the principal driving force in the polymerisation of cyclic monomers. It is a thermodynamic property which is caused by either forcing the bonds between the ring atoms into an angular distortion or by steric interaction of substituents on the ring. In cyclic hydrocarbons(7), the increase in ring strain can be correlated with the higher heat of combustion. Thus, the high heat of combustion of cyclopropane and cyclobutane are due to the angular distortion of the ring carbon-carbon bonds. Cyclopentane, on the other hand, while showing very little ring strain, has a high heat of combustion due to unfavourable steric interactions between neighbouring hydrogen atoms.

Ring strains similar to those encountered in cyclic hydrocarbons are found in cyclic ethers, and when they occur, they constitute the principal driving force for polymerisation(8). Tetrahydropyran, a six-membered ring, like cyclohexane exhibits no ring strain, and has not been polymerised. On the other hand, tetrahydrofuran has a ring strain of only 2.9 kcal/mole compared with 6 kcal/mole for cyclopentane, but this strain is sufficient to impart a negative free energy to the polymerisation reaction at moderate temperatures. Hall and Schneider(9) have described the polymerisabilities of cyclic compounds containing carbonyl groups. With certain systems such as lactones, the five-membered ring will not homopolymerise, whereas the six-membered ring does. In contrast, with lactams the reverse situation is observed. Small(10) has suggested that with lactones a maximum in free-energy change for polymerisation is observed with the five-membered ring, while with lactams it occurs with the six-membered ring. It is apparent that a generalisation on the polymerisability of rings, wholly dependent upon ring size is impossible.

Substituents play an important part in modifying the polymerisability of cyclic monomers. For example, glycollide, the cyclic dimer ester of glycollic acid, (III; $R^1 = R^2 = H$), was reported[(26-29)]



(III)

to polymerise by the action of heat on zinc chloride. In the case of lactide, the cyclic dimer ester of lactic acid, (III; $R^1 = H$, $R^2 = CH_3$), polymerisation was also reported[(28)] but with more difficulty. Hall and Schneider[(9)] reported that tetramethyl glycollide, (III; $R^1 = R^2 = CH_3$), did not polymerise at all.

The diminishing effect in polymerisability of alkyl substituents to the rings can be explained in terms of thermodynamics. The tendency to polymerise of a cyclic monomer yielding an open chain is understood by comparing the favourably lower potential energy (rotational) of the chain to the unfavourably high potential energy of a ring, due to ring strain. A substituted ring (which possesses similar ring strain to the unsubstituted ring) upon the polymerisation gives a substituted chain which possesses high potential energy. The difference in potential energy of a monomer and a chain is thus decreased by ring substitution, thereby reducing the driving force of the polymerisation.

Ring-opening polymerisation may however be divided into two types. The first type, to which all the foregoing arguments apply is the polymerisation of heterocyclic monomers in which no small molecule is split off in the reaction as every element in a monomer is used to form part of a polymer chain, and the ring is in some sort of equilibrium with the chain. In the second type, small molecules are extruded or eliminated during the polymerisation from the cyclic monomer, this type of polymerisation has been called an extrusion polymerisation(3). A recent review of ring-opening polymerisation(4) covers many aspects of polymerisation of epoxides, lactones, lactams etc., which belong to the first type and polymerise without extrusion of small molecules, and of the very well-known N-carboxy-α-amino acid anhydrides, which belong to the latter.

Although both classes of ring-opening polymerisation possess the advantage of often being able to produce polymers which are difficult to produce by condensation reactions, extrusion polymerisation has the additional advantage of not having ring-chain equilibrium in the polymerisation. This is clearly demonstrated in the work of Dainton and Ivin(5) who established the thermodynamics of ring-chain equilibria in this type

$$T_c = \frac{\Delta H_p}{\Delta S_p^o + R\ln[M]} \qquad (1\text{-}1)$$

where T_c = the ceiling temperature (the temperature above which the formation of long-chain polymers from monomer at concentration $[M]$ is impossible),

ΔH_p = the enthalpy change of polymerisation,

ΔS_p^o = the entropy change of polymerisation for $[M]$ = 1 mole litre^{-1}.

of polymerisation respectively. The ceiling temperature may be defined as the temperature at which a substantial amount of monomer may exist in equilibrium with the polymer. In another way it means, the temperature at which the rates of polymerisation and depolymerisation are equal or the temperature above which depolymerisation predominates over polymerisation. The ceiling temperature concept applies equally well to other (e.g. vinyl) polymerisation in which polymerisation and depolymerisation can lead to an equilibrium situation. In the case of cyclic monomers with rings of five, six or seven members, the ceiling temperatures may often be quite low compared with vinyl polymers (e.g. T_c of polystyrene is about 300°C). This is especially true of lactone systems.

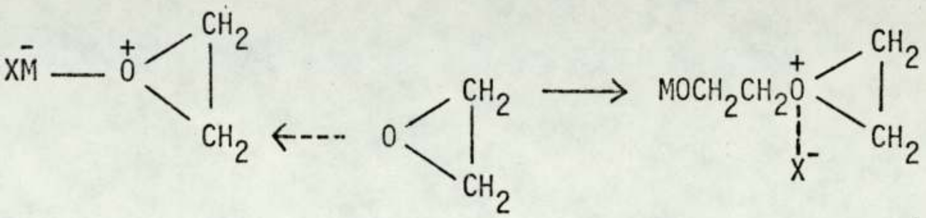
For poly-δ-valereolactone, a six-membered ring, it has been observed(6) that under conditions of polymerisation where the temperature is in excess of 150°C, a substantial amount of monomer remains in equilibrium with the polymer. Consequently, monomeric lactone can readily be generated by heating this polymer to temperatures in excess of 150°C.

One aspect of the polymerisability of heterocyclic monomers previously referred to is of particular importance in relation to the work described in this thesis. This is the variety of initiating systems which are encountered with the different monomers.

The polymerisation of ethylene oxide, for example, was first reported by Wurtz(11) to be catalysed by water, later a small amount of alkali or zinc chloride was also used(12) as catalyst. Extensive fundamental studies were carried out by Staudinger et al.(13,14) for the purpose of synthesising model cellulose substances by polymerising epoxides with various kinds of anionic and cationic catalysts. The preparation of solid high molecular weight polymer from 1,2-epoxides was developed only recently. In 1955 Pruitt and Bagget(15) used ferric chloride - propylene oxide complex catalyst in the polymerisation of epoxides and obtained high polymers. Various metal alkoxide catalysts were used by Price and Osgan(16).

The polymerisation of 1,2-epoxides may be classified under the headings cationic, anionic, and co-ordination polymerisation.

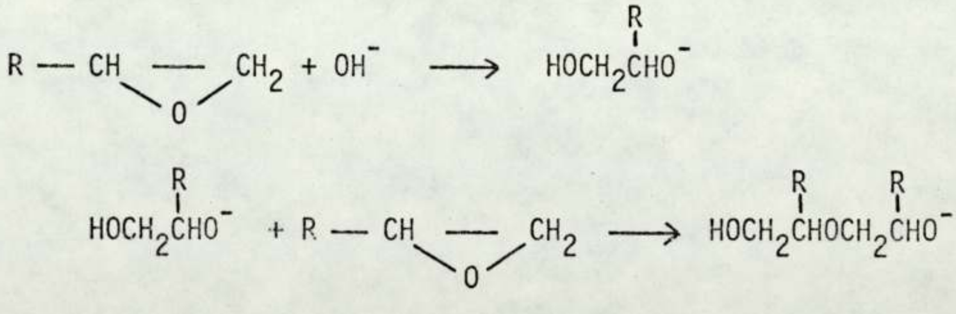
Cationic polymerisation is induced by Lewis acids such as BF_3, $AlCl_3$, $SnCl_4$, $TiCl_4$, and other metal halides. The mechanism involves a rearward, nucleophilic attack of an epoxide molecule on a carbon atom of the epoxide forming the propagating oxonium ion. Cationic ring-opening of propylene oxide occurs at primary and secondary carbon with about equal ease(17).



(1-2)

The polymers obtained from this route usually have low molecular weight.

In anionic polymerisation alkali hydroxides(16,18) and alkoxides(19,20) are used as catalysts. Nucleophilic attack occurs predominantly on a primary rather than a secondary carbon(21)



(1-3)

Optically active propylene oxide gave low molecular weight optically active polymer. Polyethylene oxides prepared by this method are generally low molecular weight viscous oils or waxy solids.

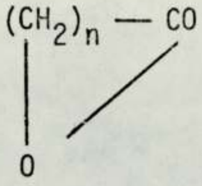
Co-ordination polymerisation produces very high molecular weight polymers(17). Typical catalysts belonging to this group are complex metal alkoxides, ferric chloride-alkylene oxide complexes, and organometallic compounds such as dialkylzinc, and aluminium alkyls. In this type of polymerisation, monomer co-ordinates to an electrophilic centre of the catalyst and is activated for the ring opening. Two or more metal atoms of the catalyst participate in the co-ordination. Attack may occur both at primary and secondary carbon atoms selectively, leading to two polymer fractions, one crystalline and isotactic, the other amorphous and atactic(17,22,23).

A recent report(24) described a new type of catalyst in polymerisation of propylene oxide. The use of compounds of the general form $R_2AlOAlR_2$ to catalyse the polymerisation of propylene oxide gave three types of polymer; i.e., a high molecular weight and highly isotactic polymer, $M_v = 10^5 - 10^6$, a low molecular weight and partially isotactic polymer, $M_v = 600\text{-}1000$, and an oligomer, $\simeq$ tetramer. The isotacticity together with the molecular weight of polymer varies with the nature of the alkyl groups in the catalyst in the order of decreasing efficiency

$$\text{Me} > \text{i-Bu} > \text{Et.}$$

The polymerisation of higher epoxides was not reported until the late 1930's(25). In contrast to 1,2-epoxides, which polymerise by either an anionic or a cationic mechanism, 1,3- and higher epoxides can polymerise only cationically. The catalysts are of strong acid or Lewis acid type or of salts derived from them.

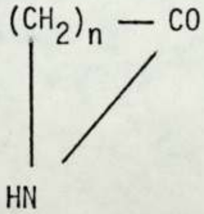
Lactones (IV) can be regarded as internal or cyclic esters, and also as the monomer precursors to polyesters since under certain conditions the rings can be made to open and polymerise to form linear polyesters. Lactones can undergo



(IV)

anionic, cationic, and initiated stepwise polymerisation. A great number of organometallic compounds, metals, metal hydrides, Lewis acids, protonic acids, and amines have been examined as catalysts for lactone polymerisations. There are two possible ways in opening of a lactone molecule to polymerise, one is via acyl-oxygen bond cleavage, the other is via alkyl-oxygen bond scission. There appears little doubt that acyl-oxygen cleavage is the preferred polymerisation mechanism for all lactones, with possible exception of substituted β -propiolactones. With these lactones it has been observed that the hydrolytic mechanisms are somewhat anomalous. It appears that alkyl-oxygen fission can occur with these highly strained four-membered ring lactones in polymerisation as well.

The conversion of lactams (V) to linear polyamides may be



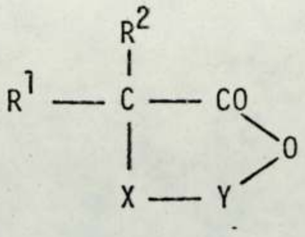
(V)

accomplished by either hydrolytic or nonhydrolytic processes. Similarly to lactones, they also undergo anionic and cationic polymerisations. A detailed account of the initiating systems and proposed polymerisation mechanisms is given in the collection of reviews on ring-opening polymerisation edited by Frish and Reegan(4).

Here, the nature of ring and substituents play their parts in governing the polymerisabilities of these two types of carbonyl-containing cyclic monomers.

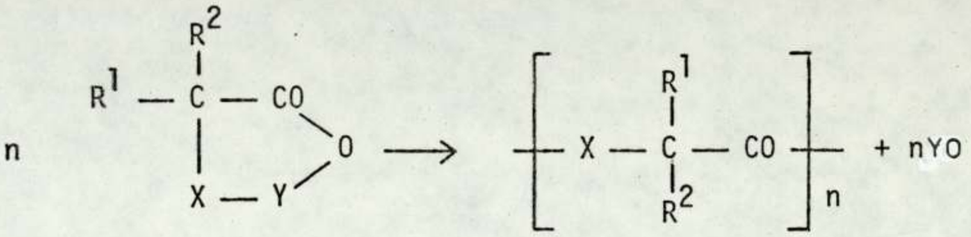
General qualitative studies on the polymerisabilities of carbonyl-containing cyclic monomers by Hall and Schnieder(9) showed that four-, seven-, and eight-membered rings polymerise in almost all cases, but the polymerisabilities are decreased by alkyl and aryl substituents on a ring. The polymerisability of five- and six-membered rings depend markedly on the class of compound. In the light of this earlier work, the importance of choice of initiator is emphasised by Konomi's recently published report of the successful polymerisation(30) of a six-membered ring lactone, α-piperidone, by using metallic aluminium alkylate as catalyst ($MAlEt_4$, where M = Li, Na and K) at temperatures below $80^{\circ}C$, and claimed to obtain the highest degree of polymerisation so far reported. This situation is typical of many recent examples of the use of novel organometallic compounds to produce enhanced polymerisation of otherwise, intractable monomers.

Perhaps the best known category of cyclic monomers which undergo 'extrusion polymerisation' are the N-carboxy-α-amino acid anhydrides (NCA s). In recent years, however, several additional types of ring which undergo 'extrusion polymerisation' have been studied foremost being the anhydrocarboxylate and anhydrosulphite of α-hydroxy acids. The general structure of these monomers may be written as



(VI)

They may be described as cyclic esters of carboxylic acids which contain α-functional groups, and the basic equation for their polymerisation is:-



(1-4)

where x may, in principle, be NR^3, O, S, Se and y = $>C=O$, $>S=O$, $>Se=O$, or $>C=S$.

The simplest synthetic route, which is in some cases applicable, consists of the reaction of the parent acid with phosgene, thiophosgene or thionyl chloride. Some typical examples of these rings are given in Table 1.1.

In recent years extrusion polymerisations have received a considerable amount of attention. NCAs are very distinguished members of this category of monomers, since their polymerisation products, namely poly α-amino acid, may be used as simple building blocks for peptides and polypeptides(31,32). They have thus received a very great deal of study and investigation.

NCAs undergo polymerisation by a variety of mechanisms,

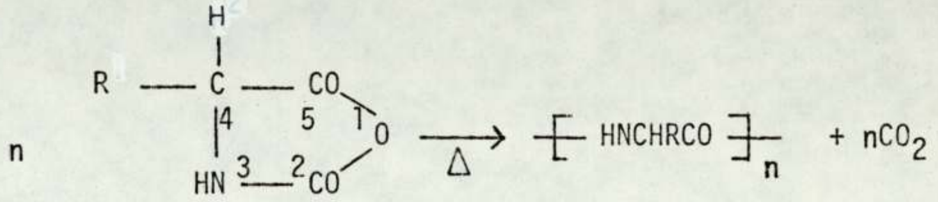
Table 1.1

Some examples of cyclic derivative of α -functional carboxylic acids

Parent acid	X	Y	Systematic name	Common name
α -amino acid	NR^3	>C=0	1,3-oxazolidin-2,5-dione	α -amino acid anhydrocarboxylate
	NR^3	>C=S	2-thioxo-1,3-oxazolidin-5-one	
α -hydroxy acid	0	>C=0	1,3-dioxolan-2,4-dione	α -hydroxy acid anhydrocarboxylate
	0	>C=S	2-thioxo-1,3-dioxolan-4-one	
	0	>S=0	4-oxo-1,3,2-dioxathiolan-2-oxide (1,3,2-dioxathiolan-4-one-2-oxide)	α -hydroxy acid anhydrosulphite
α -thio acid	S	>C=0	1,3-oxathiolan-2,5-dione	α-thio acid anhydrocarboxylate
	S	>C=S	2-thioxo-1,3-oxathiolan-5-one	
	S	>S=0	5-oxo-1,2,3-oxadithiolan-2-oxide (1,2,3-oxadithiolan-5-one-2-oxide)	α-thio acid anhydrosulphite

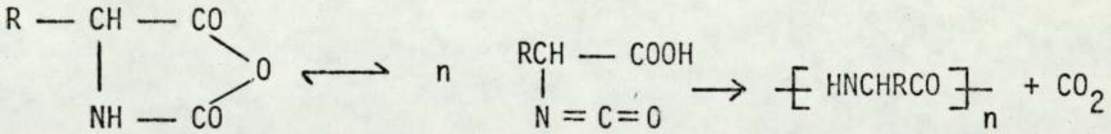
depending on the ring substituents, nature of initiators and catalysts. In some cases the mechanism is quite simple, while under different conditions the mechanism is complex and not fully understood. A comprehensive discussion of the mechanism of NCA s polymerisation has been published by Bamford et al.(33) and more recently, reviews by Szwarc(34) and Shalitin(35).

NCA.s undergo polymerisation under heat, with evolution of carbon dioxide yielding poly α-amino acids.



(1-5)

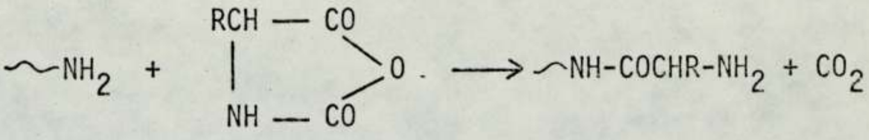
The released carbon dioxide is formed exclusively from the C-2 atom of the NCA ring. The mechanism of this thermal decomposition is still obscure, and the nature of the polymer end groups is unknown. Bayer(36) and Kopple(37) suggested that NCA reacts via its isomer, the isocyanate acid form.



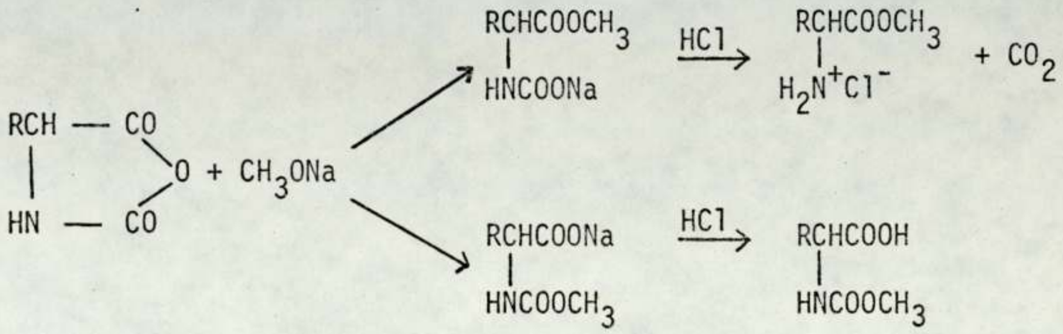
(1-6)

Another suggestion is that polymerisation is initiated and propagated by anionic activated monomer.

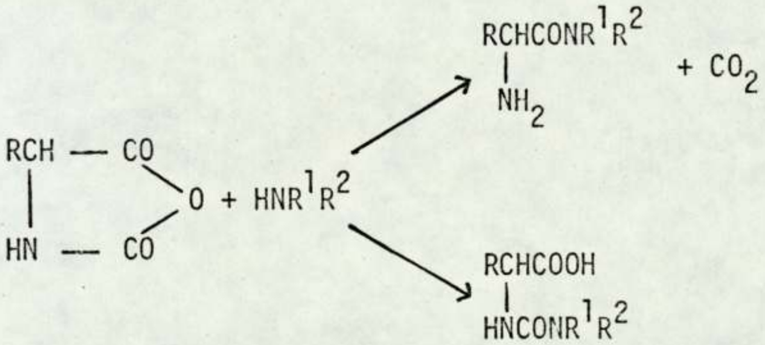
The reactions of NCA s with methoxides and different amines show a similar pattern of "normal" and "wrong" additions resulting from the attack at C-5 and C-2 carbonyls of the ring respectively. Wrong addition of this type interferes with the so-called "normal" mode of polymerisation, e.g.



(1-7)



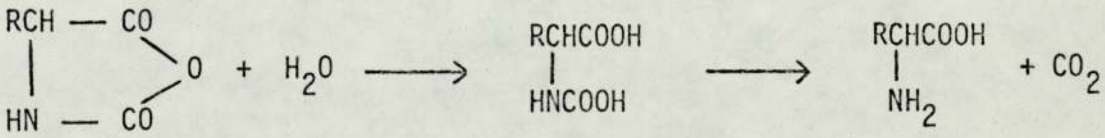
(1-8)



(1-9)

Carbon dioxide was liberated only when the C-5 atom was attacked.

Trace amounts of water are also able to serve as initiator. The reaction is characterised by a short induction period followed by a first-order reaction.



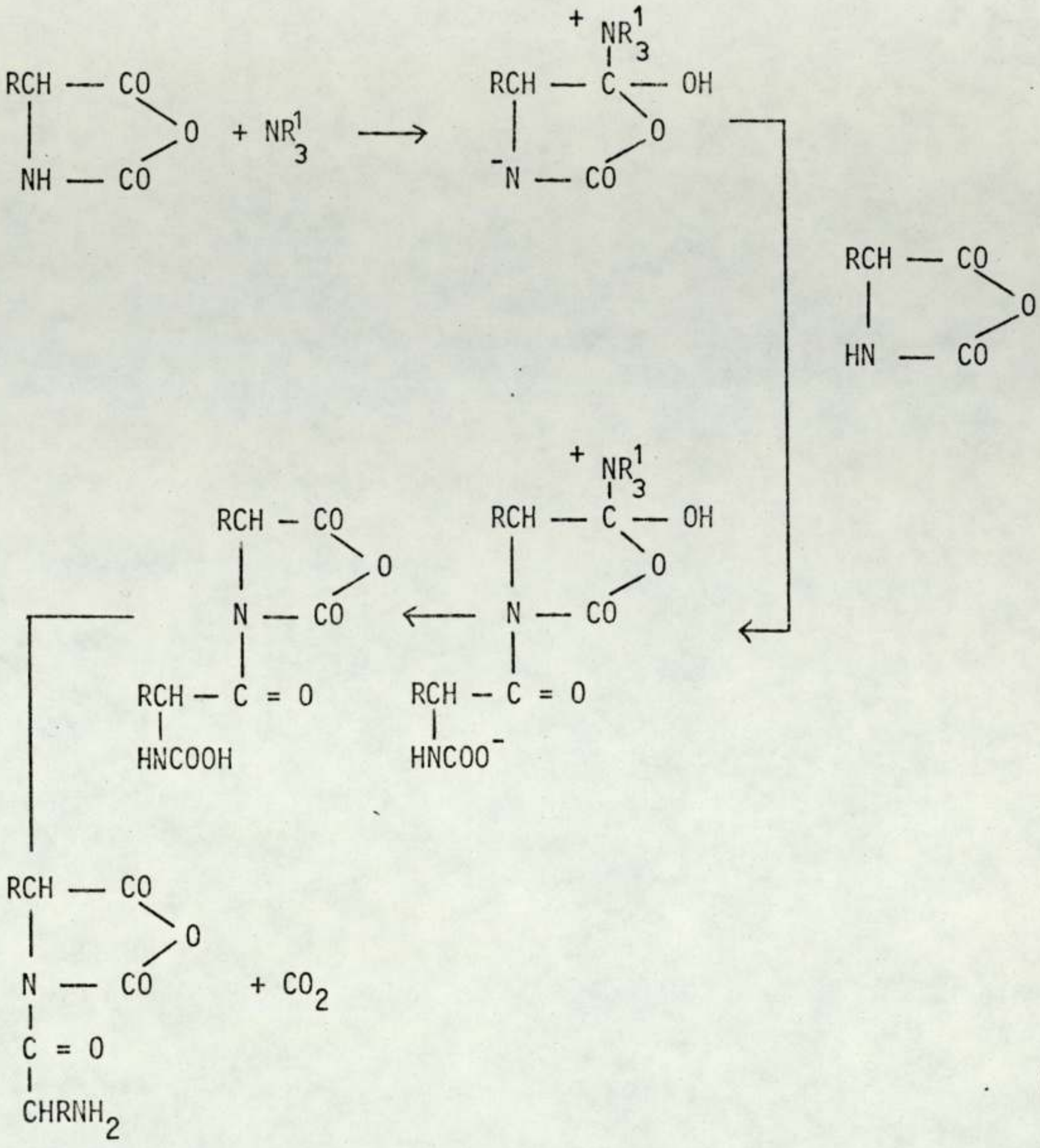
(1-10)

The newly formed amino group reacts with more monomers, thus enabling propagation to take place (Eqn. 1-7).

NCAs react with amines to yield the corresponding amino acid amide. Oligomer is formed in the presence of an excess amount of amines. This is a multistep reaction, where the amino group of one product reacts with another NCA molecule, and by several successive steps an oligomer is formed. When succeeding reactions are faster than the initial step, polymers are formed rather than the monomer derivatives. Termination can take place by "wrong" addition but this is a relatively rare occurrence. When no termination takes place the degree of polymerisation (DP) is related to initial monomer (M_0) and initiator (I_0) concentrations as follows:
$DP = [M]_0/[I]_0$.

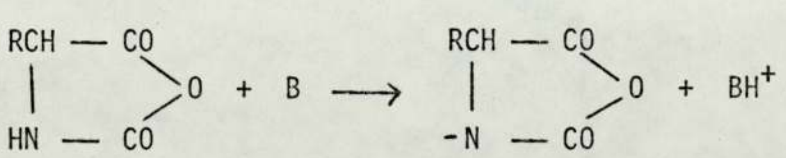
NCAs can undergo polymerisation initiated by various nucleophilic reagents: protic and aprotic bases, metal salts and perhaps the most important for preparation of high molecular weight polymers, strong bases.

For tertiary amine initiated NCAs polymerisation the molecular weight of the polymer is independent of $[M]_0/[I]_0$. Wieland(38,39) suggested that the mechanism involves nucleophilic attack of an amine on the C-5 carbonyl, forming a tetrahedral complex which opens to a zwitterionic molecule. The reaction between the oppositely charged termini propagates the polymerisation. Ballard and Bamford(40), suggested a different mechanism in which the role of the base is to abstract the proton from the ring nitrogen via attack on the C-5 carbonyl and proton transfer resulting in an anionic activated NCA which then attack the C-5 carbonyl of a nonactivated molecule.



(1-11)

More recently, Bamford and Block$^{(41,42)}$ simplified the mechanism by assuming that the tertiary amine just act as a base, and abstracting a proton from the ring nitrogen rather than as a nucleophile attacking the C-5 carbonyl.

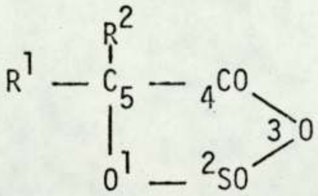


(1-12)

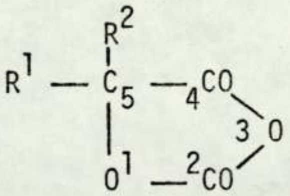
The mechanism is subsequently identical to Eqn. (1-11).

Polymerisation of NCAs by sodium methoxide or sodium hydroxide has the characteristic of a slow induction period of up to 30% conversion, followed by a fast first-order reaction, which is about 100 times faster than that found in the primary amine initiated polymerisation. The polymer formed has a very high molecular weight. Many mechanisms have been suggested. Blout suggested a mechanism in which the propagation is via nucleophile attack on either the C-2 or the C-5 carbonyl. Idelson and Blout(43), later proposed another mechanism involving the formation of a terminal amide ion, whereas Szwarc(34) has assumed the proton abstraction from the N-3 or the C-4 of the NCA molecule, yielding an "activated monomer. Despite continuous attention over many years the polymerisation of NCAs under different conditions still presents many mechanistic problems.

Other ring compounds, although structurally similar to NCAs, have received much less attention. Anhydrosulphite and anhydrocarboxylate of α-hydroxy carboxylic acids (VII) and (VIII),



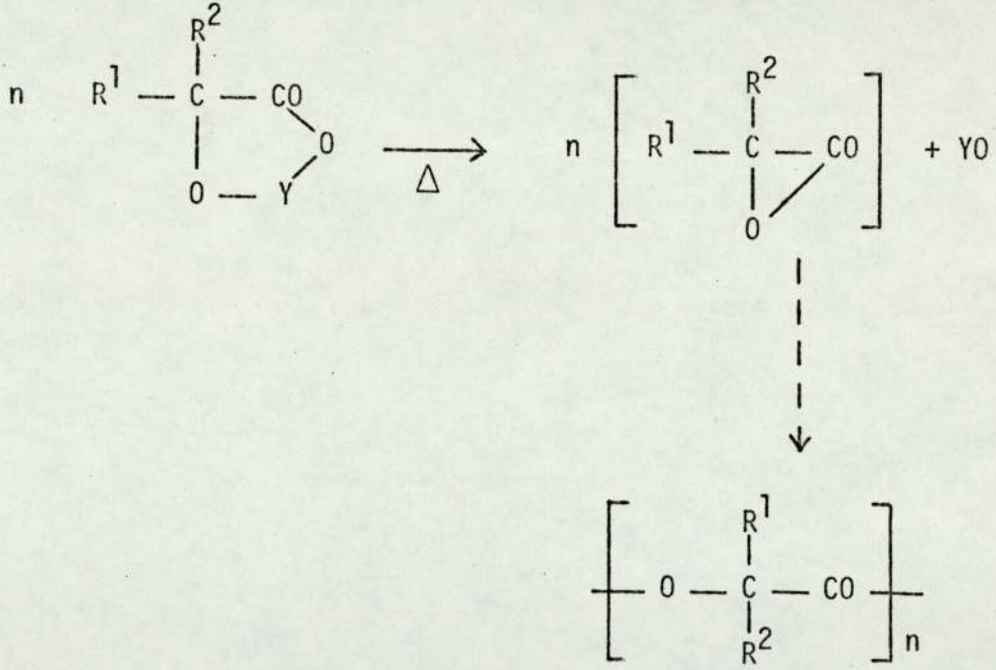
(VII)



(VIII)

polymerise to give poly α-ester with evolution of sulphur dioxide and carbon dioxide respectively. Blaise and Montagne(44) first reported methods of synthesis of anhydrosulphite of lactic acid, (VII; $R^1 = H$, $R^2 = CH_3$), and of α-hydroxybutyric acid (VII; $R^1 = R^2 = CH_3$). More recently, extensive works have been carried out on polymerisation of different substituted anhydrosulphites.(45-56) A Reaction mechanism has been put forward to account for the rapid formation of high molecular weight poly α-hydroxyisobutyric acid anhydrocarboxylate (poly HBAS) in thermal polymerisation.(57)

The mechanism suggested the formation of a highly reactive α-lactone as an intermediate species, with a thermal elimination of sulphur dioxide from the ring. The α-lactone then undergoes spontaneous polymerisation. The same concept of formation of α-lactone intermediate was used in the proposed mechanism(63) of thermal decomposition of anhydrocarboxylate of α-hydroxy carboxylic acids:

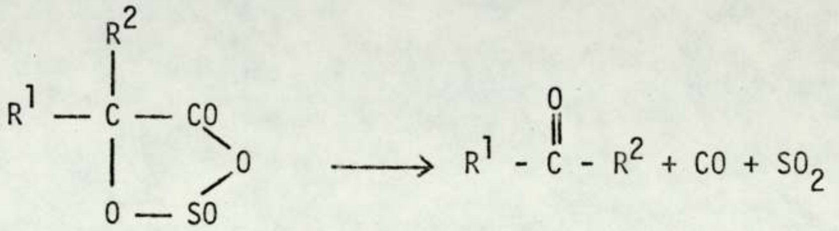


(1-13)

where Y = S=O or C = O. In both cases the decomposition showed good first-order behaviour with respect to residual monomer concentration.

In contrast to most ring compounds, the thermal stability of the disubstituted anhydrosulphite ring decreases as the size of the substituents increases. Thus it becomes more susceptible to decomposition. This is shown in the increasing magnitude of the rate constant for the unimolecular decomposition as the length of n-alkyl substituent at the C-5 carbon position is increased.

With large substituents such as phenyl, or strong electron withdrawing substituents such as chloromethyl, a secondary fragmentation process (forming ketone, carbon monoxide and sulphur dioxide) is appreciable and becomes competitive in the thermal decomposition reaction at high temperatures.


(1-14)

This forbids the possibility of obtaining highly substituted poly α -ester by thermal decomposition.

In the case of anhydrocarboxylates of α -hydroxy acids, the secondary fragmentation (forming ketone, carbon monoxide, and carbon dioxide) were reported by Tighe(62) in the decomposition of dimethyl substituted anhydrocarboxylate. Surprisingly, in the decomposition of pentafluorophenyl lactic acid anhydrocarboxylate (VIII; $R^1 = CH_3$, $R^2 = C_6F_5$) which has a very strong electron-withdrawing group ($-C_6F_5$) as substituent, there has been no report of such ketone formation.

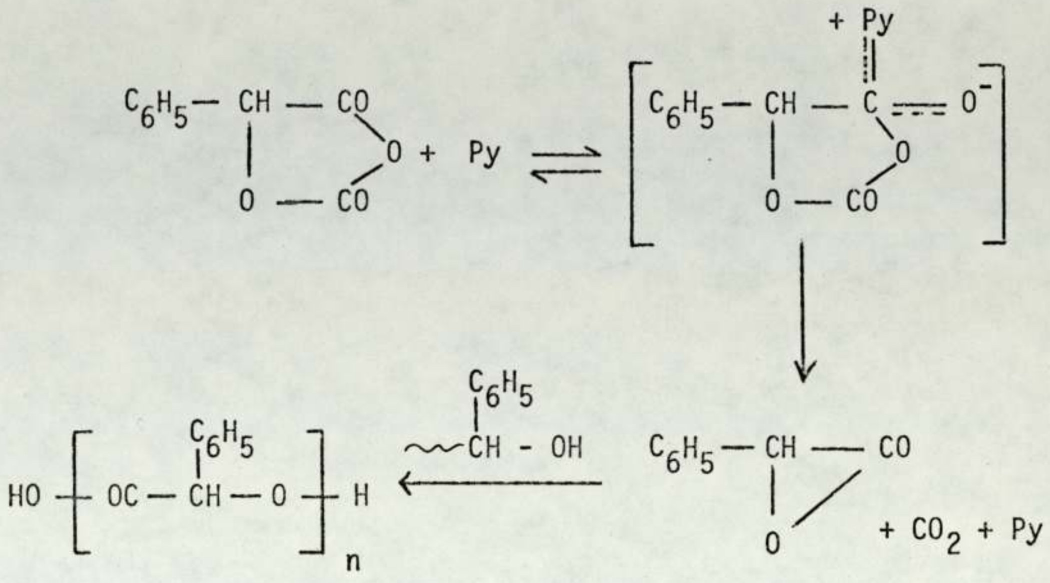
α -Hydroxy carboxylic acid anhydrosulphites have been reported(60) to undergo initiated polymerisation using such initiators as triethylamine, dimethylformamide, pyridine, and also with organometallic compounds such as sodium methoxide, lithium butyl and zinc diethyl-water. Little detail was given and no information on the molecular weight of the products.

A very recent work(59) was carried out on the initiated polymerisation of anhydrosulphites by lithium tertiary butoxide in dekalin at room temperature. It was found that not every anhydrosulphite gave the same reaction profile and the results showed the fundamentally different mechanisms involved in the decomposition of anhydrosulphite in the presence of alkoxide at ambient temperature and in thermal decomposition.

Anhydrocarboxylates of α -hydroxy carboxylic acids, which were first reported to be synthesised by Davies(61), did not, from Davies' reports, appear to possess the tendency in decreasing ring stability as ring substitution is increased but the reactions described were not studied kinetically. Davies reported that glycollic acid anhydrocarboxylate (VIII; $R^1 = R^2 = H$) decomposed to yield polyglycollide when it was heated at 100°C for 18 hours, while lactic acid anhydrocarboxylate (VIII; $R^1 = H$, $R^2 = CH_3$) was recovered unchanged when heated at the same temperature and for the same period.

Pyridine and various of its derivatives have been employed as catalysts in polymerisation of phenyl and pentafluorophenyl substituted anhydrocarboxylates at different temperatures in nitrobenzene(63). The kinetics of polymerisation were found to be first-order with respect to both monomer and pyridine. The pyridine was not consumed in the course of the reaction and its concentration did not affect the molecular weight of the product.

A suggested mechanism for the decomposition of mandelic acid anhydrocarboxylate (VIII; $R^1 = H$, $R^2 = C_6H_5$) with pyridine involves an initial equilibrium reaction between monomer, pyridine and an intermediate, formed by the attack of pyridine on the C-4 carbonyl of the ring. Decomposition of this intermediate yields a polymerisable species, believed to be the highly reactive α -lactone which takes part in a rapid chain propagation step with the terminal hydroxyl group of a polymer chain.



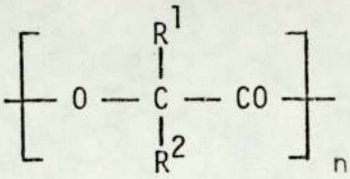
(1-15)

Adventitious traces of moisture regenerate a parent acid by hydrolysis of the ring, thereby providing initiation sites for this process.

Smith also investigated the effects of introducing a strongly electron-withdrawing group, pentafluorophenyl, as a substituent in an anhydrocarboxylate ring. It was found that the pentafluorophenyl group increased the thermal stability of the ring, but at the same time made the C-4 carbonyl more susceptible to attack by a nucleophilic species, thus the polymerisability of the ring was also increased.

Polymer obtained from the pyridine initiated polymerisation of the pentafluorophenyllactic acid anhydrocarboxylate (VIII; $R^1 = CH_3$, $R^2 = C_6F_5$) had a number-average molecular weight of about 2400 or degree of polymerisation of about 10. Little understood problems were encountered in this work. Although the reaction bears some considerable resemblance to anhydrosulphite polymerisation the molecular weights obtained were relatively low (corresponding to degree of polymerisation, around 10). The reason for this is not clear, nor for the fact that the polymerisation of the anhydrocarboxylate of pentafluorophenyl lactic acid showed a marked deviation from the first-order dependence on pyridine at higher pyridine concentrations.

Poly α -esters (IX) have not been well studied, mainly

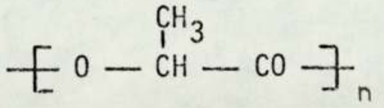


$$\left[O - \overset{R^1}{\underset{R^2}{C}} - CO \right]_n$$

(IX)

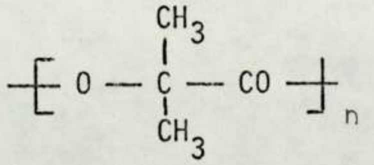
because of the limited number of synthetic routes. Aliphatic polyesters in general have low melting points and tend to be susceptible to organic solvents and to hydrolysis, aliphatic poly α -esters, however, exhibit higher melting points, i.e.

$\left[O - CH_2 - CO \right]_n$ mp = 220°C



$\left[O - \overset{CH_3}{CH} - CO \right]_n$ mp = 185°C

and



$\left[O - \overset{CH_3}{\underset{CH_3}{C}} - CO \right]_n$ mp = 240°C

The properties of fluorine-containing polyesters of any type have not been widely studied. Poly hexafluoropentamethylene isophthalate yields tough flexible film and fibre, and is reported to have a decomposition temperature above 450°C. Results obtained with perfluoroaromatic polymer have been generally disappointing even when allowance is made for the fact that high molecular weights are difficult to obtain. Polymers containing perfluoroaromatic groups pendant from the main chain have received less attention than those containing tetrafluorophenylene unit in the chain. Poly-(2,3,4,5,6-pentafluorostyrene) however, shows appreciably better thermal stability, oxidation resistance and UV resistance than polystyrene.

There has not yet been any published work about the properties of poly α-esters containing pentafluorophenyl groups.

1.2 Scope and Object of the Present Work

It is the object of this work to continue and extend the study of phenyl and pentafluorophenyl substituted 1,3-dioxolan-2,4-diones. In particular it is intended to examine the factors responsible for the limitation apparently placed on the molecular weight of the polymers and to investigate the possible existence of termination reaction corresponding to the "wrong addition" step in polymerisation of N-carboxy acid anhydrocarboxylates.

It is hoped to make a primary study of the properties of these polymers and to compare, to some extent, the relative effects of phenyl and pentafluorophenyl substituents on the poly α-ester backbone.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Instrumental Techniques

Infrared Spectra - A general purpose Perkin-Elmer Infrared grating spectrophotometer Model 237 was used. All spectra, unless otherwise stated, were recorded with the sample in the form of a KBr Disc. Air was used as reference in every case.

Mass Spectrometry - An AEI MS9 instrument was used for recording mass spectra. The instrument produces three spectra concurrently whose sensitivity varies in increments of ten enabling an accurate mass analysis to be made.

Nuclear Magnetic Resonance Spectra - Proton resonance spectra in the majority of cases were recorded using a Perkin-Elmer R14 spectrometer operating at 100 MHz and of ambient temperature 33.4°C. In some cases a Perkin-Elmer R10 spectrometer operating at 56.5 MHz was used. Fluorine resonance spectra were recorded on the latter instrument. An internal reference of tetramethylsilane was used for recording proton resonance spectra and deuterochloroform was found to be an ideal solvent.

Gas Liquid Chromatography - Traces were obtained using a Pye Gas Chromatograph Series 104 with katharometer detector. An E30 column consisting of silicone gum on firebrick was used and the carrier was helium.

Thermogravimetric Analysis - The analyses were carried out on a Du Pont Thermogravimetric Analyser 950 under an atmosphere of nitrogen.

Differential Scanning Calorimetry - Thermal properties of the materials synthesised in this work were obtained using a Perkin-Elmer Differential Scanning Calorimeter Model 2 equipped with a liquid nitrogen subambient accessory.

The analyses were made under a helium atmosphere and the heating rates used are 5 and 10 $^{\circ}C.min^{-1}$.

X-Ray Photographic Analysis - X-ray powder photographs were taken using a Phillips 11.46 cm diameter powder camera fitted with a 0.5 mm collimator. The samples were mounted in lithium beryllium borate tubes and the X-rays generated from a copper target at 40 kv using a nickel filter enabling only copper K_{α} radiation to be used.

Temperature Controlled Oil Baths - A set of temperature controlled oil baths fitted with contact thermometer/relay/heater systems enable the kinetic experiments to be carried out within an accurate temperature of $\pm$ 0.2 - 0.3^{0} depending on the volume of the baths. Risella oil was used for temperatures below 80^{0}C and for higher temperatures silicone oil was employed.

UV Exposure Cabinet - The UV exposure cabinet used was a circular unit manufactured by Laboratory Thermal Equipment. Exposed samples were mounted on a rotating holder and irradiated by means of a series of adjacently set Actinic Blue fluorescent UV tubes which were mounted vertically around the internal wall of the cabinet.

Dry Box - A dry atmosphere was necessary in storing and handling the monomers and some initiators since they were very sensitive to moisture. A glove box manufactured by SLEE Ltd. was used for this purpose. Atmospheric moisture was initially removed by replacement of the air with dry nitrogen followed by circulation of the atmosphere in the box through four glass coils immersed in a solid carbon dioxide-acetone mixture. The pumping rates of 6 l.min.$^{-1}$ through the main chamber and 4 l.min.$^{-1}$ through the access chamber were found to be suitable. In addition, regular replacement of drying agent, molecular sieve Type 5A supplied by B.D.H. Ltd., helped in maintaining the dry atmosphere when the circulation pump was not in use. The atmosphere was regularly checked by a Shaw Hygrometer connected to a Red Spot (Sensitive) Type Element which was fitted to the main chamber of the glove box. This element was effective over the range 1-500 ppm (v/v) water. The moisture content in the box was found to be at the level of 5-10 ppm (v/v).

Goniophotometry - A modified light scattering photometer(94) was used as goniophotometer for the study of the deterioration of the surface of poly- α -ester films. A high torque (Citenco) motor was adapted to rotate the disc of the Brice-Phoenix Light Scattering Photometer (Series 2000) by a connection/disconnection device fixed at the back of the photometer. The motor was connected to a variac and both were calibrated to give a required practical range of photocell rotation rates. The output signal was recorded by a Multi-range Potentiometric Flatbed Recorder (Smith Industries type RE 544.20) connected to the photometer.

A new specimen mount was designed as shown in Figure 2.1. The mount consisted of a large disc A (7.2 cm in diameter) made from one piece of brass joined with a round base B so that it could be easily rotated through 360° on the specimen table of the photometer. At the same time the mount could be fixed at various angles, which were calibrated on the edge of the disc C as half circles lockable by a pin as shown in Figure 2.2.

A device to narrow the beam, shown in Figure 2.3, consisted of

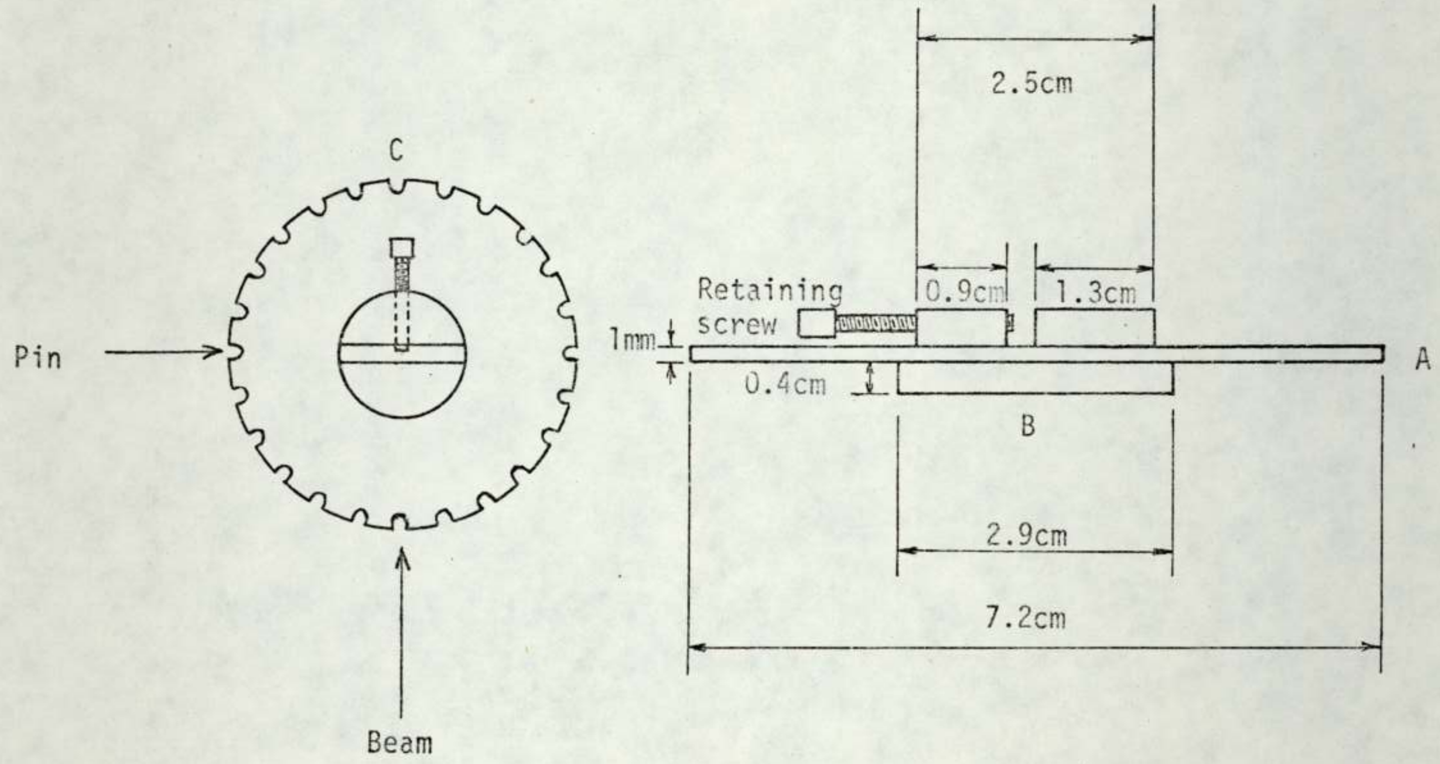


Figure 2.1 Specimen mount design

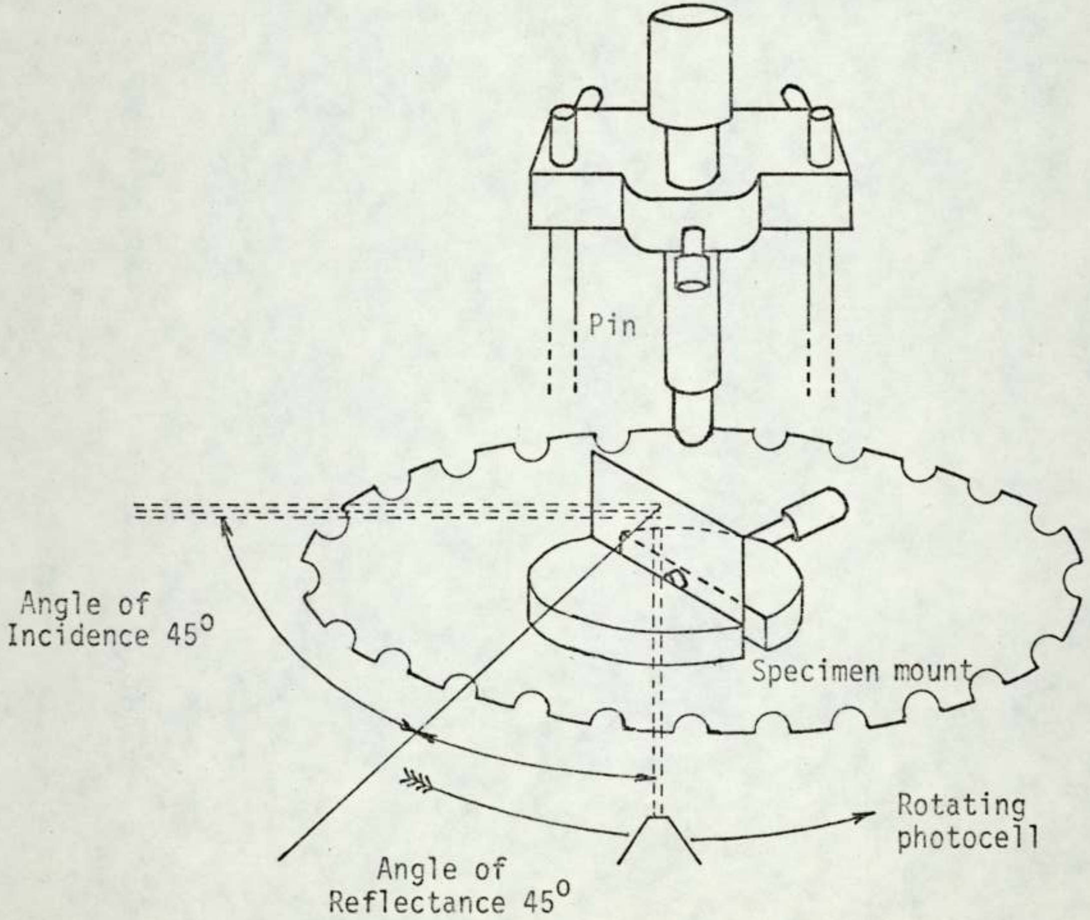


Figure 2.2 Locking of the specimen mount

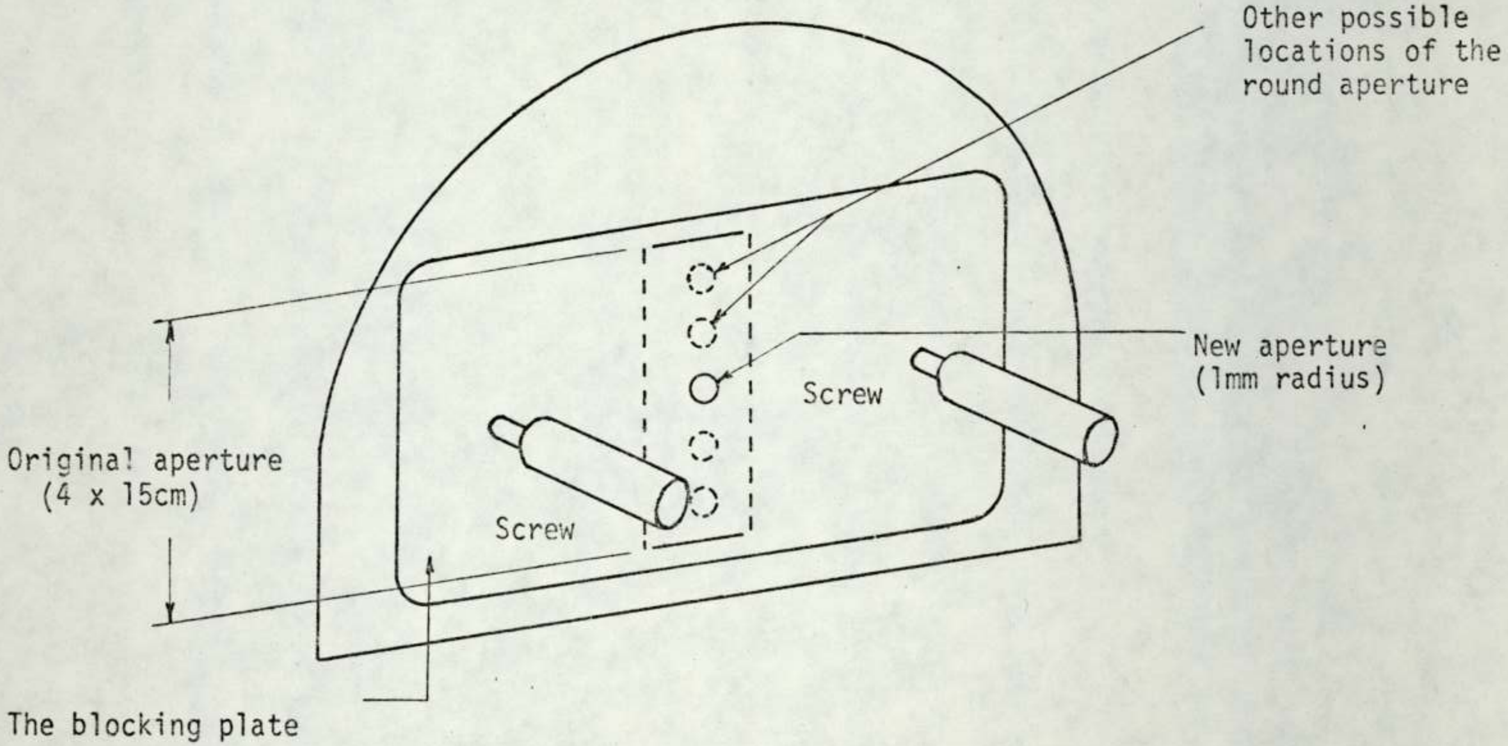


Figure 2.3 Beam narrower

a brass plate with a small hole in the centre and two screws to enable it to be attached to the slit of the photometer.

Gel Permeation Chromatography - All gel permeation chromatographic analyses were carried out by the Polymer Supply and Characterisation Centre of R.A.P.R.A., Shawbury, Shrewsbury. Computerised molecular weight data supplied was based on the assumption that the polymer (poly α-ester) "behaves" as polystyrene in solution. In order to obtain reasonably accurate molecular weights of poly α-esters from the data provided, 'Q factors' were calculated for each poly α-ester.

'Q factor' = weight per Å length of the polymer chain assuming planar zig-zag configuration.

Q factor for polystyrene = 41.4

Q factor for poly PFAAC = 63.5

$$\text{Hence, m.w. of poly PFAAC} = \text{m.w. of polystyrene} \times \frac{63.5}{41.4}$$

In most cases the solvent used in analyses was tetrahydrofuran. In a few cases, samples were sent to be analysed in solution in nitrobenzene, dimethyl sulphoxide and anisole.

2.2 Practical Techniques

Vacuum Sublimation

This technique was used for the purification of solid α-hydroxy acid anhydrocarboxylates, although it was also found that the method was applicable to the purification of the anhydrocarboxylate of phenyl lactic acid which is liquid at room temperature.

Vacuum sublimation was carried out using the apparatus shown in Figure 2.4. The apparatus was baked in an oven at temperatures above 110°C for several hours before use and then transferred into the dry box and allowed to cool. The impure anhydrocarboxylate was

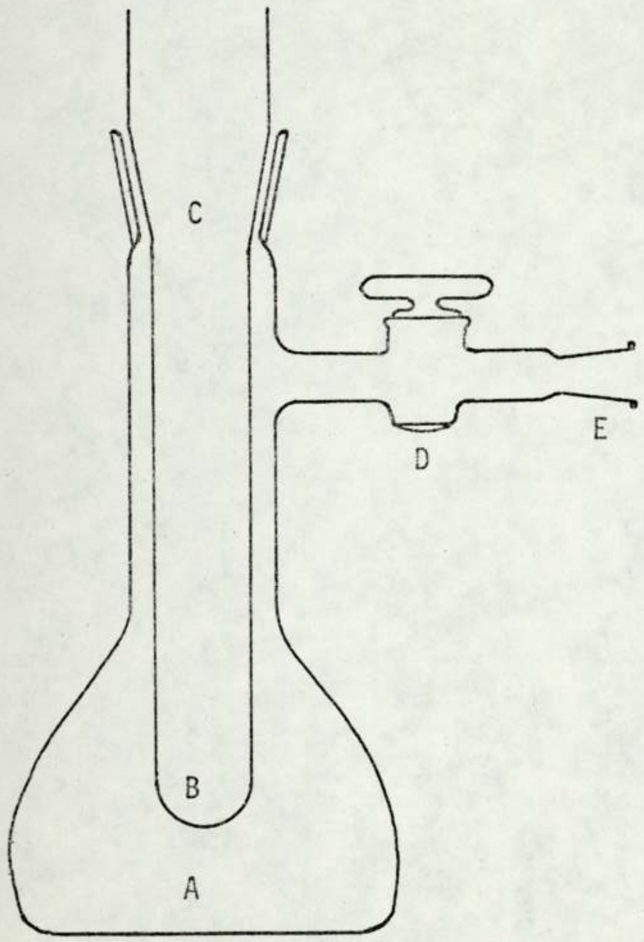


Figure 2.4

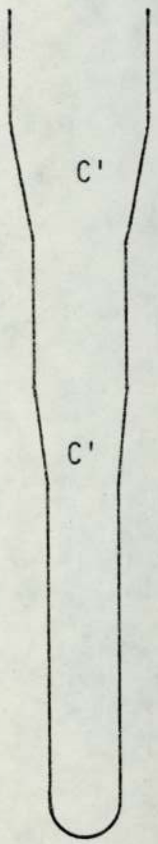


Figure 2.5

placed in the chamber A, the cold finger B then replaced and the tap D closed. All the joints were treated with high vacuum silicone grease to avoid any leakage during sublimation. All the manipulations were carried out in a dry box in order to prevent any moisture from being adsorbed inside the apparatus. The apparatus was then removed from the dry box and connected to a vacuum line via E. The lower part of the chamber A was immersed in an oil bath at a temperature 2-3^{o}C below the melting point of the anhydrocarboxylate. After the apparatus had been evacuated by opening of the tap D, a crushed solid carbon dioxide-acetone mixture was used to fill the cold finger around the lower part of which the sublimed anhydrocarboxylate was collected.

When the sublimation had been completed, the tap was closed and the apparatus was allowed to stand to attain room temperature. The outside of the apparatus was then dried by means of a hot-air blower before it was placed in the dry box when the purified anhydrocarboxylate was removed and collected.

The above method worked well with solid anhydrocarboxylates, but required a slight modification for an anhydrocarboxylate with a melting point below room temperature. Figure 2.5 shows a modified cold finger used in this case incorporating an additional smaller sized cone C' connected below the cone C . When the sublimation was complete the tap D was closed, the apparatus disconnected from the vacuum line and filled with dry helium gas. Then, in the access chamber of the dry box described in Section 2.1, and as quickly as possible, the cold finger was removed and joined via the Cone C to a previously bake-dried tube in order to collect the melting anhydrocarboxylate from the cold finger. These modifications in design and technique were necessary because it was impossible to allow for the whole apparatus to reach room temperature before transferring into a dry box (for the removal of the anhydrocarboxylate) since the anhydrocarboxylate would have melted and dropped onto the remaining impurities in the chamber A.

Polymerisation Techniques

Since anhydrocarboxylates are very sensitive to moisture, all manipulations concerning these compounds required additional protection from adventitious moisture. All manipulations were carried out in a dry box whenever possible.

(a) Polymerisation under reduced pressure

The apparatus used for this purpose is shown in Figure 2.6. Each piece of the apparatus was heated in an oven at temperatures above 110°C for a few hours before use and then placed in a dry box. The required amount of anhydrocarboxylate was placed in a tube A, fitted with a tap B and designed in such a way as to provide extra volume for the carbon dioxide evolved during the polymerisation. A suba-seal was fitted to the socket C, the tap B opened, and an initiator solution injected through the suba-seal by means of a syringe into the tube A. Tap B was closed and the tube was quickly emmersed in liquid nitrogen in order to freeze the reacting solution. The apparatus was connected to a vacuum line via the socket C, tap B opened and the apparatus evacuated. After evacuation the apparatus was then placed in a constant temperature bath at the required temperature to complete the polymerisation. This apparatus enabled bulk polymerisation to be carried out under reduced pressure in cases where the insertion of solid anhydrocarboxylate through the very narrow neck of a Carious tube (which can be used in solution

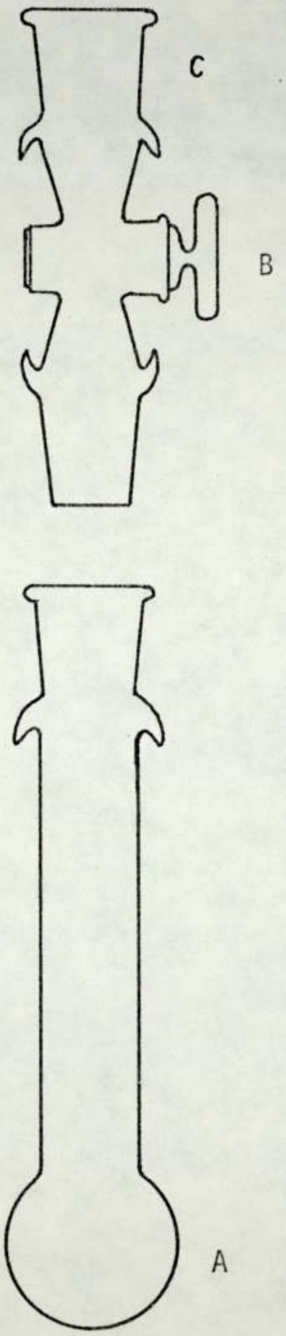


Figure 2.6

polymerisation) became difficult.

(b) Polymerisation at atmospheric pressure

Polymerisation at atmospheric pressure was necessary in order to allow for samples to be taken during polymerisation. The apparatus, shown in Figure 2.7, was a simple three-neck round bottomed flask fitted with an inlet tube for dry helium gas, a drying tube containing anhydrous calcium chloride or molecular sieve in order to prevent access of moisture and, finally, a suba-seal. Solutions of monomer and initiator were introduced into the flask by means of syringes. The helium gas was slowly and continuously passed through the apparatus via the inlet A and the outlet C. Polymerisation samples, at various reaction times, were removed by means of a syringe through a suba-seal at the neck B. An inhibitor was used to terminate polymerisation of the samples extracted. In both polymerisations (1 and 2) high vacuum silicone grease was used for sealing all the joints.

(c) Techniques of kinetic measurement

Decomposition of anhydrocarboxylates results in elimination of carbon dioxide, the rate of decomposition can, therefore, be followed by monitoring the pressure of the evolved gas with time at constant volume and temperature. The derived expression for the rate of decomposition of monomer is given in a later section.

The kinetic apparatus used, as shown in Fig. 2.8, was designed by Tighe(57). It consists of a chamber A where the polymerisation takes place, a mercury reservoir B, and capillary C, which act as a manometer scale. This type of apparatus is very useful at high temperatures, since it has no joints and can be evacuated and sealed off via the side arm D, thus eliminating any possibility of

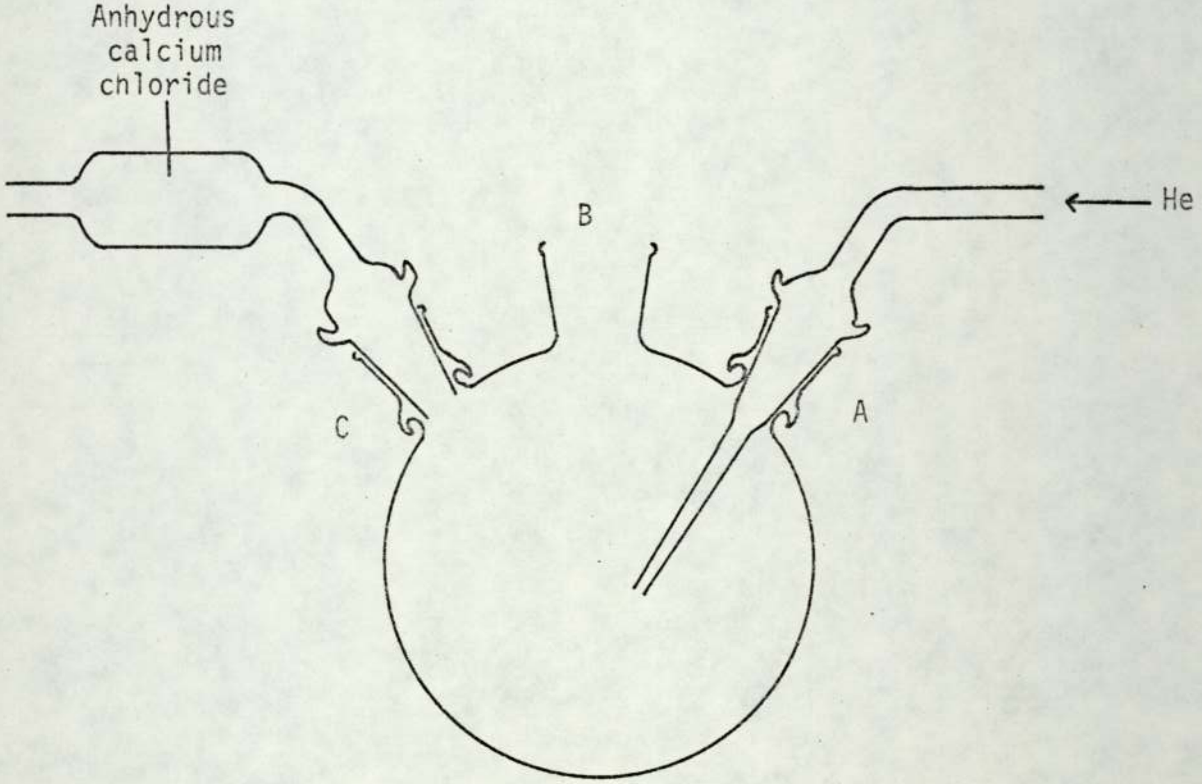


Figure 2.7

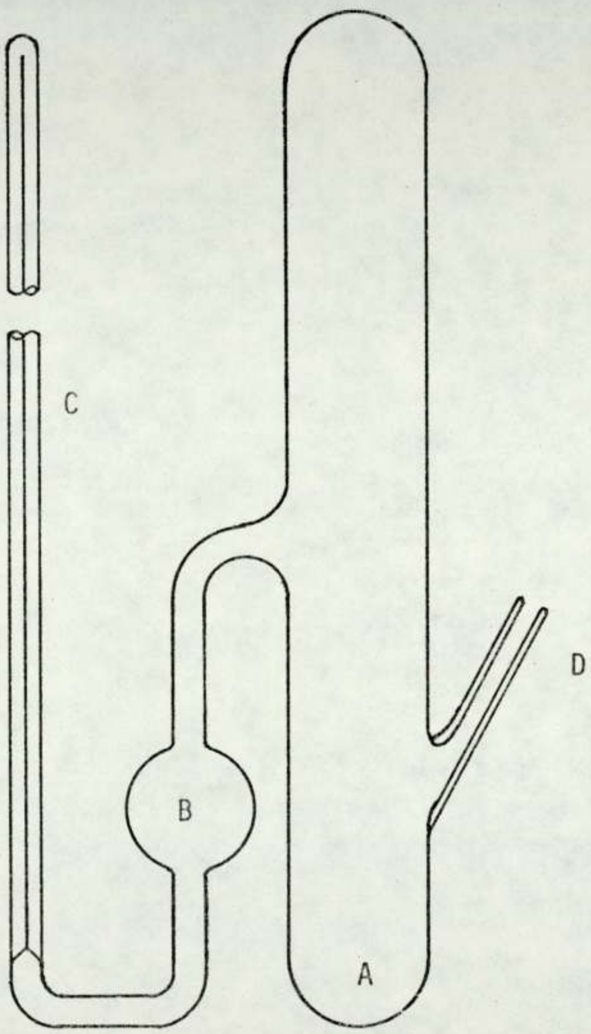


Figure 2.8

any leakage or ingress of moisture into the system.

The level of mercury in the manometer C was followed by means of a cathetometer. Before each reading was taken it was necessary to equilibrate the concentration of evolved carbon dioxide in the solution and in the gas phase. The use of a Pifco vibrator proved to be satisfactory for this purpose. Sufficient time of vibration gave more accurate readings as judged by a cessation in the rise of the mercury level after vibration.

Assuming that the behaviour of carbon dioxide at constant temperature and volume is the same as that of an ideal gas, a simple relationship between monomer concentration and the gas evolved at any given time may be derived.

If $[M]_0$ is the initial monomer concentration,

$[M]$ is the monomer concentration at any time,

$[G]$ is the concentration of evolved carbon dioxide at any time,

and if one mole of monomer decomposes to give one mole of carbon dioxide, then

$$[M]_0 = [M] + [G] \tag{2-1}$$

If the reaction proceeds to completion,

$$[M]_0 = [G]_\infty \tag{2-2}$$

For an ideal gas at constant temperature and volume, Henry's law applies and thus the pressure P of the gas is directly proportional to the number of moles of gas evolved.

i.e., $$P \propto [G] \tag{2-3}$$

Hence $$P_\infty \propto [G]_\infty \tag{2-4}$$

and $$\pi P = [G]_\infty = [M]_0 \tag{2-5}$$

where π is a proportionality constant.

If P is the pressure of carbon dioxide at any instant, equation (2-1) may be rearranged and written as:

$$\pi P = [G] = [M]_0 - [M] \qquad (2\text{-}6)$$

Equation (2-5) and (2-6) now combine to give the relationship:-

$$\frac{[M]}{[M]_0} = \frac{P_\infty - P}{P_\infty} \qquad (2\text{-}7)$$

or

$$\frac{[M]_0 - [M]}{[M]_0} = \frac{P}{P_\infty} \qquad (2\text{-}8)$$

The use of equation (2-7) and (2-8) enables kinetic parameters to be evaluated.

Precipitation of Polymers

Low molecular weight poly α-esters are soluble in some solvents, e.g. toluene, nitrobenzene, tetrahydrofuran and chloroform. When a polymerisation had been completed, the solvent was evaporated under reduced pressure and the remaining solid was redissolved in a small amount of chloroform. Polymer was precipitated out of solution by addition to a non-solvent such as petroleum ether of 40-60°C boiling range. The solution was left in a refridgerator for the precipitation to become complete. For small quantities of polymer, separation was achieved by means of centrifugation.

2.3 Purification of Solvents and Reagents

The main requirement for solvent purification was the exclusion of trace amounts of water. In general the methods used were taken from Weissberger(69) and Vogel(70) with modifications of techniques and drying agents employed. The distillations at atmospheric pressure were carried out using a stream of dry nitrogen, vented to air through anhydrous calcium chloride drying tubes to prevent entering of moisture.

Nitrobenzene - The A.R. grade of nitrobenzene supplied by Fison Scientific Apparatus Limited was allowed to stand over phosphorus pentoxide and then refluxed for twenty four hours. It was then distilled under reduced pressure using a dry nitrogen bleed system. The middle fraction was collected over anhydrous barium oxide.

The solvent was kept in a dry box and distilled under reduced pressure prior to use. The middle fraction was collected at 70°C, 0.5 mm of mercury.

Dimethyl Sulphoxide - Dimethyl sulphoxide was shaken several times with anhydrous calcium sulphate and then refluxed over anhydrous barium oxide for twenty four hours. It was fractionally distilled under reduced pressure and collected over anhydrous barium oxide. The solvent was redistilled under reduced pressure prior to use, the middle fraction boiling at 70°C at 16 mm mercury was collected.

Anisole - Anisole was dried over anhydrous calcium chloride for the period of twenty four hours and fractionally distilled under reduced pressure onto anhydrous barium oxide. The solvent was redistilled, and the middle fraction collected prior to use.

Toluene - The solvent was distilled at atmospheric pressure with precautions for exclusion of moisture. The distilled toluene was then refluxed over sodium wire for twenty four hours, followed by distillation. The distillate was stored over sodium wire which was also used to indicate the dryness of the solvent by its change in surface brightness. The solvent was redistilled before use.

Diethyl Ether - Two different grades of diethyl ether supplied by Fison Scientific Apparatus Limited were used. Diethyl ether anhydrous pruiss. A.R. grade specially suitable for grignard reactions was used in preparations of pentafluorophenyl magnesium bromide. In other cases the dried distilled grade with a maximum water content of 0.01% was used in the general preparation of anhydrocarboxylates.

Tetrahydrofuran - The solvent was allowed to stand over anhydrous calcium chloride for several days then fractionally distilled at atmospheric pressure. The distillate was refluxed over sodium wire with a small amount of naphthalene in the system. The dryness was indicated by the green colour of the solution resulting from the forming of naphthanate ion. The solvent was stored in a dry box and redistilled before use.

Pyridine - The anhydrous grade of pyridine supplied by B.D.H. Limited, with a maximum water content of 0.02%, was refluxed with analytical grade potassium hydroxide for twenty four hours with precautions for exclusion of moisture. It was then distilled under reduced pressure and the middle fraction was collected over A.R. potassium hydroxide.

Diphenyl-2-Pyridyl Methane - This solid substituted pyridine was supplied by Phase Separation Limited. It was dried under high vacuum in a desiccator containing fresh silica gel and a tray of phosphorus pentoxide for several weeks.

2,2'-Bipyridyl - The reagent supplied by Fison Scientific Apparatus Limited was dried in the same manner as diphenyl-2-pyridyl methane.

Decane-1,10-Diol - The reagent supplied by B.D.H. Limited was also dried in a high vacuum desiccator containing fresh silica gel.

Lithium Tertiary Butoxide - The reagent supplied by Alfa Inorganics was stored in a dry box and used without further purification.

Bromopentafluorobenzene - The chemical used in the early period of the work was generously provided by the Imperial Smelting Corporation, Avonmouth, further supplies were obtained from Bristal Organics Limited, both were used without further purification.

DL-2-Phenyllactic Acid - This was obtained from Koch-Light Laboratory Limited.

Cyclopentanol-1-carboxylic Acid - This was obtained from Newton Main Limited.

Glycollic Acid - This was supplied in 65-67% w/v solution by B.D.H. Limited.

Phosgene - This was supplied by B.D.H. Laboratory Gas Service Ltd.

Pyruvic Acid - This was supplied by B.D.H. Limited and Aldrich Chemical Company Inc. This reagent dimerises slowly to form α-keto-γ-valerolactone-γ-carboxylic acid. To minimise the cyclisation reaction the acid was stored at $0^{o}C$.

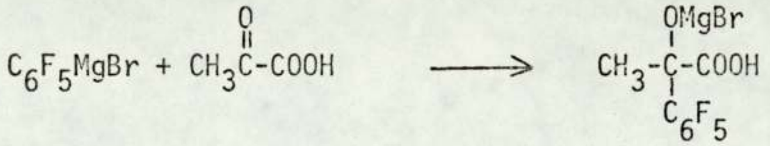
CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF α -HYDROXY CARBOXYLIC ACIDS AND ANHYDROCARBOXYLATES - RESULTS AND DISCUSSION

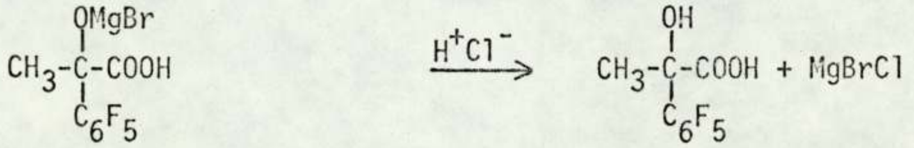
3.1 Synthesis of 2-Hydroxy-2-Pentafluorophenyl Propanoic Acid

The method employed involved the reaction between an α-keto acid, pyruvic acid, and a Grignard reagent, pentafluorophenyl magnesium bromide, followed by hydrolysis of the reaction product.

$$C_6F_5Br + Mg \longrightarrow C_6F_5MgBr \qquad (3\text{-}1)$$



$$C_6F_5MgBr + CH_3\overset{\overset{O}{\|}}{C}\text{-}COOH \longrightarrow CH_3\text{-}\underset{C_6F_5}{\overset{OMgBr}{C}}\text{-}COOH \qquad (3\text{-}2)$$



$$CH_3\text{-}\underset{C_6F_5}{\overset{OMgBr}{C}}\text{-}COOH \xrightarrow{H^+Cl^-} CH_3\text{-}\underset{C_6F_5}{\overset{OH}{C}}\text{-}COOH + MgBrCl \qquad (3\text{-}3)$$

30.9g(0.125 moles) bromopentafluorobenzene were slowly dropped onto 3.04 g (0.125 moles) magnesium turnings in 125 ml anhydrous diethyl ether. One or two iodine crystals would be used to start the reaction but two or three drops of 1,2-dibromoethane were preferable. When the addition was complete, the reacting solution was left refluxing for a period of two hours. 8.8 ml (0.125 moles) pyruvic acid in 25 ml anhydrous diethyl ether were slowly added to the stirred Grignard solution which was kept at a temperature of below 5^{o}C during the addition. The solution was allowed to warm to room temperature and then stirred for 24 hours. The reaction product was hydrolysed with 40 ml 4N hydrochloric acid and the etheral layer separated. Removal of solvent and volatile compounds, e.g., unreacted bromopentafluorobenzene and pentafluorobenzene formed by hydrolysis of pentafluorophenyl magnesium bromide, left crude 2-hydroxy-2-pentafluorophenyl propanoic acid as a brown solid. The crude product could be either purified by reprecipitation in benzene/petroleum ether or used in the next step (Section 3.2.1) in the preparation of anhydrocarboxylate without initial purification. The purified acid was a white crystalline product with a melting point of 129°C.

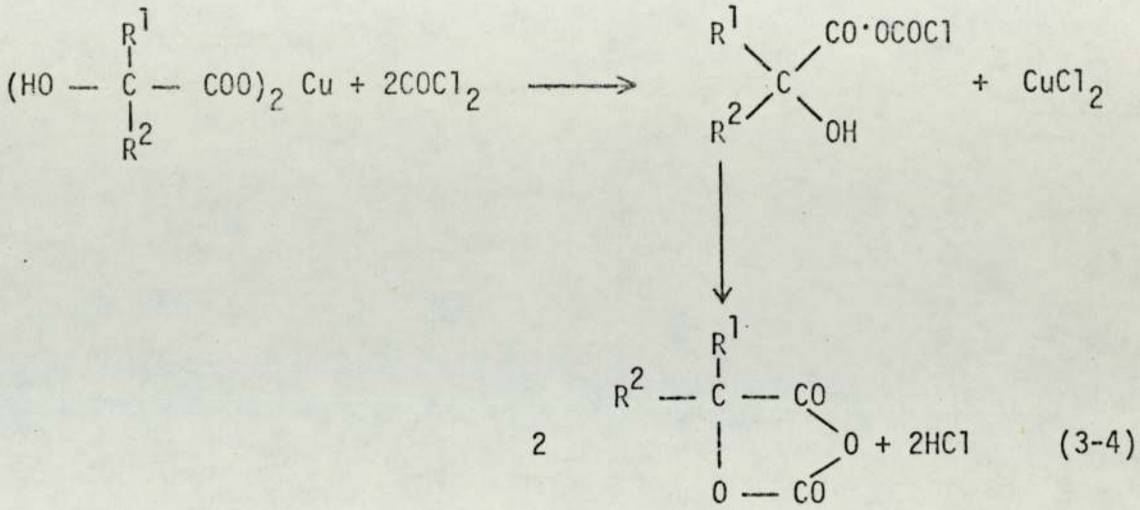
The yield of α-hydroxy acid obtained depended markedly on the purity of the pyruvic acid used. Pure pyruvic acid was essential in order to obtain a reasonably high yield. Several months during the period of the present work were spent unsuccessfully on experiments which involved using impure pyruvic acid, resulting in very low yield and a high degree of impurity. Although stored in a refridgerator, pyruvic acid polymerised slowly to form α-keto-α-valerolactone-α-carboxylic acid.

Purification of the acid was unsuccessful, resulting in an increase in the amount of dimer obtained, as reflected by an increase in viscosity and yellowing in colour. Infra-red spectroscopy and gas-liquid chromatography proved to be of little use in determining the purity of pyruvic acid.

3.2 Synthesis of α-Hydroxy Carboxylic Acid Anhydrocarboxylates

The anhydrocarboxylates were prepared by the reaction of phosgene on the anhydrous copper (II) salts of the corresponding α-hydroxy acids. The reasons why the copper (II) salt of the acid was preferred to the acid itself in the synthesis are to be discussed later in this chapter.

The equation shown overleaf is a general synthetic route for anhydrocarboxylates synthesised in the present work.


(3-4)

3.2.1 Preparation of Copper(II) Salts of α-Hydroxy Acids

An α-hydroxy carboxylic acid was converted into its copper(II) salt via the reaction of chloride with the ammonium salt. 3N ammonia solution was added to a slurry of the α-hydroxy acid in distilled water until the solution became neutral. The change in pH was checked with 1-14 pH - indicating paper or monitored by a pH meter. An excess of saturated copper(II) chloride solution was then added to the ice-cooled, neutral solution of the aqueous ammonium salt until precipitation of the copper(II) salt of the α-hydroxy acid was complete. The salt was separated by filtration, washed with distilled water and diethyl ether, and finally dried in vacuo at a temperature of 120°C for a minimum period of 48 hours. The copper(II) salts obtained ranged in colour from pale green to deep blue when hydrated and brown to green in anhydrous state, depending on the nature of the corresponding α-hydroxy acids. The absence of any weight loss at around 100°C on the T.G.A. trace indicated the anhydrous state of the salt.

Both purified and impure α-hydroxy acids were used in preparations of copper(II) salts. In the case of unpurified

α-hydroxy acid, the impurities existed in the form of tar which was not soluble in a neutral aqueous ammonium salt solution and was discarded by filtration.

3.2.2 Synthesis of 2-Hydroxy-2-pentafluorophenyl Propanoic Acid Anhydrocarboxylate

A solution of 4.95 g (0.110 moles) phosgene dissolved in 75 ml dried-distilled diethyl ether was slowly dropped onto 26.68 g (0.05 moles) copper(II) salt of 2-hydroxy-2-pentafluorophenyl propanoic acid slurried in 150 ml dried-distilled ether. The solution was stirred at a moderate speed during the addition which lasted 1 to 2 hours. The solution was then left stirring for 5 days at room temperature with precaution to avoid ingress of moisture. 7.24 ml (0.09 moles) of anhydrous pyridine dissolved in 30 ml dried-distilled ether was added to remove the hydrogen chloride formed in the cyclisation reaction. The precipitate of copper(II) chloride and pyridine hydrochloride were removed by filtration and washed with dried-distilled ether to remove any remaining anhydrocarboxylate. The solvent, unreacted phosgene and hydrogen chloride were removed by evaporation under reduced pressure at a temperature about 30°C and the solid remaining left under vacuum for 2-3 hours to remove the final traces of volatile material.

2-hydroxy-2-pentafluorophenyl propanoic acid anhydrocarboxylate, after vacuum sublimation, was obtained as a white crystalline solid which melts at 62 °C.

3.2.3 Synthesis of Atrolactic Acid Anhydrocarboxylate

A solution of 4.95 g (0.110 moles) of phosgene dissolved in 75 ml dried-distilled ether was slowly dropped to 19.6 g (0.05 moles) copper(II) salt of atrolactic acid in 150 ml dried-distilled ether.

The solution was left stirring at room temperature for 5 days, then treated with 7.24 ml (0.09 moles) anhydrous pyridine in 30 ml dried-distilled ether. The precipitate was separated and the solvent and volatile material were evaporated at a temperature well below 10^{o}C. The crude anhydrocarboxylate was obtained as a yellowish oil or a semi-solid mixture of the anhydrocarboxylate and solid impurities.

The purified anhydrocarboxylate obtained from vacuum sublimation was a viscous, colourless liquid.

3.2.4 Synthesis of Mandelic Acid Anhydrocarboxylate

A solution of 4.95 g (0.110 moles) of phosgene in 75 ml dried-distilled ether was slowly dropped onto 18.3 g (0.05 moles) copper(II) salt of mandelic acid in 150 ml dried-distilled ether. The solution was left stirring at room temperature for 4 days, then, without being treated with pyridine, filtered, followed by evaporation of the solvent and volatile material.

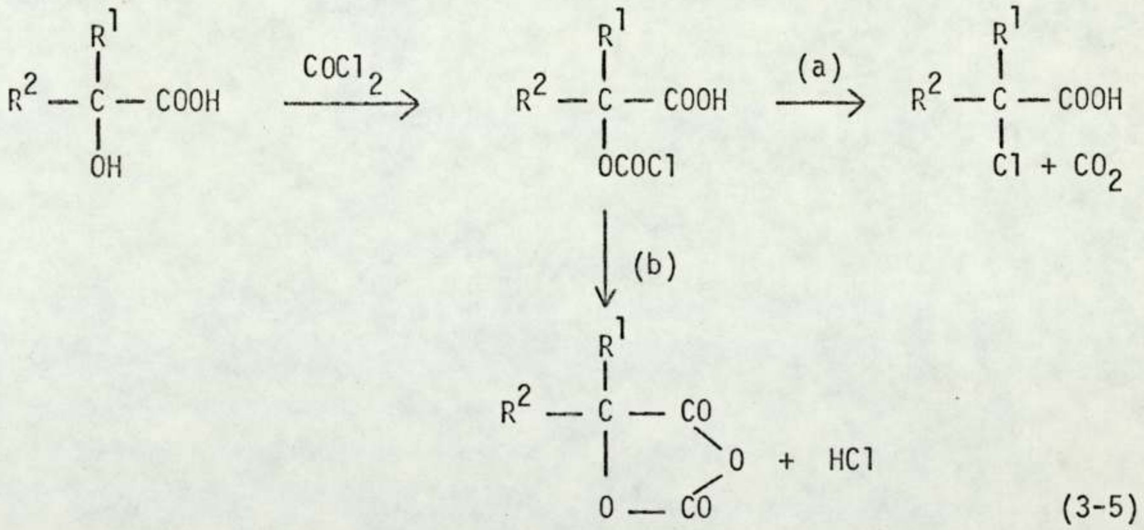
3.2.5 Synthesis of Spiro-Cyclopentyl Anhydrocarboxylate

The anhydrocarboxylate of cyclopentanol-1-carboxylic acid was prepared in the same manner as the other anhydrocarboxylates. 4.95 g (0.110 moles) phosgene in 75 ml dried-distilled ether was slowly dropped onto a slurry of 16.0 g (0.05 mole) copper(II) salt of cyclopentanol-1-carboxylic acid in 150 ml dried-distilled ether, and the solution left stirring for 5 days. After the precipitate was separated, the solvent and volatile material were evaporated under reduced pressure. The anhydrocarboxylate obtained was a white solid with a melting point of 64^{o}C.

3.2.6 Synthesis of Glycollic Acid Anhydrocarboxylate

The solution of 4.95 g (0.110 moles) of phosgene in 75 ml dried-distilled ether was slowly dropped onto 10.68 g (0.05 moles) copper(II) glycollate slurried in 150 ml dried-distilled ether, then it was left stirring at room temperature for 4 days. The solution was then (without being treated with pyridine) filtered and the solvent and volatile material were evaporated at a temperature well below 10°C. Purification of the anhydrocarboxylate, which decomposed on melting, was very difficult.

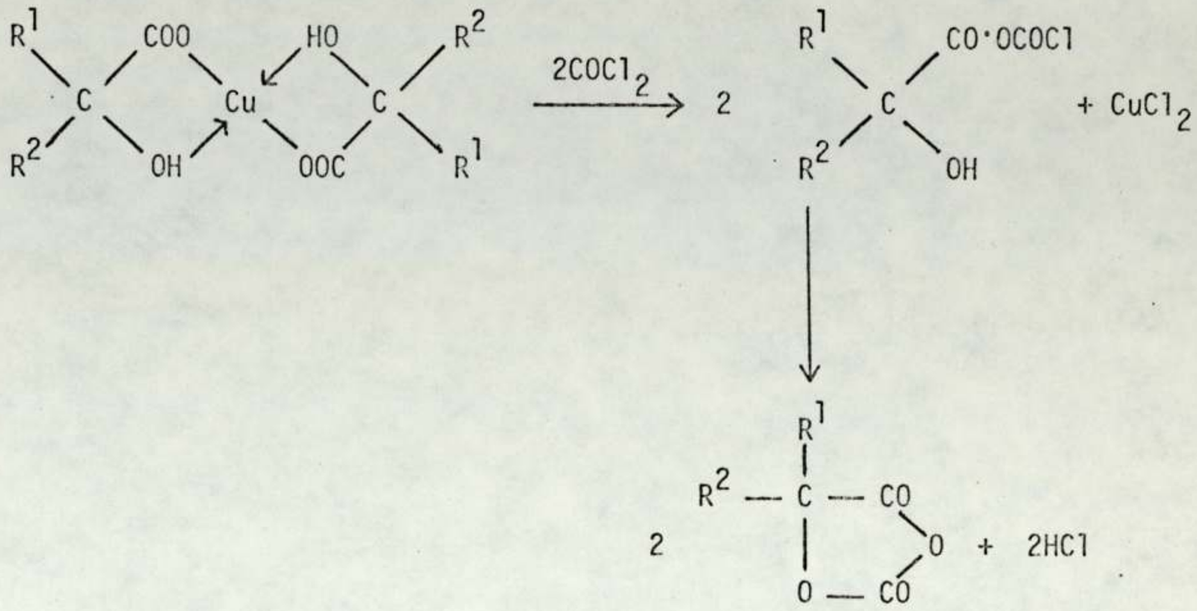
The above method of synthesis of anhydrocarboxylate of α-hydroxy acids, involving the reaction of copper(II) salts of the corresponding acids with phosgene, had been chosen because of greater advantages over the other method in which α-hydroxy acids were directly reacted with phosgene. The reaction of phosgene with phenyl substituted α-hydroxy acids gives an appreciable quantity of α-chloro acid impurity, as shown by a suggested reaction scheme below.



(3-5)

The alkyl chloroformate, addition product of phosgene on the hydroxyl terminal of an α-hydroxy acid, tends to lose carbon dioxide to form the α-chloro acid. The loss of hydrogen chloride from the chloroformate results in cyclisation to give an anhydrocarboxylate ring.

The use of copper(II) salt favours the formation of an acyl chloroformate by an attack of the phosgene molecule at the carboxylate anion as shown below.



(3-6)

Subsequent loss of hydrogen chloride from the acyl chloroformate results in formation of the anhydrocarboxylate ring.

Furthermore, copper(II) salts are easily obtained in an anhydrous state, thus reducing the amount of parent acid impurity which is generated by the reaction of the pre-formed anhydrocarboxylate with moisture.

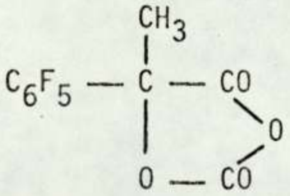
Another advantage is that half of chlorine impurity produced from the reaction is removed as a precipitate of anhydrous copper(II) chloride.

Ketone formation was found in the synthesis of one anhydrocarboxylate. Infra-red and nuclear magnetic resonance spectra showed the presence of acetophenone in a crude anhydrocarboxylate of atrolactic acid synthesised by the method described previously. It was suggested that the pyridine and resultant pyridine hydrochloride could have promoted a decomposition of the acyl chloroformate to the corresponding ketone. This suggestion was made on the basis of the known decomposition of alkyl chloroformates and alkyl chlorosulphinates to form corresponding alkyl chloride with the liberation of carbon dioxide in the presence of pyridine and pyridine hydrochloride(73).

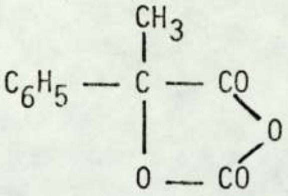
Pyridine, used in the present work as initiator, may also promote the decomposition of pre-formed anhydrocarboxylates when used in excess for the removal of hydrogen chloride during the preparation of anhydrocarboxylate. In cases of highly reactive anhydrocarboxylates (to an attack by a nucleophile), such as mandelic and glycollic anhydrocarboxylates, in order to achieve a reasonably high percentage yield it is preferable not to use pyridine in the synthesis of these anhydrocarboxylates.

3.3 Characterisation of α-Hydroxy Acids, Copper(II) Salts and Anhydrocarboxylates

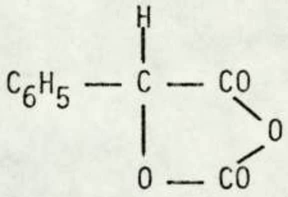
The anhydrocarboxylates prepared are as follows:-



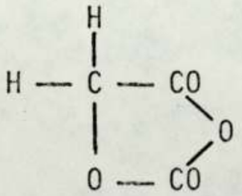
(X)



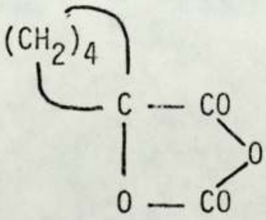
(XI)



(XII)



(XIII)



(XIV)

These ring compounds may be named systematically, however for the convenience of reference throughout the text, the trivial

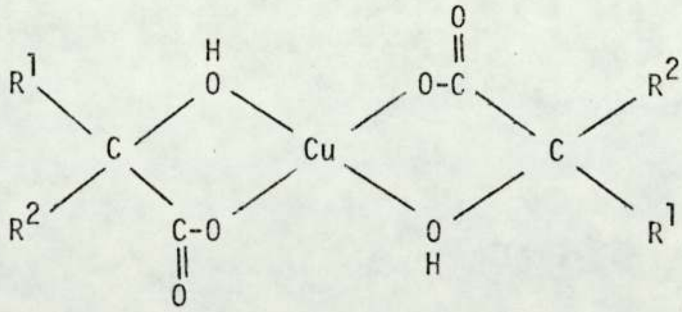
Table 3.1

α-Hydroxy acids and their anhydrocarboxylates

Parent Acid	R^1	R^2	Anhydrocarboxylate (Abbreviation)	Anhydrocarboxylate (Systematic name)
2-Hydroxy-2-pentafluorophenyl propanoic acid	C_6F_5	CH_3	PFAAC (X)	5-methyl-5-pentafluorophenyl-1,3-dioxolan-2 ,4-dione
Atrolactic acid	C_6H_5	CH_3	AAAC (XI)	5-methyl-5-phenyl-1,3-dioxolan-2,4-dione
Cyclopentanol-1-carboxylic acid	$(CH_2)_4$		C'pent AC (XIV)	Cyclopentane spiro-5-1,3-dioxolan-2,4-dione
Mandelic acid	C_6H_5	H	MAAC (XII)	5-phenyl-1,3-dioxolan-2,4-dione
Glycollic acid	H	H	GAAC (XIII)	1,3-dioxolan-2,4-dione

names or their abbreviations are preferred. Table 3.1 shows the names of the anhydrocarboxylates together with the parent acids, corresponding α -hydroxy acids.

α-hydroxy acids can be easily characterised by their infrared spectra. An infrared spectrum of an α-hydroxy acid obtained by KBr disc shows a peak around 1700-1800 cm^{-1} which is a carbonyl stretching vibration. This, is a characteristic absorption for a specific α-hydroxy acid, the precise position at which the absorption occurs is governed by the nature of the substituents on the α-C of the acid. The absorption due to the hydroxylic stretching is a sharp medium peak at about 3400 cm^{-1}. The spectrum of 2-hydroxy-2-pentafluorophenyl propanoic acid is shown in Figure 3.1. The carbonyl stretching vibration is at 1740 cm^{-1} and the free hydroxyl stretching is at 3400 cm^{-1}. The free hydroxyl stretching absorption does not appear on a spectrum of a copper(II) salt of the corresponding acid, instead a broad absorption band is found in the region of 3000-3500 cm^{-1}. This is explained by the suggested structure of a copper(II) salt.



(XV)

Hydroxyl groups in a copper(II) salt are not free, they are believed to co-ordinate with the copper(II) metal. The carbonyl stretching absorption of a copper(II) salt occurs at lower frequencies than those of the acids. Figure 3.2 shows the spectrum of the copper(II) salt of 2-hydroxy-2-pentafluorophenyl propanoic acid

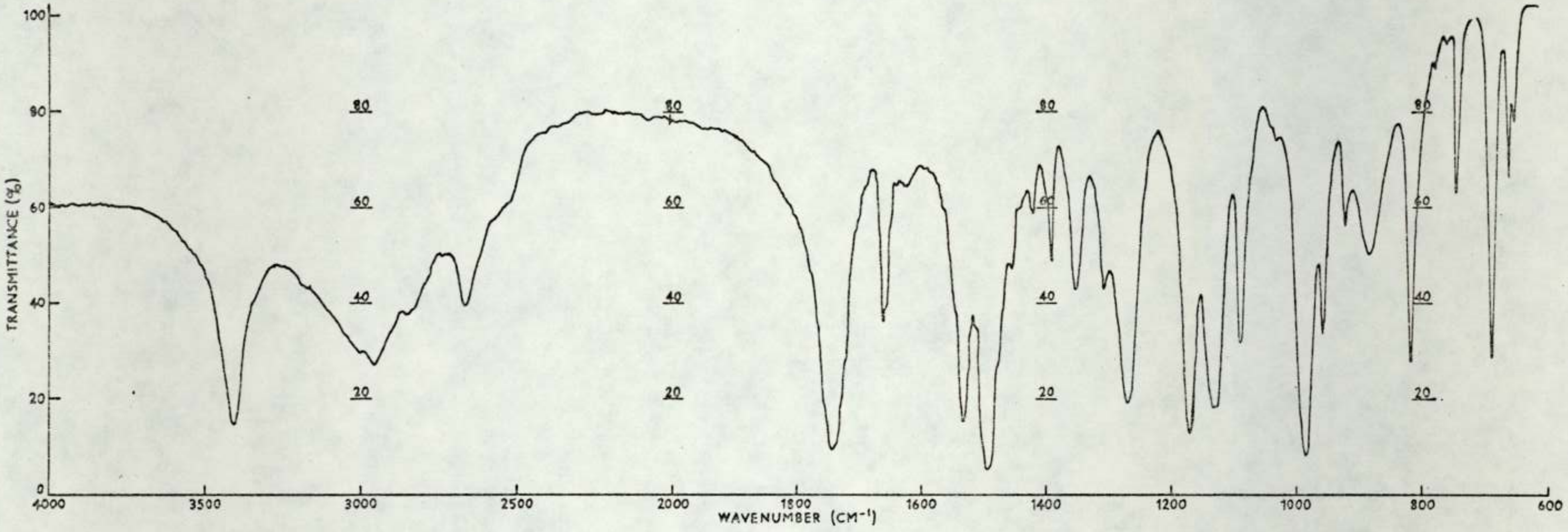


Figure 3.1 IR 3.1. Spectrum of 2-hydroxy-2-pentafluorophenyl propanoic acid

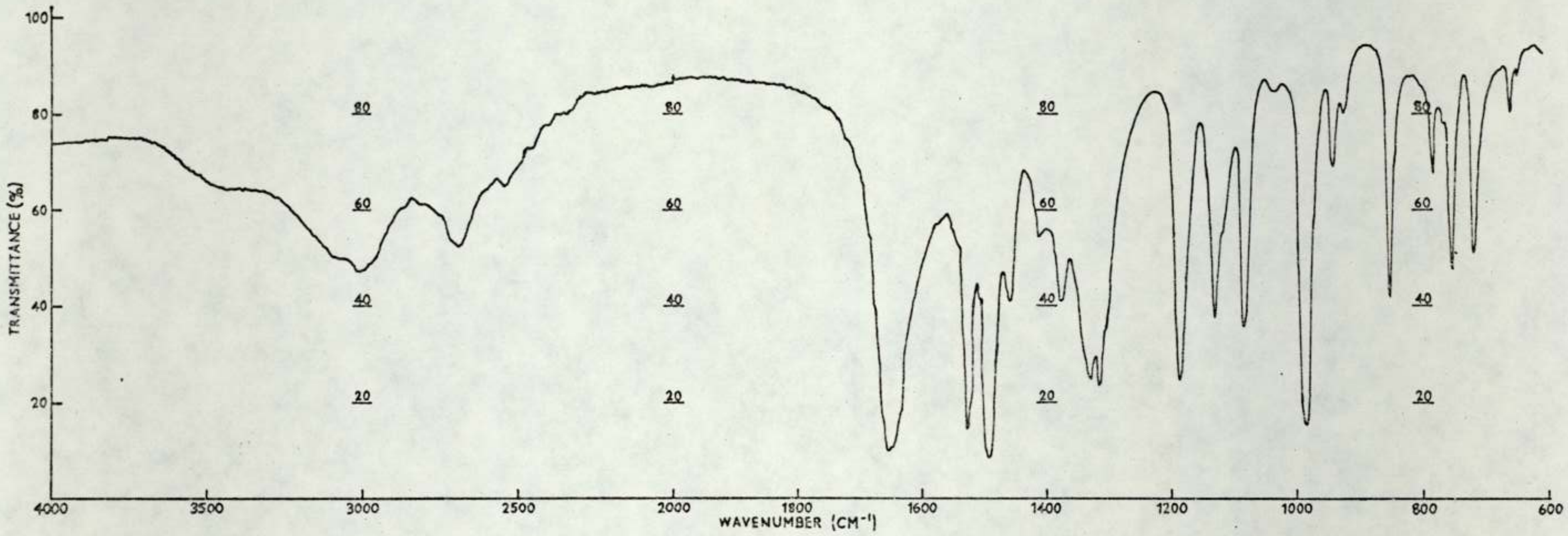


Figure 3.2 IR 3.2. Spectrum of copper(II) salt of 2-hydroxy-2-pentafluorophenyl propanoic acid

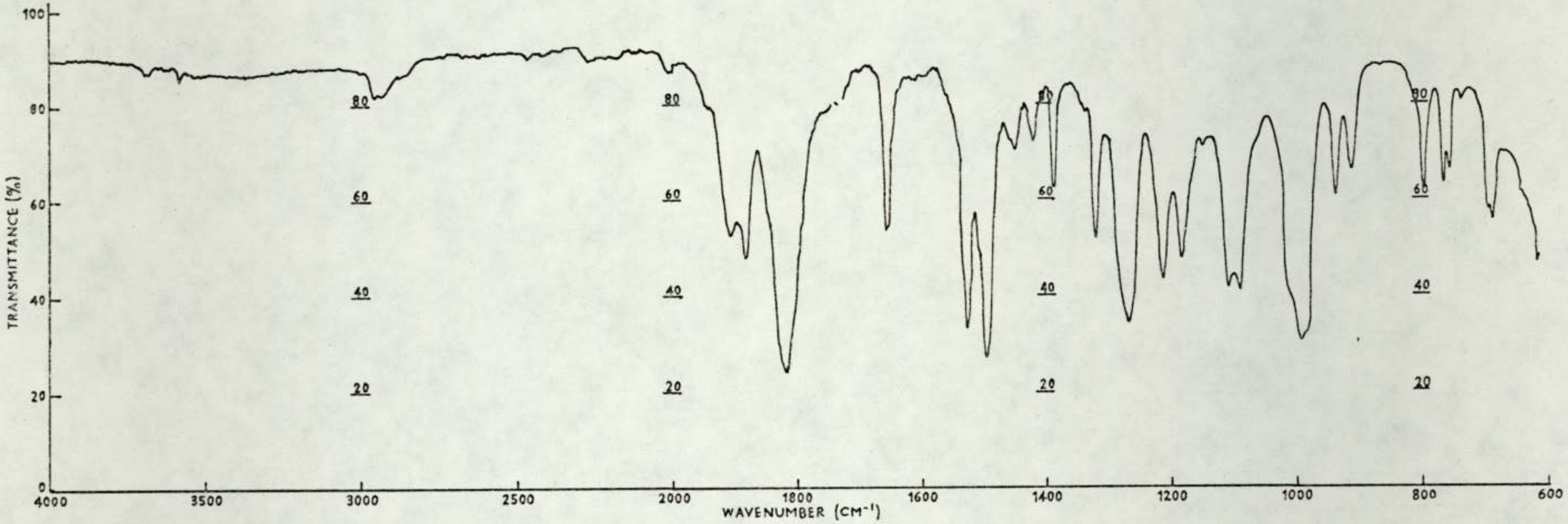


Figure 3.3 IR 3.3. Spectrum of 2-hydroxy-2-pentafluorophenyl propanoic acid anhydrocarboxylate, PFAAC

the sharp hydroxyl stretching peak is replaced by a typical broad band of bound hydroxyl absorption.

The spectra of anhydrocarboxylates show even more marked change at both hydroxyl and carbonyl stretching regions. Anhydrocarboxylates display two stretching bands in the carbonyl region and the absence of hydroxyl absorption nearer 3400 cm^{-1}. The two bands result from the stretching modes of two different carbonyl groups in the ring. The positions of the bands are at higher frequencies or shorter wavelengths than those of their parent acids. The increase of frequency of carbonyl absorption in a ring is because of ring strain resulting from the decrease in rotational freedom of the carbonyl group restricted by ring formation. A similar increase in carbonyl absorption frequencies may be seen in the five membered cyclic anhydrides of carboxylic acids. The anhydrides show absorption at higher frequencies (shorter wavelengths) than noncyclic anhydrides because of ring strain; succinic anhydride absorbs at 1865 cm^{-1} and at 1782 cm^{-1} while saturated and conjugated noncyclic anhydrides absorb near both 1818 cm^{-1} and 1750 cm^{-1} and near 1775 cm^{-1} and 1720 cm^{-1} respectively. The two carbonyl bands of anhydrocarboxylates are not equal in intensity, a higher frequency band is of medium intensity and a lower frequency band is of high intensity.

The spectrum of 2-hydroxy-2-pentafluorophenyl propanoic acid anhydrocarboxylate is shown in Figure 3.3. The characteristic C-F absorptions of the pentafluorophenyl group are shown at 1660 cm^{-1} and 1532 cm^{-1}, both are medium to strong intensity. Table 3.2 contains the carbonyl stretching vibration frequencies of α-hydroxy acids, copper(II) salts and anhydrocarboxylates.

Table 3.2

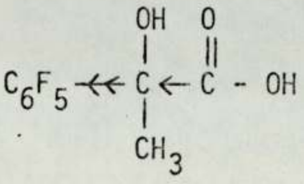
Carbonyl absorptions for α-hydroxy acids, their copper(II) salts and the corresponding anhydrocarboxylates

Parent acid	α-hydroxy acid cm^{-1}	Copper(II) salt cm^{-1}	Anhydrocarboxylate cm^{-1}*
2-hydroxy-2-pentafluorophenyl propanoic acid	1740	1650	1822 (s) 1881 (m)
Atrolactic acid**	1725	1633	1813 (s) 1885 (m)
Cyclopentanol-1-carboxylic acid	1728	1637	1800 (s) 1874 (m)

* s - strong intensity absorption
m - medium intensity absorption

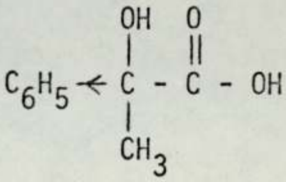
** the spectrum obtained by thin smear

The effect of the pentafluorophenyl group on the carbonyl absorption is displayed by comparison of the frequency of the carbonyl absorptions for 2-hydroxy-2-pentafluorophenyl propanoic acid and its analogue, atrolactic acid.



$$C_6F_5 \twoheadleftarrow \overset{OH}{\underset{CH_3}{C}} \leftarrow \overset{O}{\overset{\|}{C}} - OH$$

(XVI)



$$C_6H_5 \leftarrow \overset{OH}{\underset{CH_3}{C}} - \overset{O}{\overset{\|}{C}} - OH$$

(XVII)

The presence of a pentafluorophenyl group as a substituent affects the carbonyl stretching vibration by increasing the difficulty in vibration. This is shown in the displacement of the carbonyl vibration frequency to a shorter wavelength, (i.e. higher energy). The electron densities of the carbonyl carbons in the two acids, XVI and XVII, are equally affected by the identical combination of inductive effect from methyl and hydroxyl groups. However, the pentafluorophenyl group is a more strongly electron-withdrawing substituent than the phenyl group and so exerts a more effective inductive effect than that of the phenyl substituent. Thus the carbonyl carbon in XVI carries more positive charge than its analogue in XVII. The displacement to a shorter wavelength of the carbonyl absorption frequency of the pentafluorophenyl substituted acid is thus caused by the stronger C=O bond. This effect is also observed for the carbonyl absorptions in the copper(II) salts of the two acids.

The effect can still be distinguished in the respective anhydrocarboxylates although it is overshadowed by the greater effects of ring strain.

The chemical shifts from high resolution nuclear magnetic resonance carried out in 5-10% w/v solutions of α -hydroxy acids and the corresponding anhydrocarboxylates are shown in Table 3.3.

The fluorine resonance spectra of 2-hydroxy-2-pentafluorophenyl propanoic acid and its anhydrocarboxylate were consistent with a pentafluoro substituted benzene ring. Fluorine-fluorine couplings of the distinct ortho, meta and para fluorines of the pentafluorophenyl group were observed. It is noted that the proton resonance of the methyl groups in both the fluorinated α-hydroxy acid and anhydrocarboxylate are moved to lower field frequency by the presence of a pentafluorophenyl substituent, compared with the R^2 resonance of atrolactic acid. Also the methyl resonance occurs as a triplet whereas only a singlet is observed in the non-fluorinated compounds. This is attributed to the long range spin-spin coupling with the two ortho fluorine atoms on the pentafluorophenyl substituent.

The mass spectra of anhydrocarboxylates have been studied and it is interesting to note that top mass peaks observed correspond to the molecular weight of the anhydrocarboxylates. These observed top mass peaks may be used to indicate that the thermal stability of anhydrocarboxylates is greater than those shown by anhydrosulphite rings in which no such peak was observed(50),(58). Principal ring fragmentation peaks observed correspond to the following fragmentation pattern, which appears to be typical of the anhydrocarboxylate ring and represents a stepwise fragmentation of the ring system.

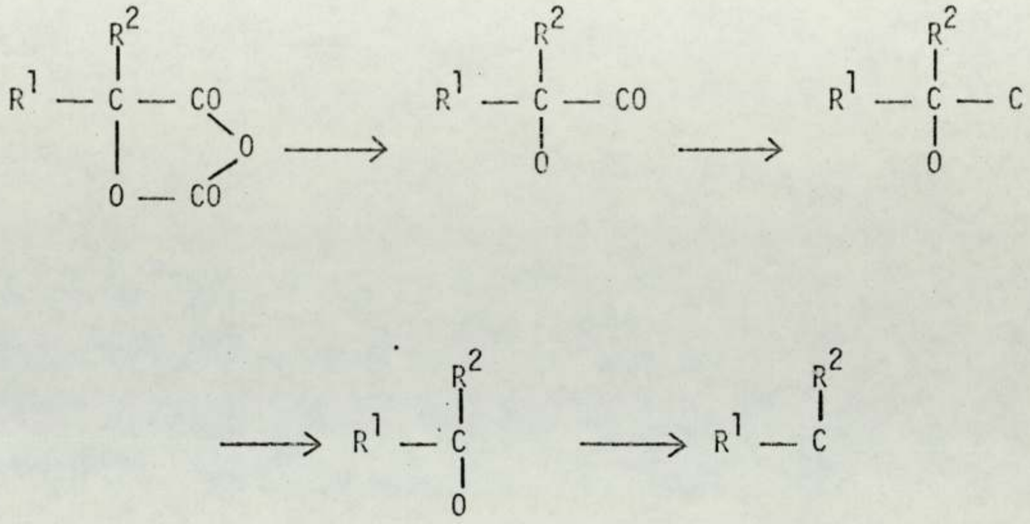
Table 3.3

Nuclear magnetic resonance spectra recorded from deuterochloroform solution, 10% w/v at 100 MHz. Reference T.M.S.

Parent Acid		α-hydroxy Acid*	Anhydrocarboxylate*
2-hydroxy-2-pentafluorophenyl propanoic acid**	$R^1 = C_6F_5$	-	-
	$R^2 = CH_3$	7.99 (t)	7.75 (t)
Atrolactic acid	$R^1 = C_6H_5$	2.63 (m)**	2.52 (m)
	$R^2 = CH_3$	8.18 (s)	8.01 (s)
Cyclopentanol-1-carboxylic acid **	$(CH_2)_4$	8.09 (umc)	7.93 (umc)
Mandelic acid	$R^1 = C_6H_5$	2.50 (s)	2.49 (s)
	$R^2 = H$	4.70 (s)	3.98 (s)

* (s) - singlet , (t) - triplet , (m) - multiplet , (umc) - unresolved multiple couplet.

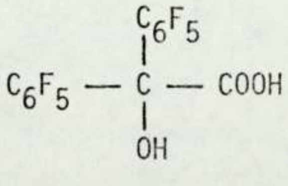
** spectra recorded at 60 MHz.



All anhydrocarboxylates are solid with the exception of atrolactic acid anhydrocarboxylate, which is liquid. The melting points of the anhydrocarboxylates were determined by a differential scanning calorimetric method which gave a higher accuracy than a conventional method. Table 3.4 and Table 3.5 show the physical properties of copper(II) salts and α-hydroxy acids and anhydrocarboxylates.

3.4 Perfluoro α-Hydroxy Carboxylic Acids

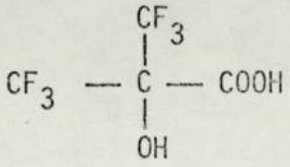
Several attempts have been made in this and related work(66) to synthesise decafluorobenzilic acid, XVIII,



$$C_6F_5 - \underset{OH}{\overset{C_6F_5}{C}} - COOH$$

(XVIII)

because of the fact that this acid and the related hexafluoro α-hydroxy isobutyric, XIX, acid provide a potential route to perfluoro aromatic and aliphatic poly α-ester respectively.



$$CF_3 - \underset{OH}{\overset{CF_3}{C}} - COOH$$

(XIX)

Table 3.4

Physical properties of copper(II) salts of α-hydroxy carboxylic acids

Copper(II) salt	C, H Analysis			
	Theoretical %		Analysed %	
	C	H	C	H
2-hydroxy-2-pentafluorophenyl propanoate*	37.68	1.40	35.3	1.5
Atrolactate	54.88	4.60	53.3	4.8
Cyclopentanol-1 carboxylate	44.78	5.63	43.2	5.5

* F, theoretical % = 33.11
analysed % = 34.3

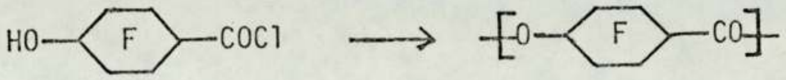
Table 3.5

Physical properties of α-hydroxy acids and the corresponding anhydrocarboxylates

Anhydrocarboxylate	Melting Point ^{o}C	%C Found (%C Required)	%H Found (%H Required)	Melting point of Parent Acid, ^{o}C
PFAAC	62	41.5 (42.57)	1.2 (1.07)	129
AAAC	-58	60.2 (62.49)	3.8 (4.20)	92*
C' pent AC	63.6	51.0 (53.84)	5.6 (5.10)	104

*from reference 71

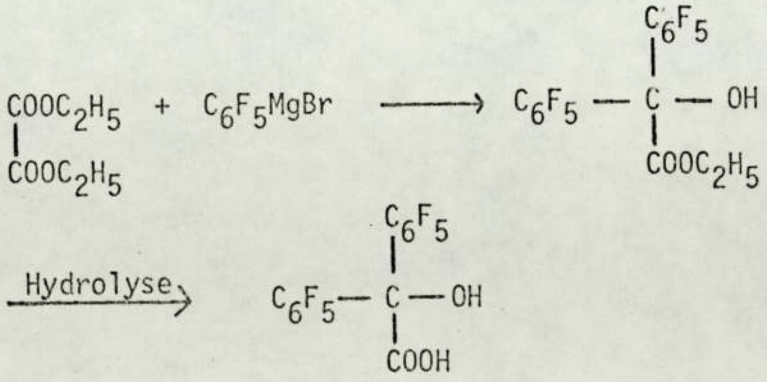
The uniqueness of this route to perfluoropoly α -ester can best be understood in terms of the unstability of the -CF$_2$OH group which makes the conventional route to diol-diacid synthesised perfluoro polyesters unavailable. The only reference in the literature to perfluoro polyester is a patent which describes the reaction shown below.



No further information on the behaviour of the polymer is given. It may be that this is because the method does not give satisfactory yields of high molecular weight polymer or alternatively that the properties, in common with other polymers containing main chain (as distinct from pendant) fluoroaromatic groups, are disappointing.

3.4.1 Decafluorobenzilic Acid Synthesis

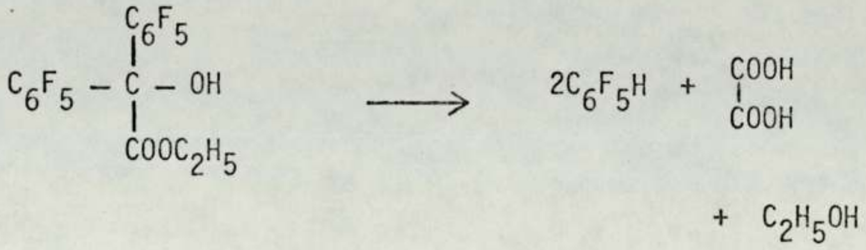
Initial synthetic techniques involved the reaction of diethyloxalate with the Grignard reagent derived from bromopentafluorobenzene and the hydrolysis of the reaction product. This technique had been successfully employed for the synthesis of the dibutyl substituted α -hydroxy acid(50). In the case of decafluorobenzilic acid the idealised equation is given below.



$$\begin{array}{c}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + C_6F_5MgBr \longrightarrow C_6F_5-\begin{array}{c}C_6F_5\\ |\\ C\\ |\\ COOC_2H_5\end{array}-OH \xrightarrow{\text{Hydrolyse}} C_6F_5-\begin{array}{c}C_6F_5\\ |\\ C\\ |\\ COOH\end{array}-OH$$

(3-7)

Although some success had been achieved on a small scale with this reaction, two major disadvantages exist; the first is the susceptibility of the C_6F_5 - C bond to cleavage by alkali resulting in the formation of oxalic acid.



$$C_6F_5-\underset{COOC_2H_5}{\overset{C_6F_5}{C}}-OH \longrightarrow 2C_6F_5H + \begin{matrix} COOH \\ COOH \end{matrix} + C_2H_5OH \qquad (3\text{-}8)$$

The second is the fact that several unidentified products are formed in the first-step of the Grignard reaction, possibly resulting from attack at both identical carbonyl groups of the diethyloxalate. In an attempt to overcome some of these difficulties ethyl oxalyl chloride was used as the substrate molecule and the reaction conditions varied.

37.0 g (0.15 moles) bromopentafluorobenzene and 3.6 g (0.15 moles) dry magnesium turning were employed in making a Grignard compound in 125 ml anhydrous ether by the conventional method as in section 3.2.

17.6 g (0.075 moles) ethyl oxalyl chloride in 50 ml anhydrous ether was slowly added to the Grignard solution. Temperature was maintained below 5^{o}C during the addition with vigorous stirring. The solution was then allowed to warm up to room temperature with continued stirring for 2 hours.

The solution was then divided into two portions. The first portion was used to form the copper(II) salt concurrently with hydrolysis of the Grignard product. The second portion was hydrolysed conventionally and copper(II) salt formation attempted after extraction of the hydrolysate*.

*The conventional method used in synthesis of 2-hydroxy-2-pentafluorophenyl propanoic acid in Section 3.1.

(a) "Instant" copper(II) salt formation (first portion)

13 g (0.1 moles) copper(II) chloride dissolved in 20 ml of 4N hydrochloric acid was added with stirring to the Grignard product. After the addition had been completed it was cooled and neutralised by ammonium solution. The precipitation was left to go to completion.

(b) "Conventional" copper(II) salt formation (second portion)

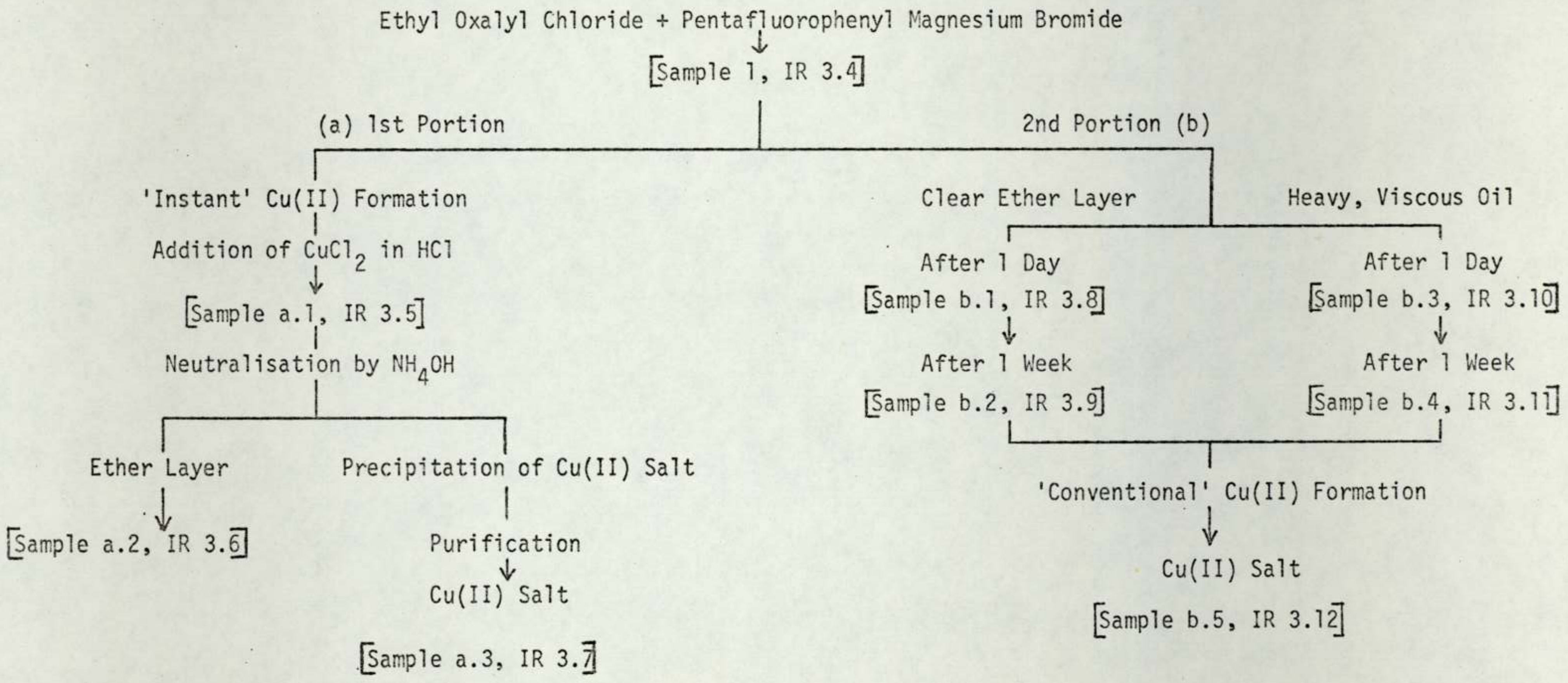
The second portion was left for one week and hydrolysed with 20 ml 4N hydrochloric acid. Reagent grade ether was used to extract the hydrolysate, some ether was evaporated and the remainder added slowly to 20 ml 0.1 N ammonium solution. A concentrated aqueous solution of 13 g (excess) copper(II) chloride was added into the solution, followed by neutralisation by ammonium solution. Precipitate was formed by cooling.

The Scheme 3.1 shows the reaction pathways where a number of selected samples were taken during the reaction for infrared analyses.

The changes of carbonyl absorptions were observed during the progress of the reaction, characteristic C-F absorptions at 1660 cm^{-1} and 1532 cm^{-1} confirmed the presence of aromatic C-F bonds. In IR 3.4 (sample 1, Figure 3.4), the sample from the reaction solution of ethyl oxalyl chloride and pentafluorophenyl magnesium bromide after 1 hour, newly formed carbonyl absorptions near 1770 cm^{-1} and 1710 cm^{-1} are shown together with two carbonyl absorption bands of the ethyl oxalyl chloride. The broad absorption band in the region of 3000 cm^{-1} - 3700 cm^{-1} cannot possibly belong to hydrogen-bonded hydroxyl group because of the anhydrous condition in the synthesis. This absorption band has too high an intensity and is too broad to be considered as the overtones of all the carbonyl absorption bands.

SCHEME 3.1

Synthesis of Copper(II) Salt of Decafluorobenzilic Acid



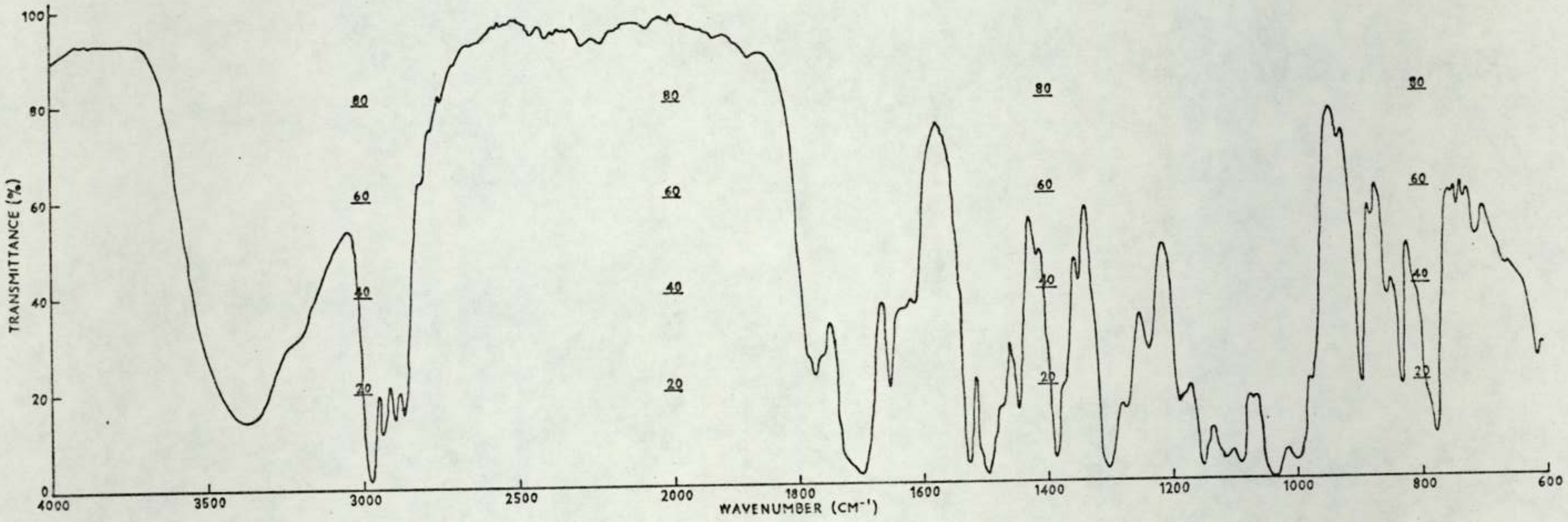


Figure 3.4 Sample 1, IR 3.4

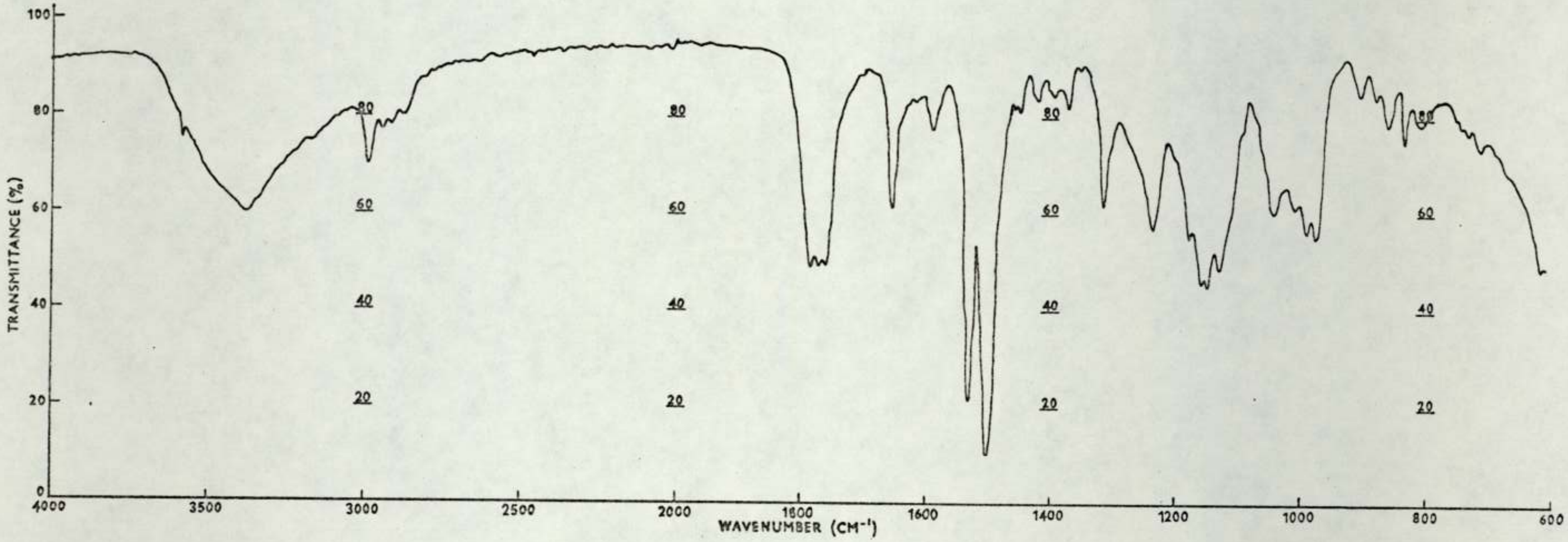


Figure 3.5 Sample a.1, IR 3.5

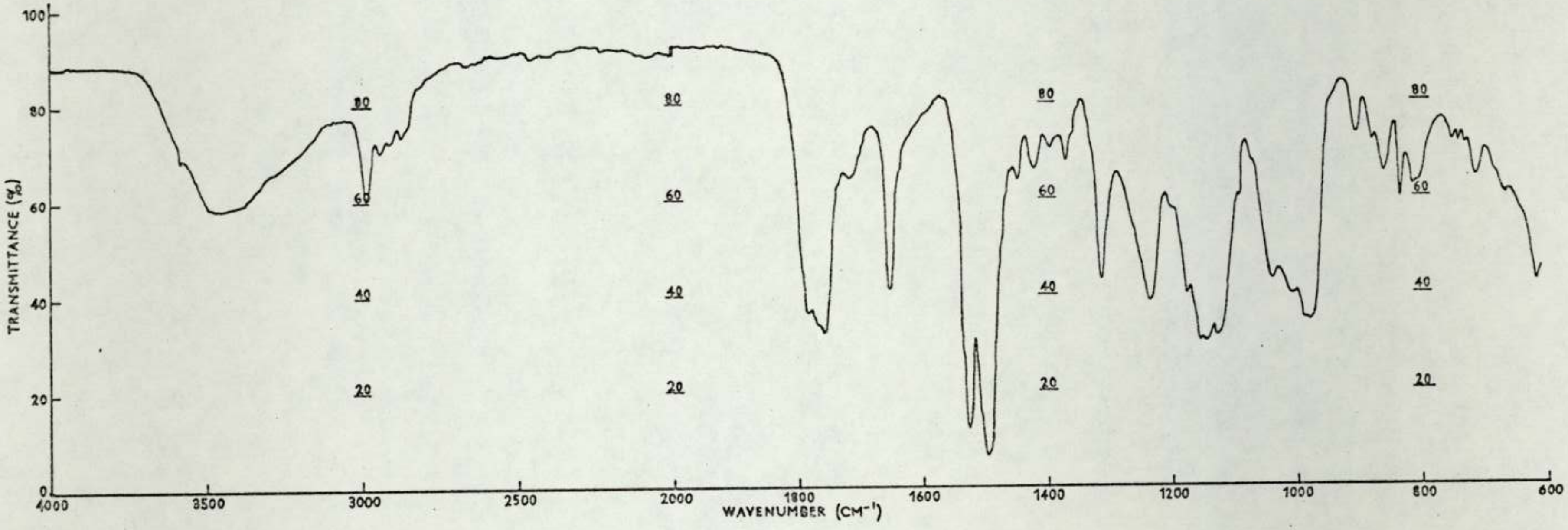


Figure 3.6 Sample a.2, IR 3.6

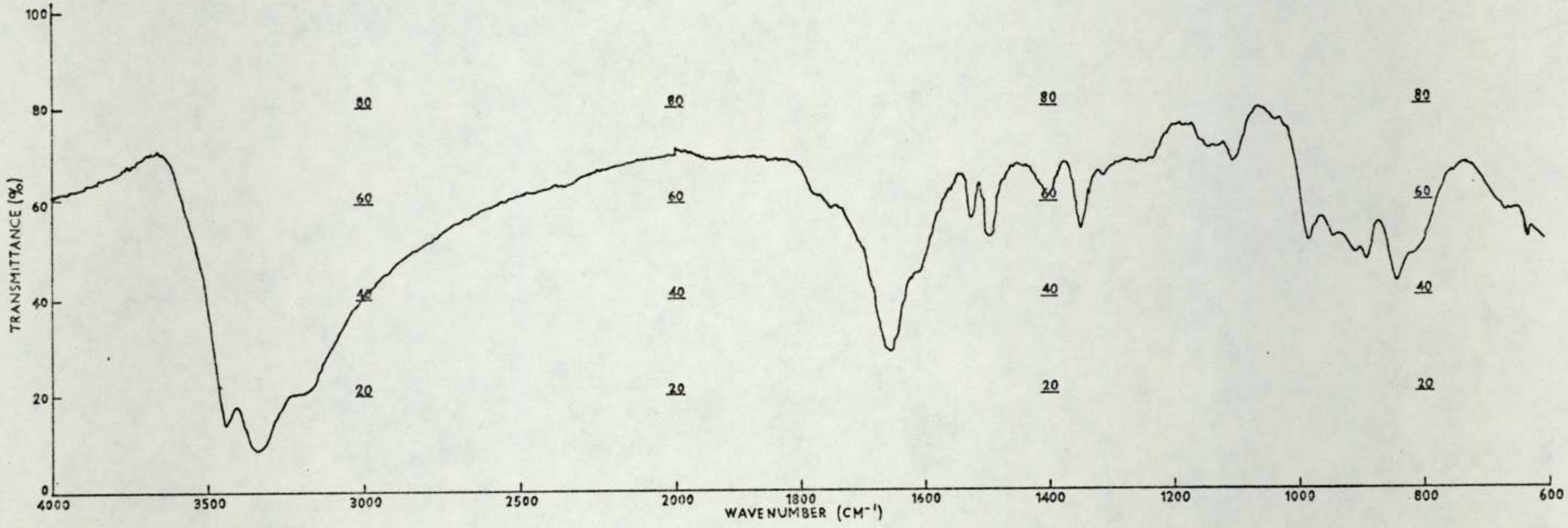


Figure 3.7 Sample a.3, IR 3.7

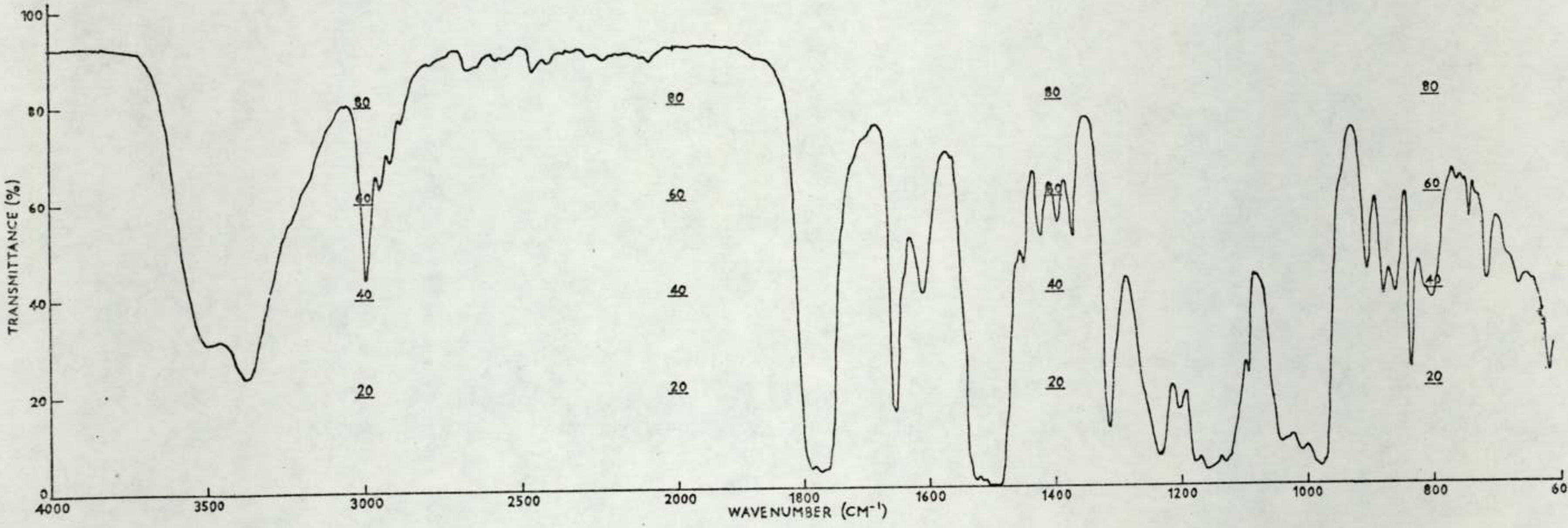


Figure 3.8 Sample b.1, IR 3.8

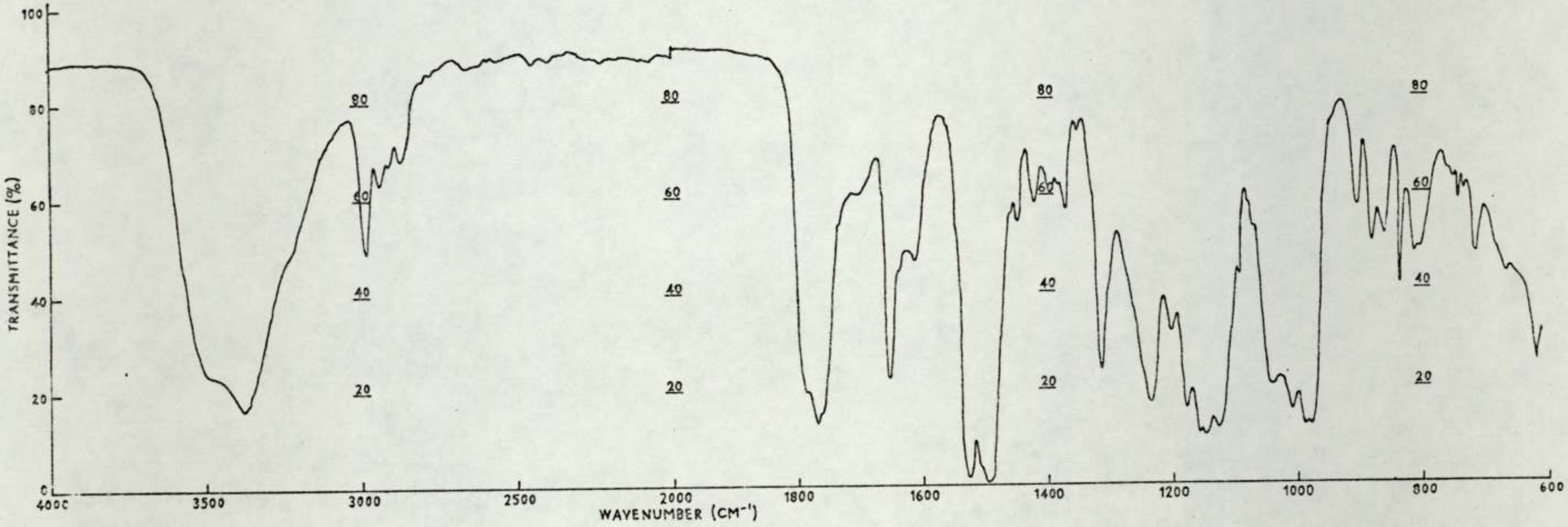


Figure 3.9 Sample b.2, IR 3.9

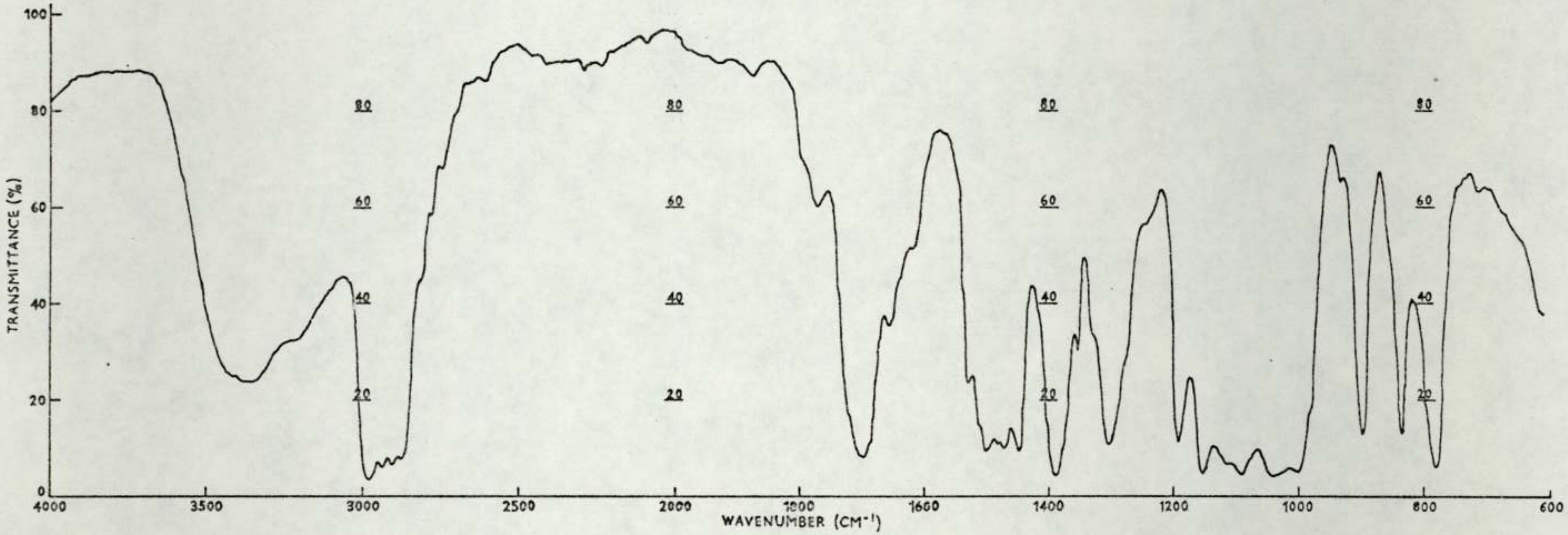


Figure 3.10 Sample b.3, IR 3.10

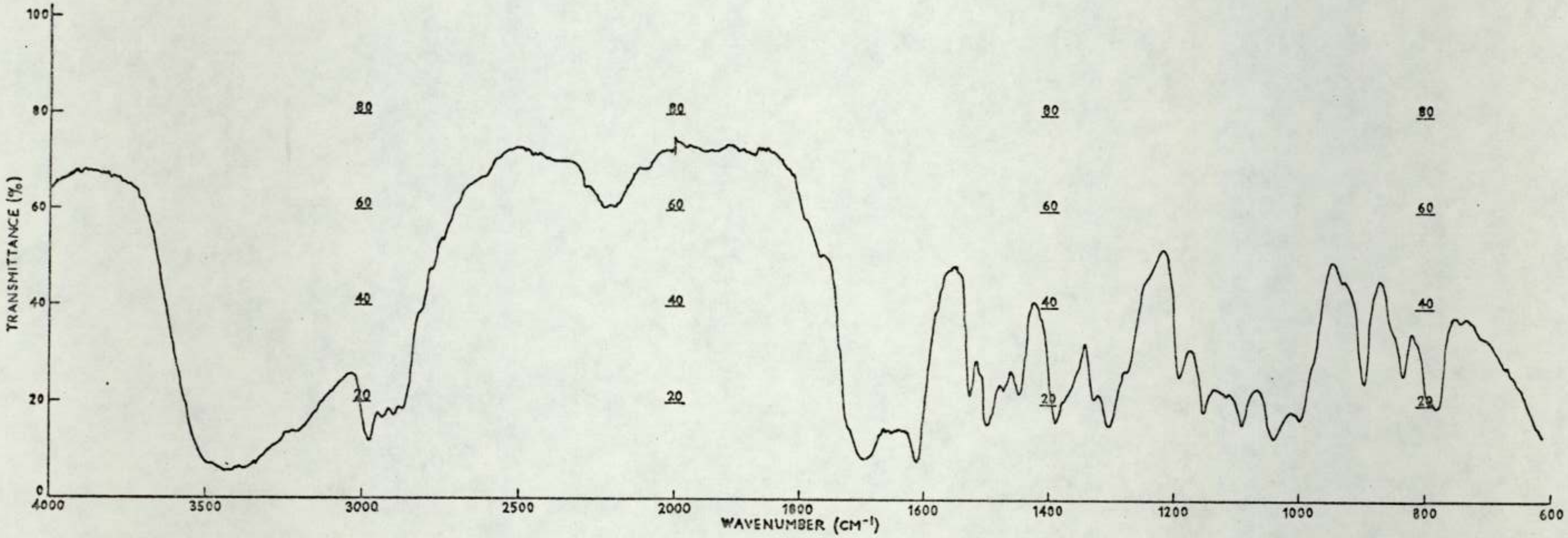


Figure 3.11 Sample b.4, IR 3.11

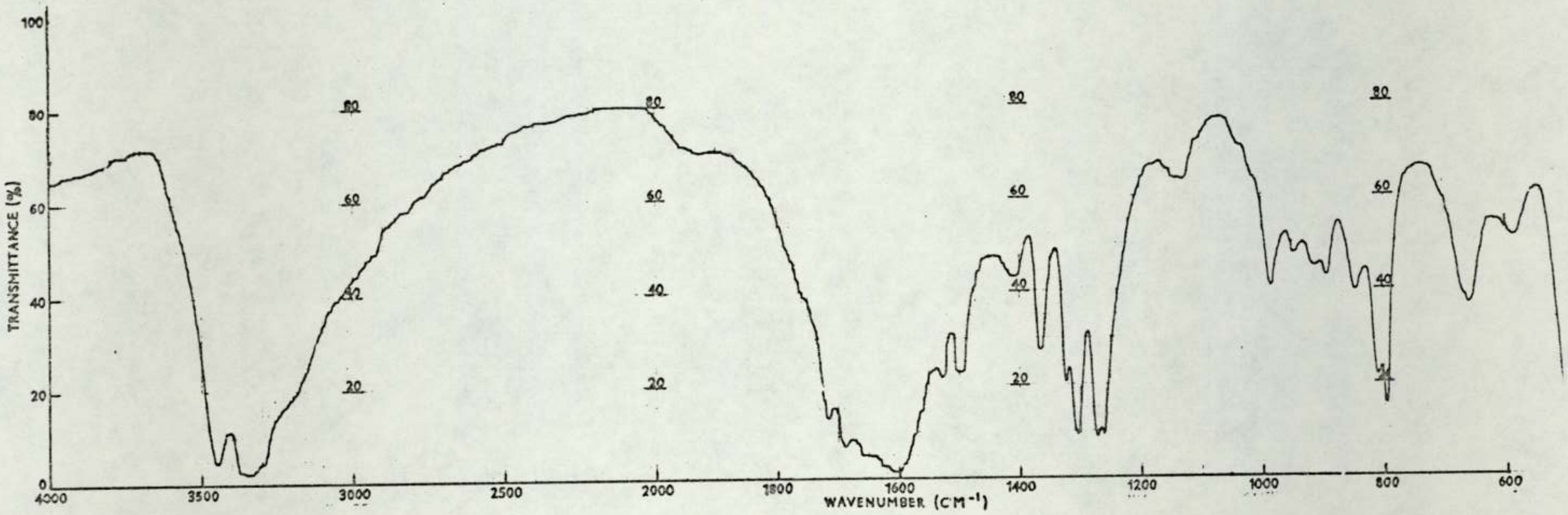


Figure 3.12   Sample b.5, IR 3.12

The infrared spectra of the etheral layers of the samples taken after the addition of copper(II) chloride and the neutralisation, IR 3.5 (sample a.1, Figure 3.5) and IR 3.6 (sample a.2, Figure 3.6) respectively, are almost identical and display no carbonyl absorption at 1710 cm^{-1}. This implies that if any of the required species had been produced, then the possible reactions involved would be as followed.

(a) IR 3.5 (sample a.1, Figure 3.5), the species were hydrolysed in the aqueous layer leaving the etheral layer oxalic acid, hydrolysis product of unreacted ethyl oxalyl chloride, together with pentafluorobenzene, hydrolysis product of unreacted Grignard reagent.

IR 3.6 (sample a.2, Figure 3.6), this sample was taken from the etheral layer after the precipitation of copper(II) salt in the aqueous layer, no change happened in the etheral layer.

(b) The other possible reaction was the conditions used in the hydrolysis and the formation of copper(II) salt were too strong resulting in the formation of oxalic acid, as in equation (3-6).

The broad absorption band in the region of 3000 cm^{-1} - 3700 cm^{-1} was still observed in both spectra, but exhibited less intensity relative to the carbonyl absorption near 1760 cm^{-1} - 1790 cm^{-1}. The aromatic C-F absorption bands could possibly, apart from bromopentafluorobenzene, belong to unknown impurities resulting from side reactions.

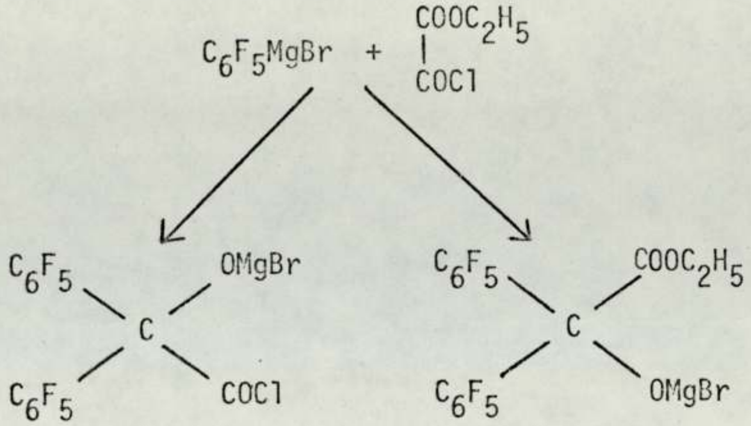
From the second portion of the Grignard reaction products, it was found that after 24 hours a heavy, viscous oil had settled at the bottom of the flask, left a clear etheral layer above. Samples from both layers were taken out for analysis after 1 and 7 days.

The spectra IR 3.8 and IR 3.9, sample b.1 (Figure 3.8) and sample b.2 (Figure 3.9), taken after 1 and 7 days respectively from the clear etheral layer are similar, showing carbonyl absorptions which are believed to belong to the oxalic acid or some unhydrolysed ethyl oxalyl chloride. Both spectra show the presence of pentafluoro phenyl group and the absence of the carbonyl absorption bands around 1700 cm^{-1}.

The spectra of the viscous oil, IR 3.10 (sample b.3, Figure 3.10) and IR 3.11 (sample b.4, Figure 3.11) obtained after 1 and 7 days respectively display similarity in absorption bands. The near 1700 cm^{-1} carbonyl absorption which disappears from the clear etheral layer is shown in the two spectra of the viscous oil. It is interesting to note that a new absorption band appeared at 1610 cm^{-1} in both spectra. They exhibit different intensities relative to the band at 1700 cm^{-1}.

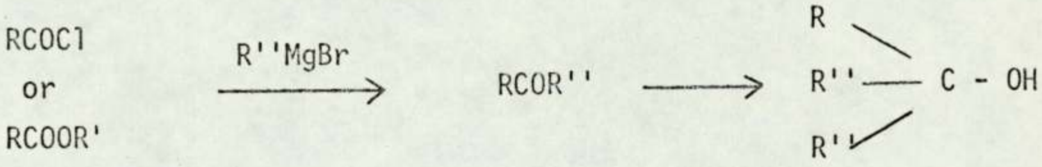
The infrared spectra of the copper(II) salts obtained from both "instant" and "conventional" methods, IR 3.7 (sample a.3, Figure 3.7) and IR 3.12 (sample b.5, Figure 3.12) exhibits some degree of impurity with the main carbonyl absorption at about 1651 cm^{-1}. One of the impurities was found to be the copper(II) salt of oxalic acid.

The Grignard reaction between pentafluorophenyl magnesium bromide and ethyl oxalyl chloride gives a mixture of products. Amongst the possible reactions are



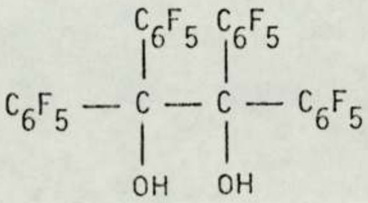
(XX) (XXI) (3-9)

In the reaction with a Grignard reagent, an acid chloride, like an ester, yields first a ketone, and with excess reagent, a tertiary alcohol.



(3-10)

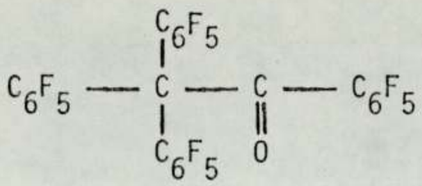
With an acid chloride the initial step proceeds more rapidly than the corresponding reaction with ester, the ketone then reacts with more reagents. In the case of ethyl oxalyl chloride which is both ester and acid chloride, it is possible that perfluorobenzopinacol (XXII) was produced.



$$C_6F_5-\overset{\displaystyle C_6F_5}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle C_6F_5}{\underset{\displaystyle OH}{C}}-C_6F_5$$

(XXII)

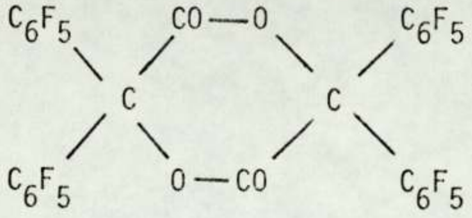
This compound could undergo "pinacol-pinacolone rearrangement" in acidic medium, to yield perfluorobenzopinacolone



$(C_6F_5)_3C-C(=O)-C_6F_5$

(XXIII)

The other possible reaction product is perfluorobenzilide (XXIV)



(XXIV)

which could be formed by either:

- direct dimerisation and elimination of MgBrCl from (XX), or,
- cyclisation of the hydrolysis products of (XX) or the acid itself.

A viscous oily product from a previous Grignard reaction of the same type had been left standing without analysis in order to attempt to induce crystallisation. Since some crystallisation occurred separation and analysis were undertaken based on the observation that the mixture consisted of a methanol soluble and a methanol insoluble fraction. It was hoped that this exercise might help to identify possible reaction products.

Infrared spectra of the two fractions are shown in IR 3.13 (Figure 3.13) and IR 3.14 (Figure 3.14). The most significant feature are the presence of a sharp hydroxyl peak (3480 cm^{-1})

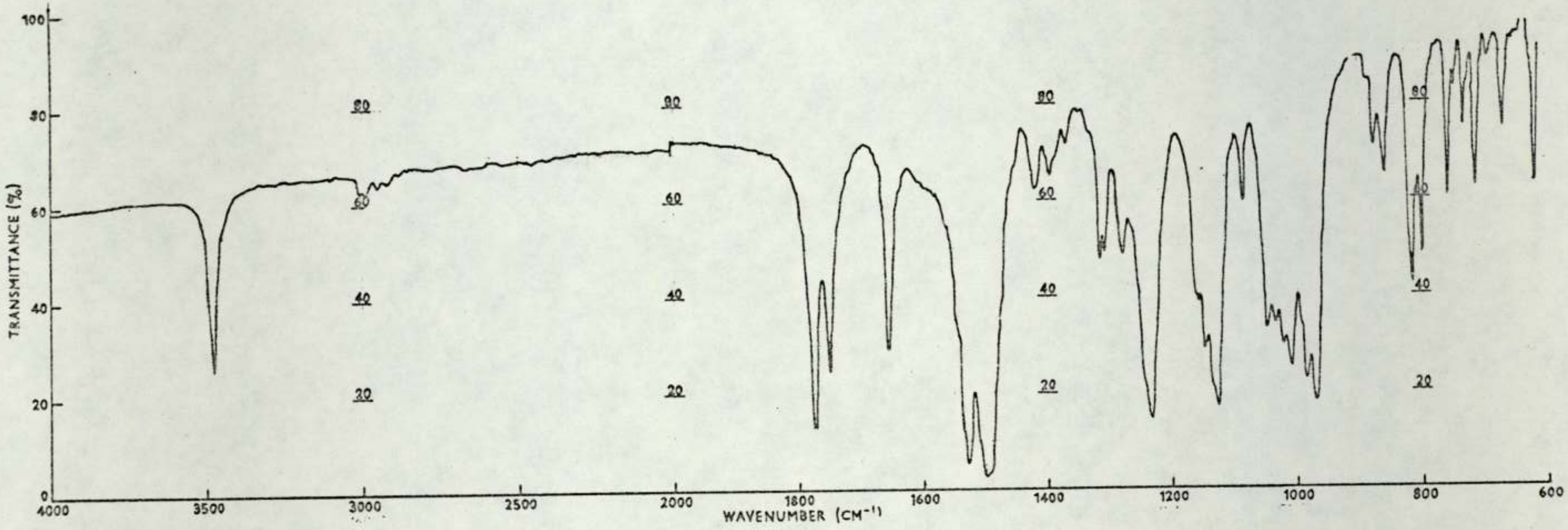


Figure 3.13 IR 3.13. Spectrum of a methanol insoluble fraction

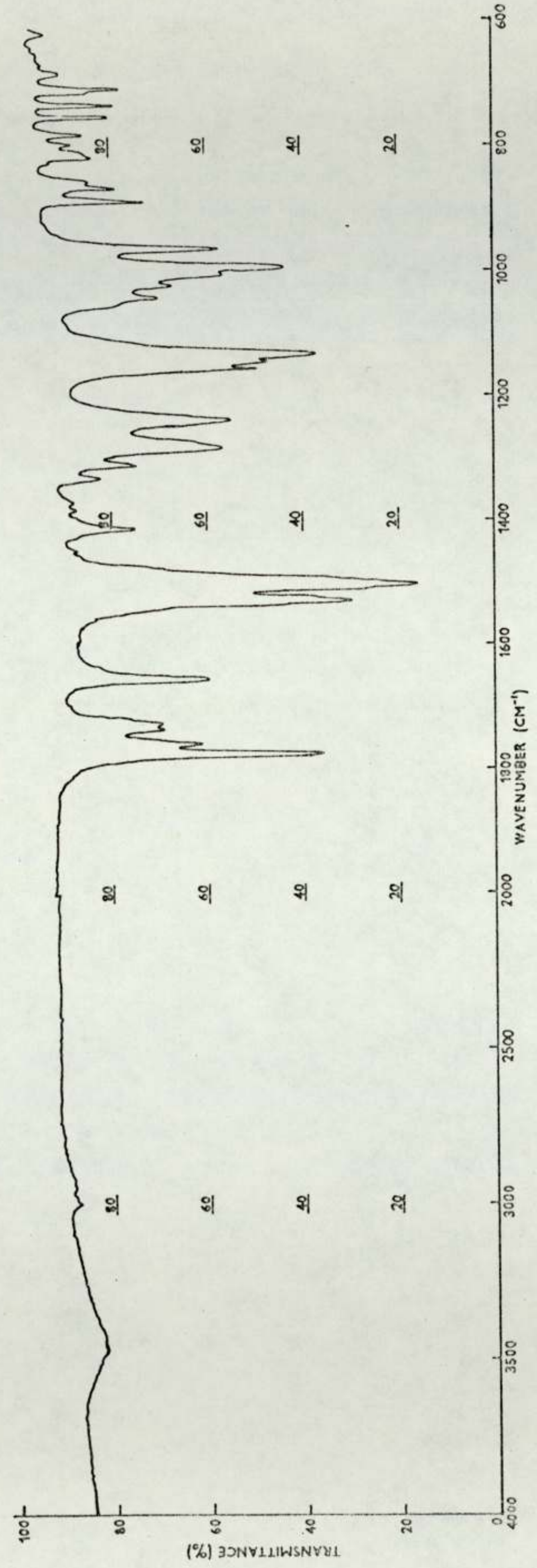


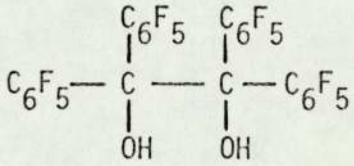
Figure 3.14 IR 3.14. Spectrum of a methanol soluble fraction

present in IR 3.13, a methanol insoluble fraction, but absent in IR 3.14, a methanol soluble fraction. Both spectra show multiple carbonyl peaks between 1700 cm^{-1} - 1800 cm^{-1}.

Mass spectra of the products provide some interesting results. The top mass peak was as high as 614 showing that the product must contain some species of higher molecular weight than the required acid (MW = 407). Table 3.6 shows some mass peaks together with possible structures of the corresponding fragments.

On the basis of these and similar results it seems probable that in addition to the desired ethyl ester of decafluorobenzilic acid several additional species are obtained as primary products of the Grignard reaction. Two products which are more likely are

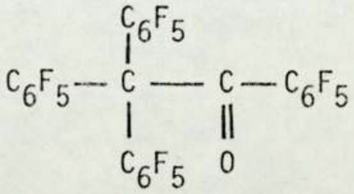
perfluorobenzopinacol (XXII)



$$\begin{array}{ccccc} & C_6F_5 & & C_6F_5 & \\ & | & & | & \\ C_6F_5- & C & - & C & -C_6F_5 \\ & | & & | & \\ & OH & & OH & \end{array}$$

which rearranges to

perfluorobenzopinacolone (XXIII)

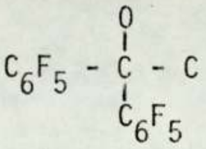
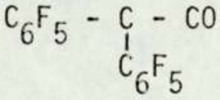
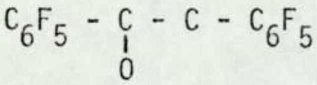
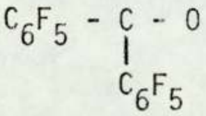
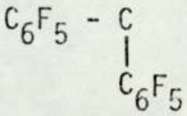


$$\begin{array}{ccccc} & C_6F_5 & & & \\ & | & & & \\ C_6F_5- & C & - & C & -C_6F_5 \\ & | & & \| & \\ & C_6F_5 & & O & \end{array}$$

Thus the separation of the crystallised products of the Grignard reaction was probably incomplete yielding XXII plus some XXIII together with other carbonyl containing species (methanol insoluble fraction, IR 3. 13); and impure XXIII containing little or no XXII (methanol soluble fraction, IR 3.14). This is consistent with the experimental observation that the sample corresponding to IR 3.14 gave a strong response to the 2,4-dinitrophenylhydrazine ketone test

Table 3.6

Some major mass peaks obtained from mass spectra of the mixture products from decafluorobenzilic acid synthesis

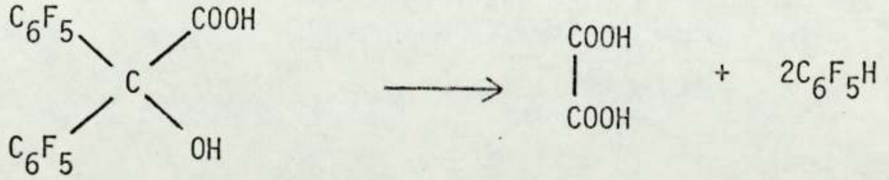
Mass peak	Possible fragments
374	 $C_6F_5-\overset{O}{\underset{C_6F_5}{C}}-C$  $C_6F_5-\underset{C_6F_5}{C}-CO$  $C_6F_5-\underset{O}{C}-C-C_6F_5$
362	 $C_6F_5-\underset{C_6F_5}{C}-O$
346	 $C_6F_5-\underset{C_6F_5}{C}$
195	C_6F_5-C
167	C_6F_5

whereas that corresponding to IR 3.13 responded more weakly.

The most probable additional component of the reaction mixture is the perfluorobenzilide (XXIV) which together with the perfluoropinacolone (XXIII) is capable of explaining the multiple carbonyl peaks observed in the infrared spectra. The perfluorobenzilide is undoubtedly formed from decafluorobenzilic acid and the prolonged crystallisation conditions would enhance its formation.

One reasonably promising way of overcoming some of the problems is the 'in situ' formation of the copper(II) salt of decafluorobenzilic acid at an early stage of the Grignard reaction (sample a.3, Scheme 3.1). The copper(II) salt thus obtained was hydrolysed by dilute hydrochloric acid and the product gave the mass spectrum corresponding to the major mass peaks in Table 3.7.

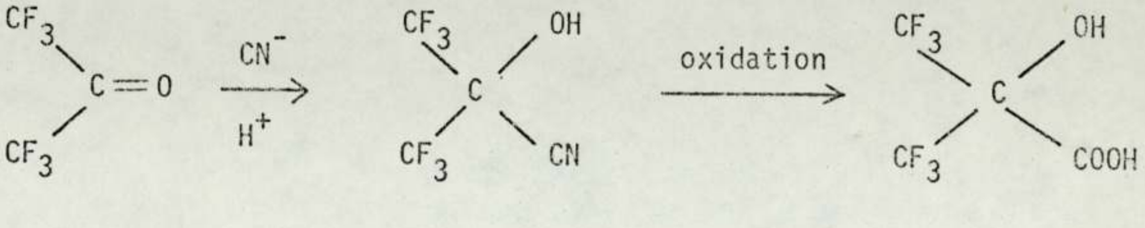
More vigorous hydrolysis produced a white crystalline product identified as oxalic acid. It is understood that this product was produced by cleavage of the C_6F_5 - C bonds of the pre-formed acid.



(3-11)

3.4.2 Synthesis of Bis-(trifluoromethyl)-Glycollic Acid

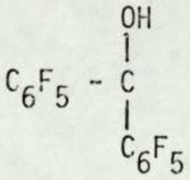
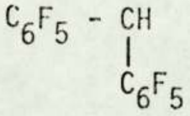
Attempts have been made for the synthesis of bis-(trifluoromethyl)-glycollic acid via the cyanohydrin route as in equation (3-12)



(3-12)

Table 3.7

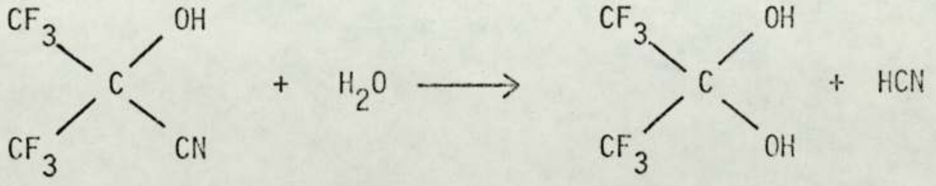
Major mass peaks obtained from hydrolysis product of copper(II) salt in the synthesis of decafluorobenzilic acid

Mass peak	Fragment
363	 $C_6F_5-\underset{C_6F_5}{\overset{OH}{C}}$
347	 $C_6F_5-\underset{C_6F_5}{CH}$
195	C_6F_5
45	COOH

(a) Hexafluoroacetone trihydrate was employed to react with sodium cyanide in a solution of 5% tetrahydrofuran in diethyl ether. Phosphoric oxide was used in order to react with water of the hydrated perfluoroacetone. Hexafluoroacetone trihydrate was slowly dropped into a stirred suspension of sodium cyanide which remained at 5°C during the addition.

According to the work of Mill et al.(96) in the synthesis of 1,3-dichlorotetrafluoroacetone cyanohydrin salts, in this synthesis of hexafluoro acetone cyanohydrin sodium cyanide was chosen instead of the potassium salts. The reason for this is that from Mill's work it was reported that although potassium cyanide reacted readily but gave lower yields than did sodium cyanide, also the sodium cyanohydrin exhibits yellow colour which would be useful for indication in the progress of the reaction.

The experiment was unsuccessful. It seemed that the reaction never started, the phosphoric oxide settled at the bottom of the flask and the suspension solution remained clear and colourless after a long period. According to Russian workers (97), in the presence of water at room temperature, partial hydrolysis of the cyanohydrin took place with the formation of hexafluoroacetone hydrate and cyanic acid.



(3-13)

Fluorinated aldehyde and ketones are strong Lewis acids, forming stable hydrates. It occurred that the hydrated perfluoroacetone was very stable and with the presence of water in the molecule it was difficult for the reaction to take place.

(b) In the further attempts, gaseous hexafluoroacetone was dissolved in tetrahydrofuran, diethyl ether and diethylether-tetrahydrofuran. The dissolved hexafluoroacetone solution was slowly dropped into a stirred, cold (5°C) suspension solution of sodium cyanide and potassium cyanide. Analyses of the reaction solution showed no evidence of the formation of the required cyanohydrin.

The same Russian workers(97) reported the synthesis of hexafluoroacetone cyanohydrin from the reaction of hexafluoroacetone with hydrocyanic acid in the presence of piperidine as a catalyst. They also claim that by slight heating of this cyanohydrin in the presence of concentrated sulphuric acid the amide of bis-(trifluoromethyl)-glycollic acid was formed and under more vigorous conditions free bis-(trifluoromethyl) glycollic acid was obtained. There was however no detail of the experimental technique reported.

Although this reaction in principle offers an attractive route to the corresponding perfluoropolyester, poly-(hexafluoroisopropylidene carboxylate), the synthetic difficulties are, at the present stage of the work, extremely daunting.

CHAPTER 4

THE PYRIDINE INITIATED POLYMERISATION OF 5-METHYL-5-PHENYL-1,3-DIOXOLAN-2,4-DIONE IN NITROBENZENE - KINETIC RESULTS AND DISCUSSION

The basic features of pyridine initiated polymerisation of phenyl and pentafluorophenyl substituted anhydrocarboxylates were established by Smith(63) who examined in some detail the behaviour of mandelic acid anhydrocarboxylate, MAAC, and 2-pentafluoro-2-hydroxy-propanoic acid anhydrocarboxylate, PFAAC. Three features of this work require further elucidation.

The first of these (a) is the factor or factors which control molecular weight.

The second (b) is the suggestion made by Smith that disubstituted anhydrocarboxylates would only polymerise if one of the substituents was pentafluorophenyl or another strongly electron withdrawing group. Thus MAAC possessing one phenyl and one α-hydrogen polymerised readily and PFAAC polymerised with reasonable ease since the steric effect of the α-methyl was counteracted by that of the strongly electron withdrawing pentafluorophenyl. It was suggested, however, that atrolactic acid anhydrocarboxylate, possessing methyl and phenyl groups as substituents, would polymerise either very slowly or not at all.

The final point (c) is the deviation from second order dependence on pyridine concentration observed in a polymerisation of pentafluorophenyl, methyl substituted anhydrocarboxylate, PFAAC. No comparable effect being encountered with mandelic acid anhydrocarboxylate.

In this chapter the polymerisability of atrolactic acid anhydrocarboxylate, AAAC, under similar conditions to those used by

Smith is discussed particularly in relation to the feature (b).

4.1 Results

4.1.1 General Kinetic Features

Initial examination of the reaction between pyridine and atrolactic acid anhydrocarboxylate, AAAC, indicated that the reaction showed, as in previous cases$^{(63)}$, first-order dependence on both monomer and initiator. Since the reactions were not fast it was necessary to work at reasonably high pyridine concentrations whilst remaining within the regime where first-order dependence on pyridine was shown. The conditions chosen were equimolar monomer and pyridine, both set at 0.25 molar with nitrobenzene as a solvent.

4.1.2 Pressure Versus Time Profile

A typical pressure versus time profile (obtained using the gas evolution technique described in Chapter 2, Section 2.2) is shown in Figure 4.1 for the reaction of AAAC with equimolar pyridine (0.25 M) at 60°C. The corresponding semilog plot (log $[(P_\infty - P)/P_\infty]$ versus time) which is presented in Figure 4.2 (c) illustrates the good experimental first order dependence on monomer concentration (well into the second decade) and the fact that the pyridine concentration remains sensibly constant throughout the reaction.

The rate of decomposition of AAAC in the presence of pyridine may, therefore, in general be expressed by

$$-\frac{d[M]}{dt} = \frac{d[CO_2]}{dt} = k_2[M][Py] \qquad (4\text{-}1)$$

where $[M]$, $[Py]$ and k_2 are the concentration of AAAC, pyridine and the second-order rate constant respectively. As the pyridine concentration is assumed to be constant during the course of the reaction, Equation (4-1) may be written as,

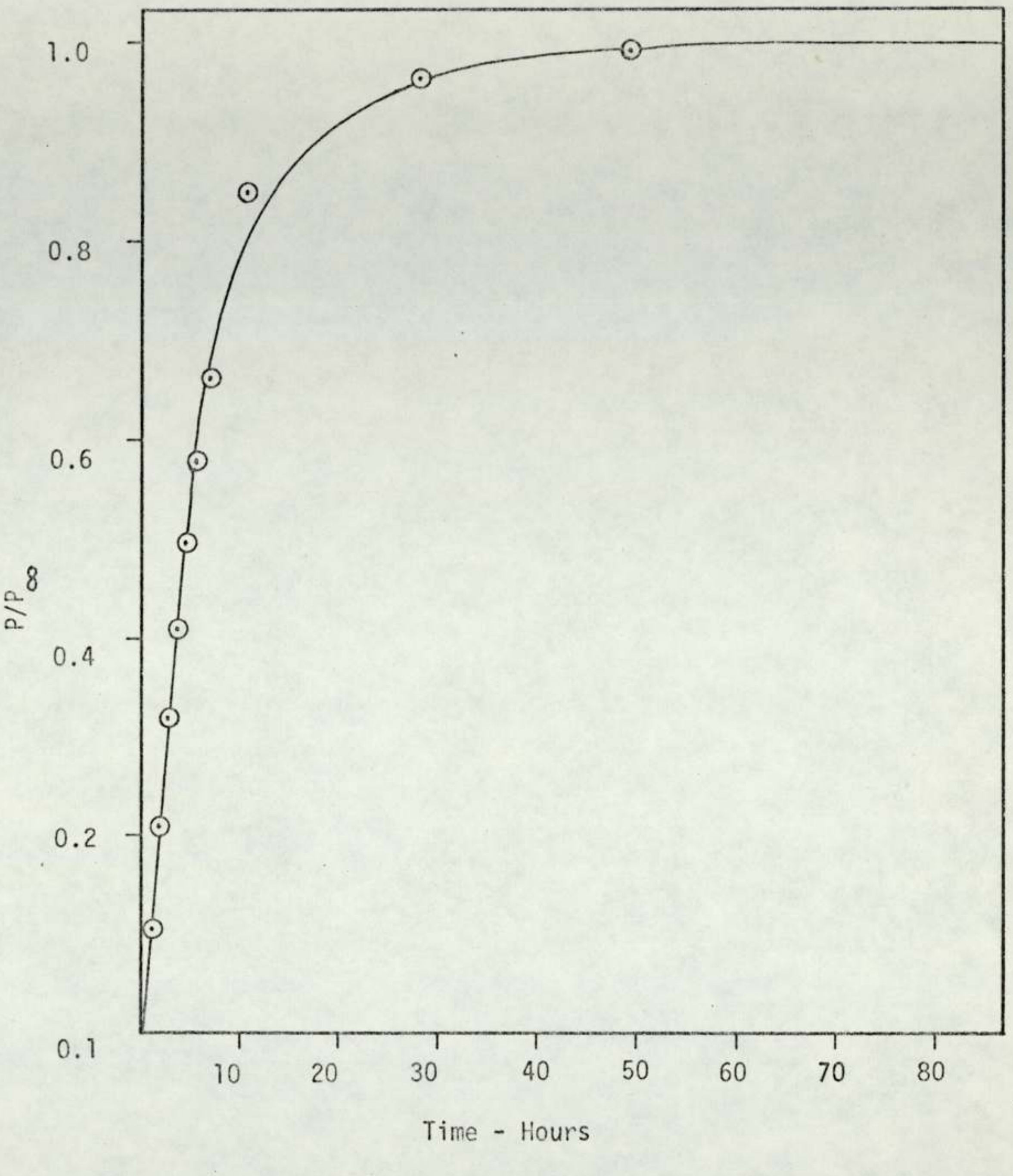


Figure 4.1 The pressure versus time profile of the pyridine initiated polymerisation of AAAC in nitrobenzene at 60°C.

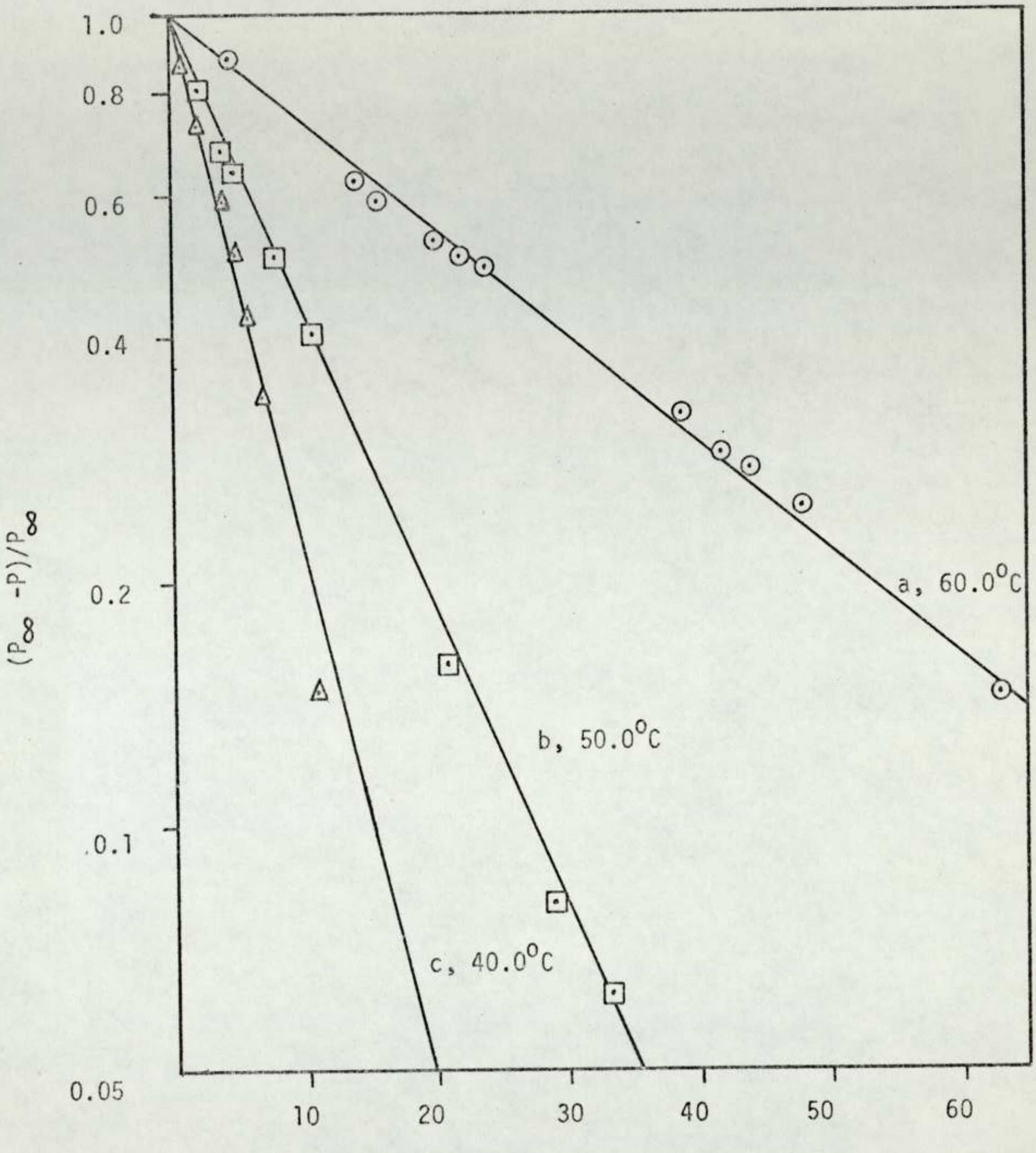


Figure 4.2 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of AAAC in nitrobenzene.

$$-\frac{d[M]}{dt} = k_1[M] \qquad (4\text{-}2)$$

Where $$k_1 = k_2[Py] \qquad (4\text{-}3)$$

and can be considered as a pseudo first-order rate constant.

4.1.3 Effect of Temperature

The reaction was studied over the temperature range 40-60°C. Good first-order dependences with respect to monomer and pyridine were observed throughout with no evidence of catalysis or inhibition by carbon dioxide or other reaction products. First-order semilog plots are shown in Figure 4.2 and the derived second-order (k_2) and pseudo first-order (k_1) rate constants in Table 4.1. Table 4.1 also shows the activation energy ($E^{\ddagger}$), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) derived from a conventional Arrhenius plot (Figure 4.3).

4.1.4 Effect of Higher Pyridine Concentration

Although this chapter is concerned with the polymerisation of atrolactic acid anhydrocarboxylate in the region where reasonably ideal homogeneous conditions exist (e.g. where the monomer concentration is insufficiently high for polymer precipitation to occur) it is relevant to note that at higher pyridine concentration (substantially greater than equimolar with respect to monomer) deviation from simple first-order dependence on pyridine concentration does occur in a similar but less marked way to that observed with PFAAC. The effect is illustrated in Figure 4.4. This point is more relevant to the discussion on deviations from the idealised mechanism which is presented in a later chapter.

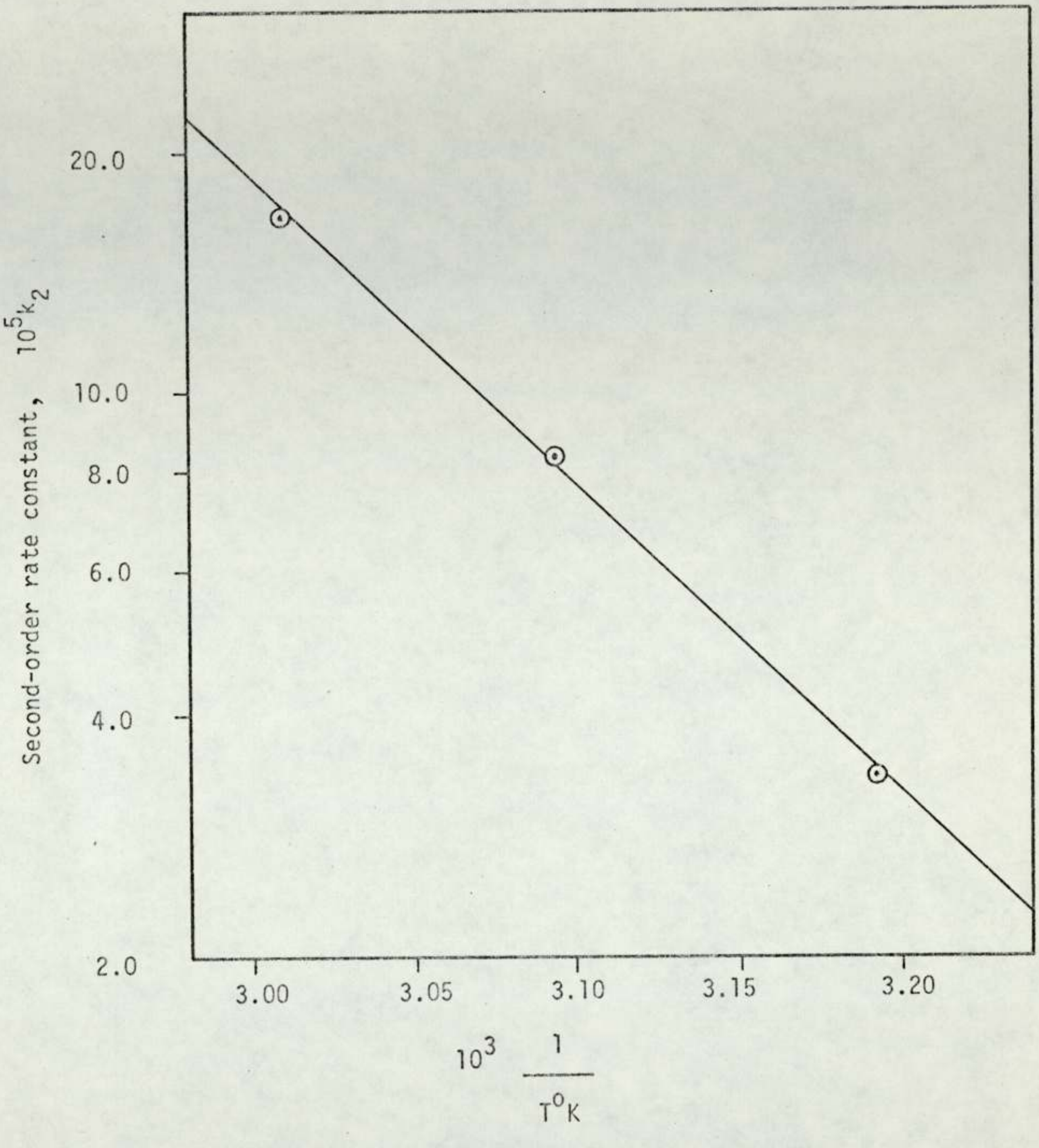


Figure 4.3 An Arrhenius plot of the second-order rate constant, k_2, versus the reciprocal of the absolute temperature for the pyridine initiated polymerisation of AAAC in nitrobenzene. Temperature range 40-60°C.

Table 4.1

Second-order rate constants (k_2), energy of activation ($E^{\ddagger}$), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the pyridine initiated polymerisation of AAAC in nitrobenzene.

Temperature ^{o}C	10^5 k_2 $1.mole^{-1}.sec^{-1}$. ($k_1 = 0.25\,k_2\ sec^{-1}$)
40.0	3.3
50.0	10.2
60.0	16.7
$E^{\ddagger}$ (kJ $mole^{-1}$.)	73.2
A ($1.mole^{-1}.sec^{-1}$.)	6.5×10^7
$\Delta S^{\ddagger}$ (J $K^{-1}.mole^{-1}$.)	-103

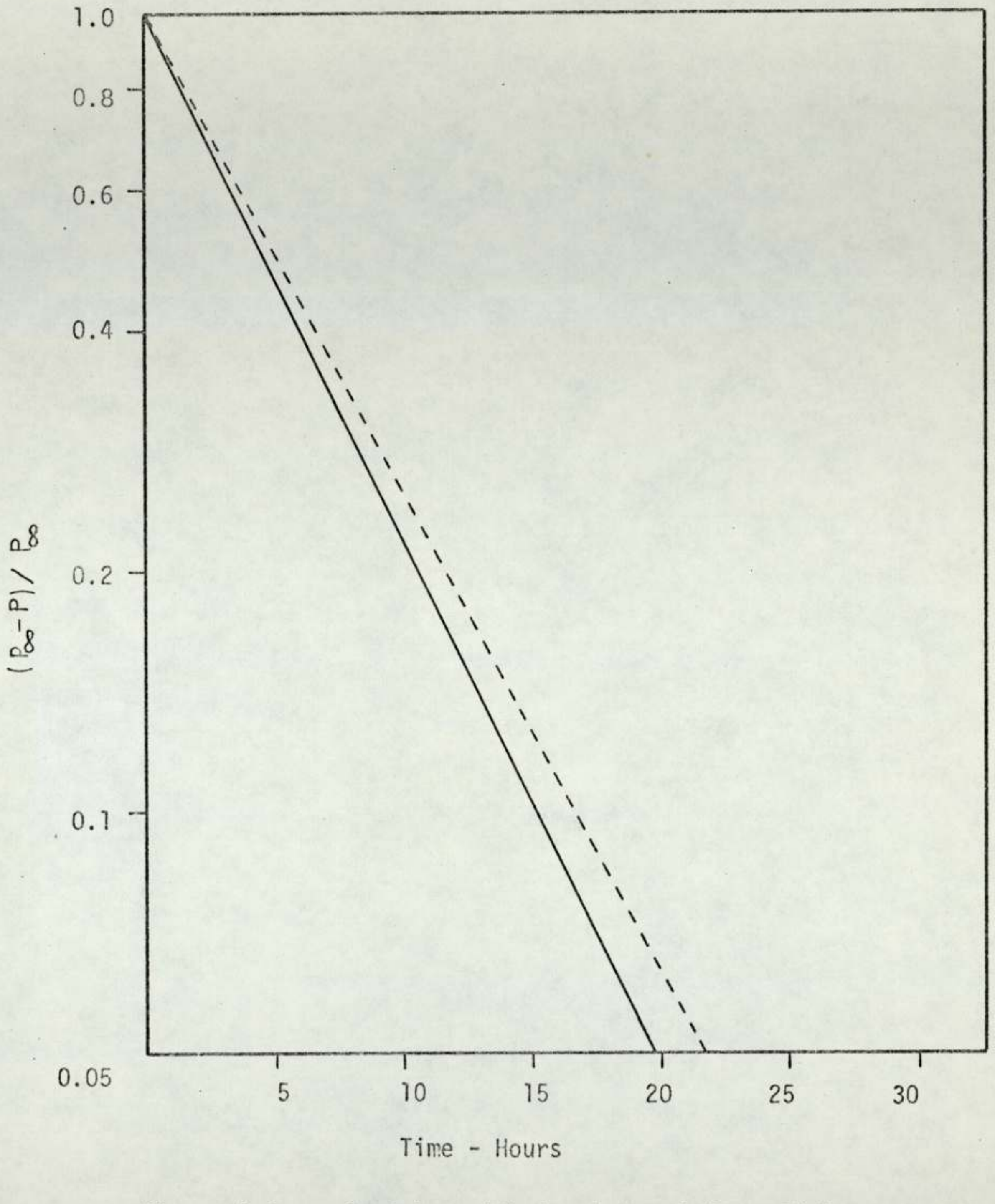


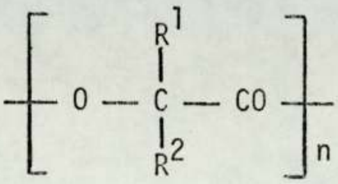
Figure 4.4 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of AAAC in nitrobenzene at 60.0°C.

——— $[AAAC]_o$ = 0.25 mole.litre^{-1}.
$[Py]$ = 0.25 mole.litre^{-1}.
k_2 = 1.67×10^{-5} litre.mole^{-1}.sec^{-1}.

- - - - $[AAAC]_o$ = 0.25 mole. litre^{-1}.
$[Py]$ = 0.50 mole.litre^{-1}.
k_2 = 7.5×10^{-5} litre.mole^{-1}.sec^{-1}.

4.1.5 Examination of the Reaction Products

Although detailed characterisation and related molecular weight studies are presented elsewhere it is relevant to indicate the nature of the results obtained at this point. As in all previous cases, the products obtained were poly α-esters of the general form:



$$\left[-O-\overset{R^1}{\underset{R^2}{C}}-CO- \right]_n$$

The sample taken at the end of the kinetic runs were studied by gel permeation chromatography techniques. The results are shown in Table 4.2.

Table 4.2

Gel permeation chromatography results of polymers obtained from initiated polymerisation of AAAC in nitrobenzene

$[M]_o$ molar	$[Py]$ molar	Temperature ^oC	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Highest MW
0.25	0.25	40	1191	1072	1.11	3520
"	"	50	759	815	1.07	1920
"	"	60	2114	1774	1.19	10000

4.2 Discussion

The kinetic parameters obtained from the pyridine initiated polymerisation of AAAC (Table 4.1) are very similar to those previously obtained from the polymerisation of PFAAC and MAAC(63) under similar conditions as shown below.

Monomer	$E^{\ddagger}$ kJ. mole^{-1}	A l. mole. sec^{-1}	$\Delta S^{\ddagger}$ J.K.^{-1} mole
AAAC	73.3	6.5×10^{7}	-103
PFAAC	62.5	6.9×10^{6}	-127.3
MAAC	48.3	4.3×10^{6}	-133

These values are quite different from both thermal and protonic nucleophile initiated polymerisation of similar rings.

Polymerisation	$E^{\ddagger}$ kJ. mole^{-1}	A l. mole. sec^{-1}	$\Delta S^{\ddagger}$ J.K.^{-1} mole
Thermal	1	10^{10}	0
Protonic initiated	34-43	10-10^{3}	250

The mechanism proposed by Smith provides, in the light of the available evidence, the best basis for understanding the reaction. The features accommodated by this mechanism are listed below.

(i) The first-order behaviour with respect to the concentration of both monomer and pyridine.

(ii) The fact that pyridine is not consumed during the course of the reaction.

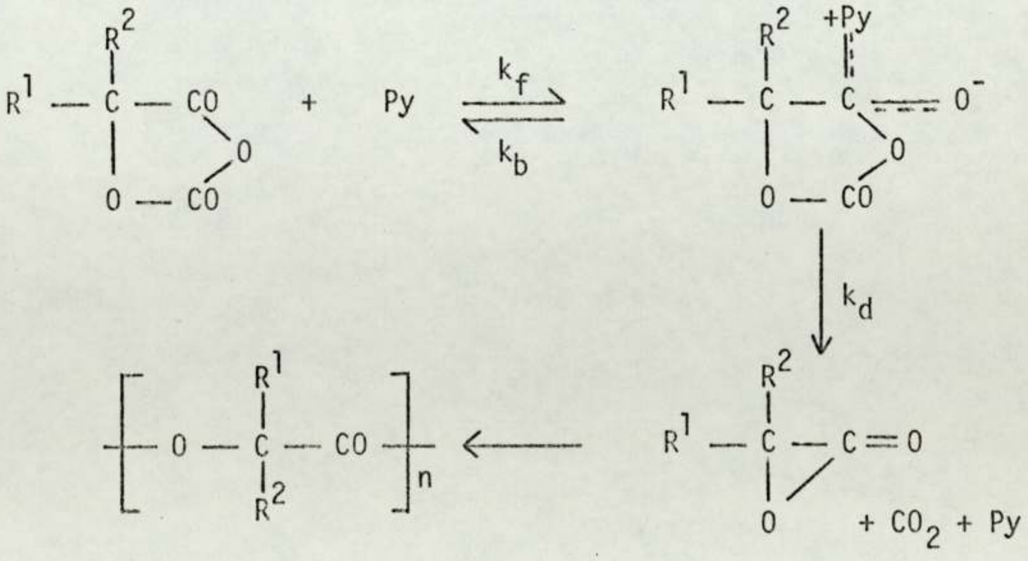
(iii) The molecular weight is not governed by the initial pyridine concentration.

(iv) The kinetic parameters cannot be equated with any "model" ring-opening reaction.

(v). The molecular weight is controlled by the presence of moisture or other nucleophiles.

(vi) Both hydroxyl and carboxyl groups are presented as end groups.

In all cases, decomposition of anhydrocarboxylate in the presence of pyridine produced a poly α-ester with the evolution of gaseous carbon dioxide. The proposed mechanism involves the attack of pyridine, acting as nucleophile, on the C-4 carbonyl of the ring producing a complex intermediate which is capable of either breaking down to reform the monomer and pyridine molecules or decompose to yield a polymerisable species (α-lactone), carbon dioxide and pyridine.



(4-4)

where k_f, k_b and k_d govern the reactions indicated. The α-lactone intermediate is known to be a very reactive species and would immediately polymerise to form a poly α-ester chain. This is a very rapid reaction, thus, has no contribution in the rate determining step and the activation energy of the overall reaction.

The equilibrium constant, K_{eq}, of the complex formation controls the presence of the complex in the system which is, at the same time, continuously consumed by decomposition to form α-lactone and subsequently a polymer.

Molecular weights of polymer obtained are very low which was unexpected, since extreme precautions to prevent adventitous entry of moisture were taken and the purities of solvent, monomer and pyridine were carefully controlled. Termination, as suggested, resulted from the reaction of adventitous moisture with α-lactone, and subsequently govern the molecular weights. These problems of very low molecular weights together with the deviation from the simple first-order dependence on pyridine concentration at high concentrations of pyridine, lead to a suggestion that there is some unspecified termination mechanism which controls the low value of molecular weight. This will be discussed later in this thesis.

So far, no comment has been made about relative rates of reaction of PFAAC, MAAC and AAAC. In fact they are not so dissimilar as predicted by Smith. One aim of ring-opening studies of this type is to develop an understanding of steric and polar interaction in propagating end group and in the monomer. The ultimate aim is the development of multiple correlation equations to enable rates of polymerisation to be predicted. In this context the use of the Taft Equation provides an interesting and effective way of assessing relative balance of steric and polar effects.

If K_{eq} is the equilibrium constant for the formation of the complex between monomer, M, and pyridine, Py, then

$$K_{eq} = \frac{k_f}{k_b} = \frac{[\text{Complex}]}{[M][Py]} \qquad (4\text{-}5)$$

Rearrangement of the Equation (4-5) gives

$$[\text{Complex}] = K_{eq}[M][Py] \qquad (4\text{-}6)$$

The overall equation rate may be written as

$$\frac{d[CO_2]}{dt} = -\frac{d[M]}{dt} = k_d\,[\text{Complex}] \qquad (4\text{-}7)$$

Substituting Equation (4-6) in (4-7) gives

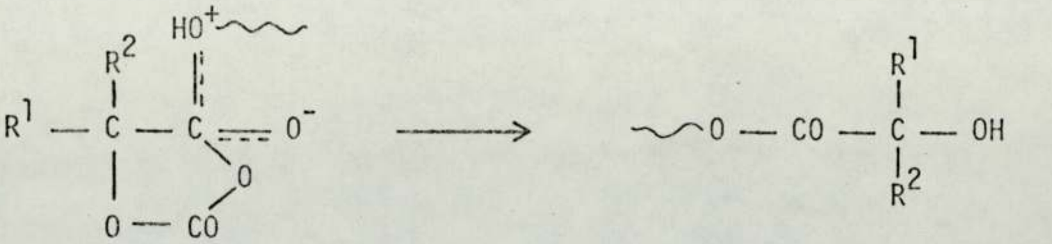
$$\frac{d[CO_2]}{dt} = k_d \cdot K_{eq}[M][Py] \qquad (4\text{-}8)$$

Comparison of Equation (4-8) to (4-1) results in

$$k_2 = k_d \cdot K_{eq} \qquad (4\text{-}9)$$

The equation (4-9) illustrates that the rate of the pyridine initiated polymerisation of anhydrocarboxylates is governed by two factors, the equilibrium constant of the complex formation and the rate of decomposition of the complex to α-lactone. Also, the equation implies that the activation energy of the overall reaction (as may be derived from the Arrhenius plot) does not refer to a simple single process.

In the presence of other nucleophiles, for example hydroxyl compounds, the attack at the C-4 carbonyl by these nucleophiles leads to the opening of the ring with the hydroxyl end group.


(4-10)

Hydroxyl end group in a chain is not a strong enough nucleophile to compete with pyridine in direct attack on the ring, but by reacting with the α-lactone (Equation 4-4) will effectively limit the molecular weight attainable.

As the suggested mechanism involves the attack of a nucleophile at the C-4 carbon of the anhydrocarboxylate ring, the substituents on the C-5 carbon must play an important role in the reaction profile. When the nucleophile and the solvent medium used are not varied the reactivities of series of anhydrocarboxylate rings may be determined by the nature of the substituents on the rings, and subsequently on the growing chain of a polymer. The electronic properties of the substituents govern the electrophilicity of the C-4 carbonyl of the ring and the nucleophilicity of an attacking polymer chain, the steric hindrance plays its part in impeding the attacking path of the nucleophile.

Correlation of the relative magnitude of the steric effect and the electronic or polar effect of the substituent with the measured rate of a reaction can be achieved with reasonable accuracy by using the Taft Equation. The Taft $\rho^* \sigma^*$ Equation (4-11) correlates a reaction rate, k, with σ^*, a parameter representing the polar or electronic effect of a substituent, and ρ^*, an empirical parameter dependent upon the nature of the reaction and on the reaction conditions.

$$\log \frac{k}{k_0} = \rho^* \sigma^* \qquad (4\text{-}11)$$

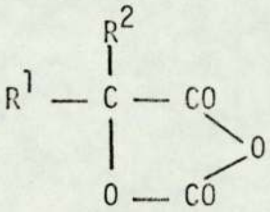
For the reaction series in which deviation occurred, when using Equation (4-11), due to steric effects associated with the reaction, the Equation (4-12) may be used.

$$\log \frac{k}{k_o} = \rho^* \sigma^* + sE_s \qquad (4\text{-}12)$$

Or $$\log k = \rho^* \sigma^* + sE_s + C \qquad (4\text{-}13)$$

Similarly E_s is considered as a steric substituent constant governed by an empirical parameter s. Thus the parameter ρ^* and s reflect the relative importance of polar and steric effects.

In the monomer of general type



studied here, the reaction rates at 60°C in the presence of equimolar pyridine in nitrobenzene provide a basis for comparison. The substituents, rate constants together with combined polar and steric parameter values are shown in Table 4.3. The best fit is obtained where a value of 1.88 is given to ρ^* and 1.29 to s, this is illustrated in Figure 4.5.

Two major features emerge from this analysis. The first is the realisation that aromatic or fluoroaromatic substituents are effective only in terms of their generalised steric and electronic feature and have no specific activating effect on the polymerisability of anhydrocarboxylates. The second is related to this and is, in fact, the prediction which follows from Figure 4.5 that two α-hydrogen substituents (i.e., the anhydrocarboxylate of glycollic acid) would

Table 4.3

Substituents on the C-5 carbon of an anhydrocarboxylate ring, second-order rate constants for pyridine initiated polymerisation at 60°C in nitrobenzene and the polar and steric parameters

R^1	R^2	k_2 at 60°C mole^{-1} litre sec^{-1}	σ^{*+}	E_s^+	$1.88\,\sigma^* + 1.29\,E_s$
C_6H_5	H	1200×10^{-4}	1.09	.74	2.99
$C_6H_5$$^{++}$	CH_3	1.62×10^{-4}	0.6	-0.5	0.48
$C_6F_5$$^{+++}$	CH_3	14.3×10^{-4}	1.10	-0.5	1.42
C_6H_5	C_6H_5	5.9×10^{-4}	1.2	-1.0	.96

[+] Value obtained from Reference (72).

[++] E_s value was approximately calculated by the E_s values of cyclohexyl and cyclopentyl.

[+++] σ^* obtained from Reference (76).

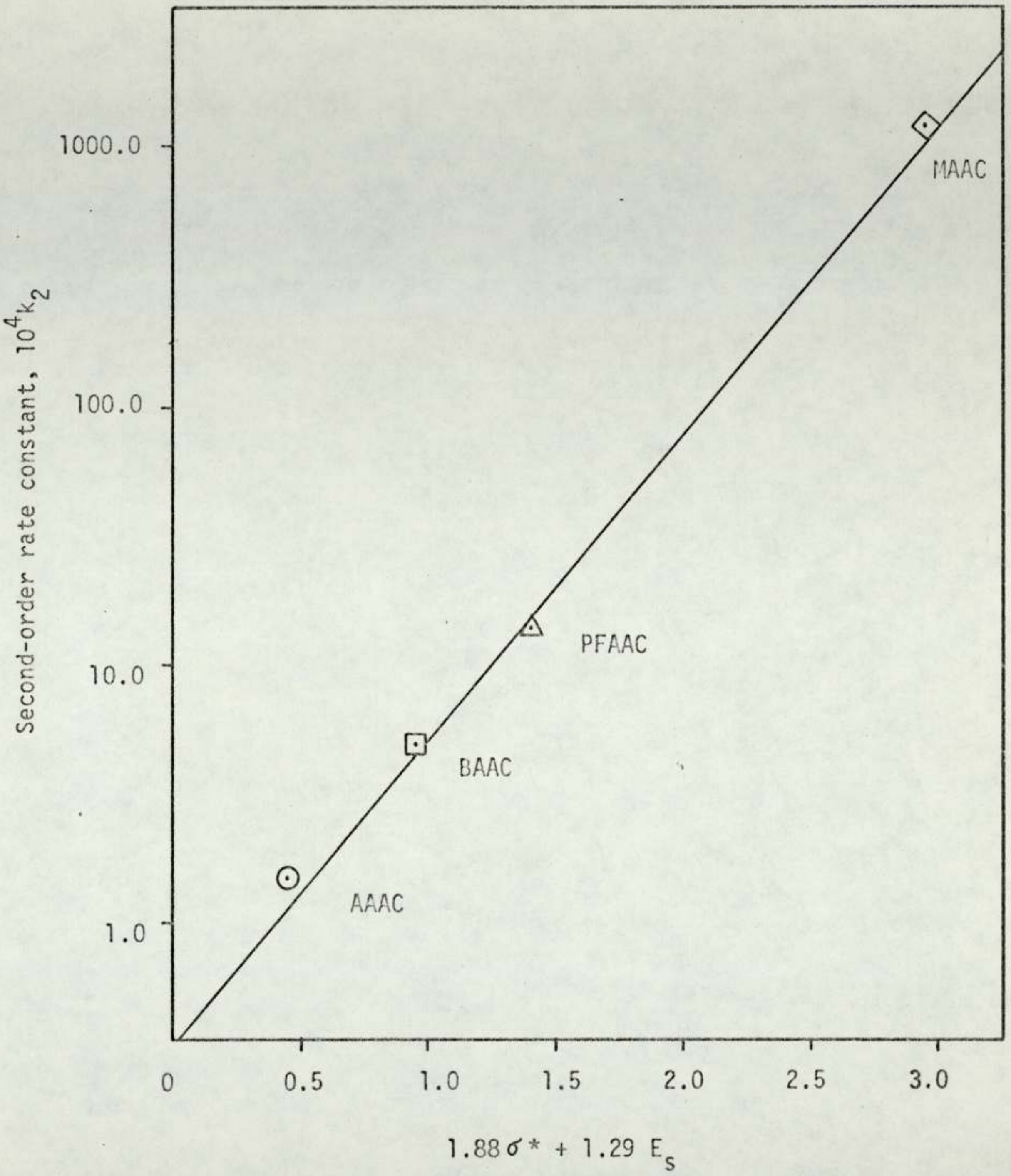


Figure 4.5 A semi-logarithmic plot of the second-order rate constant (k_2) versus the substituent factor ($1.88\sigma^* + 1.29 E_s$) for the pyridine initiated polymerisation of a series of α-hydroxy acid anhydrocarboxylates at 60°C in nitrobenzene.

be the most reactive of the common monomers.

The balance of steric and polar effects as indicated by the relative values of ρ^* and s is interestingly enough almost identical to that encountered in the reaction of anhydrocarboxylates with alcohols(63). The importance of this is that it provides support for the concept of pyridine attacking the C-4 carbonyl in the ring and being subjected to the steric restrictions imposed by the C-5 ring substituents.

It is apparent, however, that the mechanism as presented here has two particular limitations, the first of these is the absence of a termination step which is capable of explaining the unexpectedly low molecular weight encountered with all three monomers, AAAC, PFAAC and MAAC. The second, which may well be related to the first, is its failure to predict the deviation from simple first-order dependence at high pyridine concentration observed with the PFAAC(63) and AAAC. The molecular weight problem is of course fundamental to the validity of the mechanism and will be examined in more detail in a subsequent chapter.

CHAPTER 5

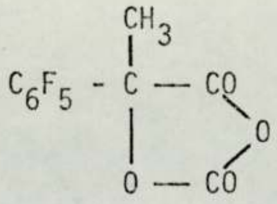
MECHANISTIC ANOMALIES IN THE TERTIARY BASE INITIATED POLYMERISATION OF ANHYDROCARBOXYLATES: KINETIC STUDY

This chapter presents the kinetic results and relevant information for the pyridine and substituted pyridines initiated polymerisation of anhydrocarboxylates. Discussion of these results will be presented in Chapter 7.

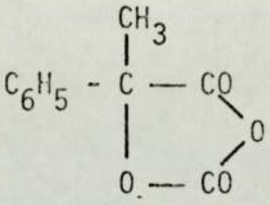
Investigations of the effect on kinetic behaviour of monomers, initiators and solvents were carried out within the temperature range of 40-70^{o}C. All materials were purified and dried to obtain a substantially anhydrous state by methods described in Chapter 2. The relevant molecular weight information is presented in Chapter 6.

5.1 Effect of Monomer on Kinetic Behaviour

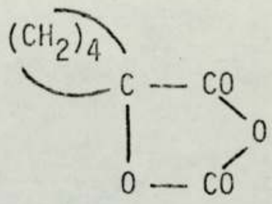
It is possible on present evidence that the pyridine initiated polymerisation described in earlier chapters may be peculiar to those anhydrocarboxylates with aromatic or perfluoroaromatic substituents. It was initially thought that possibly only PFAAC (X), the pentafluorophenyl and methyl substituted anhydrocarboxylate, and other fluoroaromatic substituted monomers would polymerise with appreciable rates (e.g. the derived second-order rate constants obtained from the polymerisations under the temperature range of 40-60^{o}C are in the order of 10^{-4} l. mole^{-1}. sec^{-1}.), but the results in Chapter 4 show that it is not so. AAAC (XI), the phenyl and methyl substituted anhydrocarboxylate, behaves similarly to PFAAC in both "pyridine response" and the molecular weight of polymer attainable under similar conditions.



(X)



(XI)



(XIV)

PFAAC and AAAC provide some light in understanding the contribution of electronic and steric effects from the bulky aromatic substituent to the polymerisability of an anhydrocarboxylate ring. It was then logical to study a suitable non-aromatic substituted anhydrocarboxylate under similar polymerisation conditions. Cyclopentane spiro-5-1,3-dioxolan-2,4-dione (C' pent AC, XIV) was thought to satisfy the requirements since it should be both less sterically hindered and electronically activated than PFAAC and AAAC.

The pyridine initiated polymerisations of C' pent AC were carried out in nitrobenzene within the temperature range 50-70^{0}C. The semi-log plots of log $[(P_{\infty}-P)/P_{\infty}]$ versus time shown in Figure 5.1 illustrate the first-order kinetic behaviour to be similar to those of PFAAC and AAAC. The first-order plots give straight lines well into the second decade. The derived second-order rate constants are of the same order ($\simeq 10^{-4}$ l. mole^{-1}. sec^{-1}.) as those obtained from PFAAC and are higher than the derived second-order rate constants of AAAC (of the order of 10^{-5} l. mole^{-1}. sec^{-1}.) obtained over the same temperature range. Table 5.1 gives the derived second-order rate constants of the pyridine initiated polymerisation of C' pent AC together with the activation parameters obtained from the Arrhenius plot, Figure 5.2.

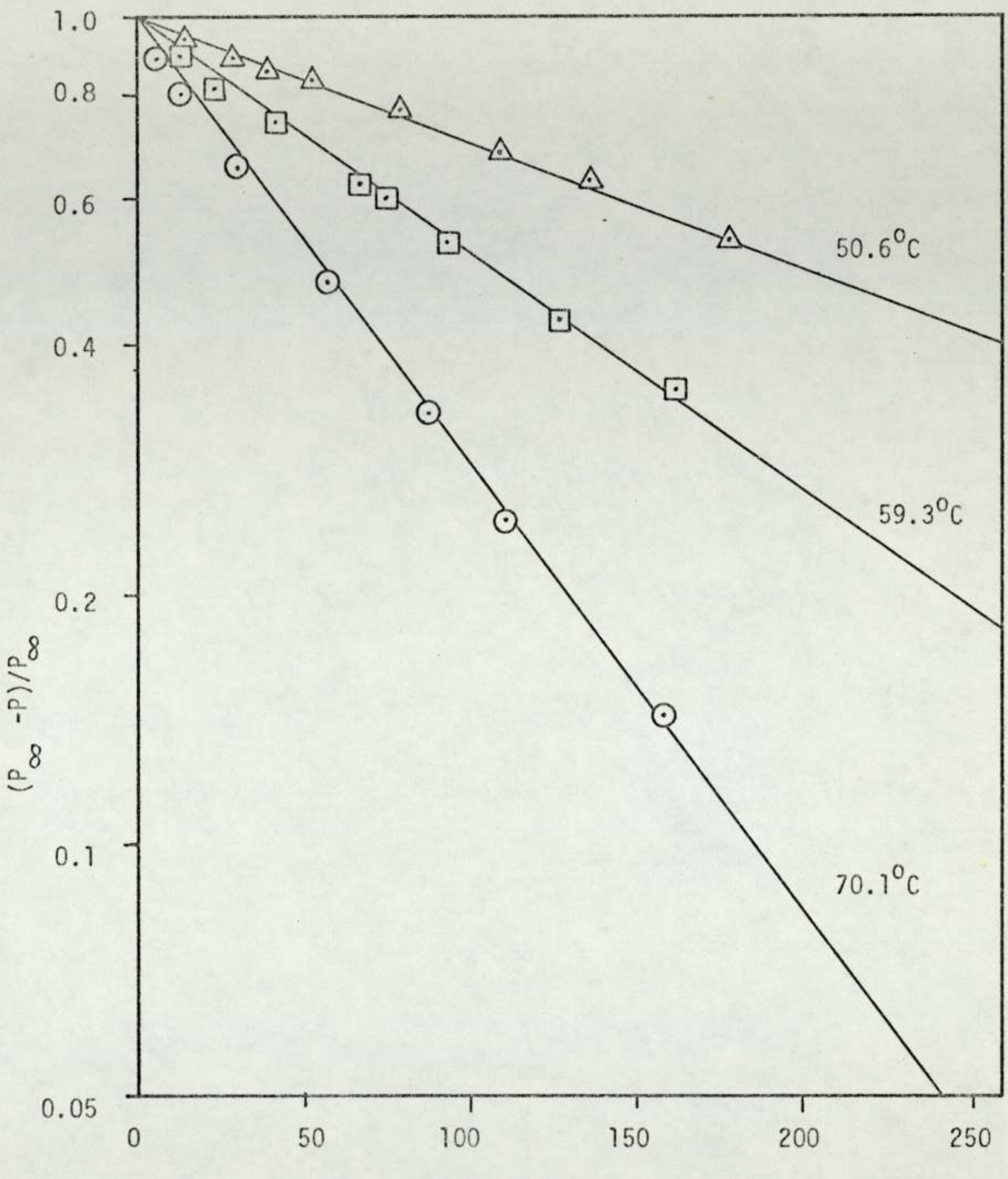


Figure 5.1 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of C' pent AC in nitrobenzene.

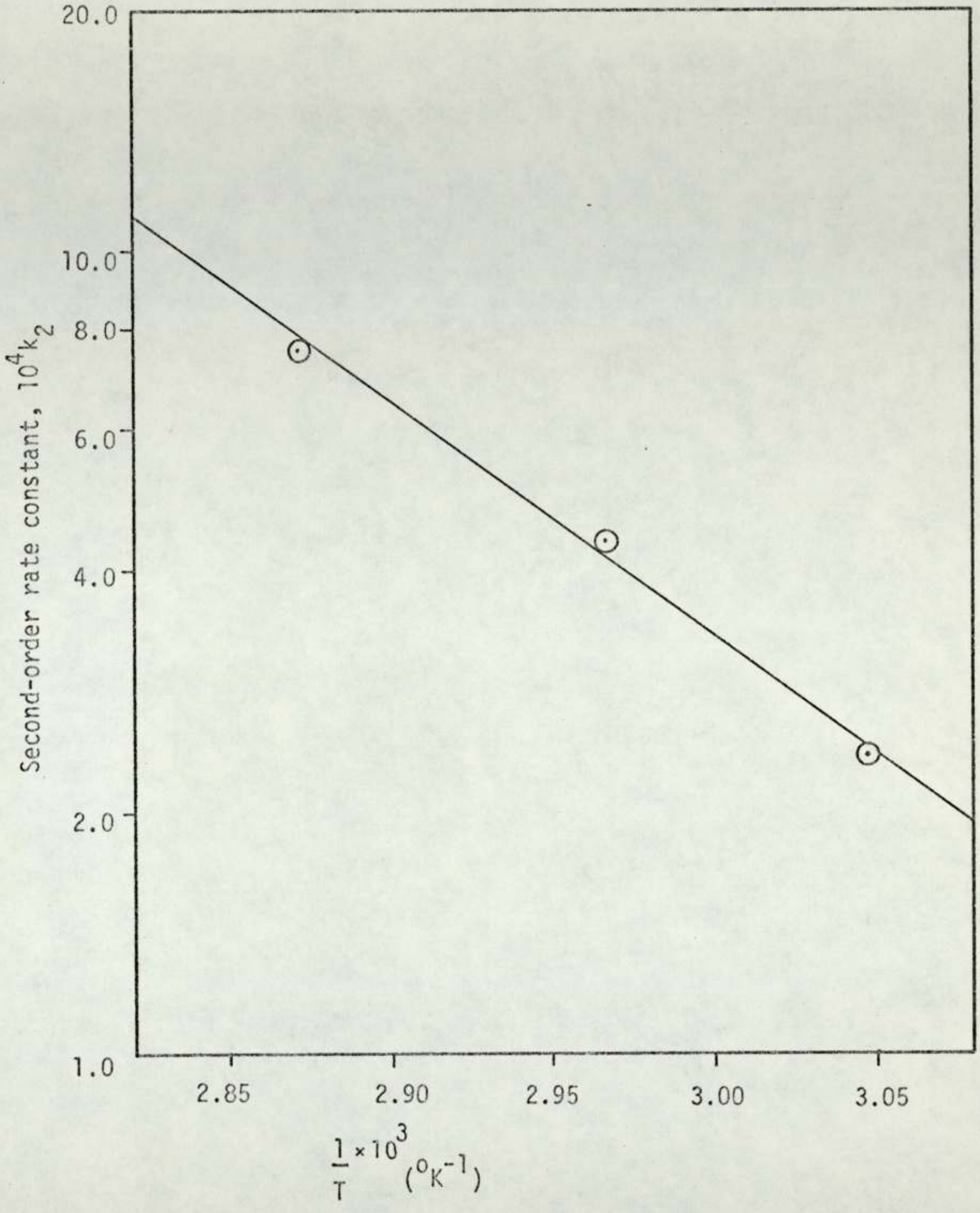


Figure 5.2 An Arrhenius plot of the second-order rate constant, k_2, versus the reciprocal of absolute temperature for the pyridine initiated polymerisation of C' pent AC in nitrobenzene. Temperature range 50-70^{o}C.

Table 5.1

Second-order rate constants (k_2), energy of activation ($E^{\ddagger}$), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the pyridine initiated polymerisation of C' pent AC in nitrobenzene

Temperature ^{o}C	10^4 k_2 $l.mole^{-1}.sec^{-1}$.
50.6	2.34
59.3	4.35
70.1	7.51
$E^{\ddagger}$ (kJ $mole^{-1}$.)	55.0
A ($l.mole^{-1}.sec^{-1}$.)	2.5×10^5
$\Delta S^{\ddagger}$ (J $K^{-1}.mole^{-1}$.)	-149

5.2 Effect of Solvent on Kinetic Behaviour

In anhydrous nitrobenzene medium the kinetics of pyridine initiated polymerisation of PFAAC(63), AAAC and C' pent AC under the conditions employed in this work are first-order with respect to the monomer concentration, as shown in Chapter 4 and this Chapter, Section 5.1. Investigation of the effect of solvent on the reaction was thought to be interesting since it might provide some information concerning the reaction pathways. Dimethyl sulphoxide (DMSO) and anisole were chosen as the medium for pyridine initiated polymerisation under the temperature range of 40-60^{o}C.

5.2.1 Pyridine Initiated Polymerisation of PFAAC in Dimethyl Sulphoxide and Anisole

The results of pyridine initiated polymerisation of PFAAC in dimethyl sulphoxide at equimolar concentration of 0.25M over the temperature range 40-60^{o}C exhibit a deviation from simple first-order behaviour as shown in the first-order plots between log $[(P_{\infty}-P)/P_{\infty}]$ and time in Figure 5.3. The reactions at 50.2 and 60.0^{o}C, as followed by the gas evolution technique, started with fast reaction rates up to about 40-50 per cent of the monomer being consumed. At this point the reaction rates began to decrease to constant values which were maintained up to the end of the reaction. At 40.0^{o}C the reaction, however, behaved in a different manner following more closely a first-order kinetic pattern. The second-order rate constants calculated from the initial parts of the reaction are given in Table 5.2.

Table 5.2

Second-order rate constants (k_2), energy of activation ($E^{\ddagger}$), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the pyridine initiated polymerisation of PFAAC in dimethyl sulphoxide at equimolar concentration $[PFAAC]_0 = [py] = 0.25$ mole.litre^{-1}.

Temperature ^{o}C	10^3 k_2 l.mole^{-1}.sec^{-1}.
40.0	1.15
50.2	2.57
60.0	5.77
$E^{\ddagger}$ (kJ mole^{-1}.)	69.3
A (l.mole^{-1}.sec^{-1}.)	4.2×10^8
$\Delta S^{\ddagger}$ (J K^{-1}.mole^{-1}.)	-87

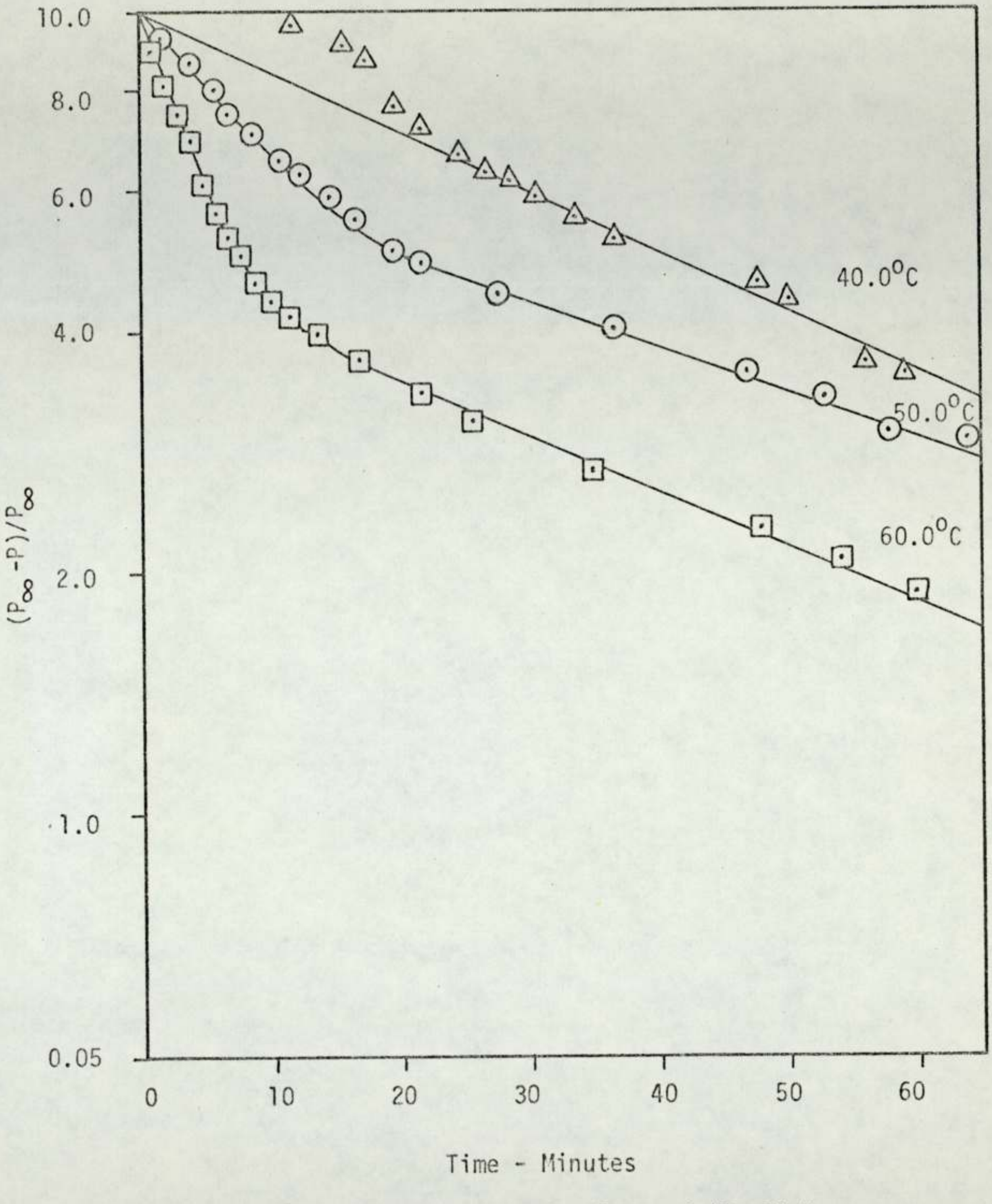


Figure 5.3 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of PFAAC in dimethyl sulphoxide.

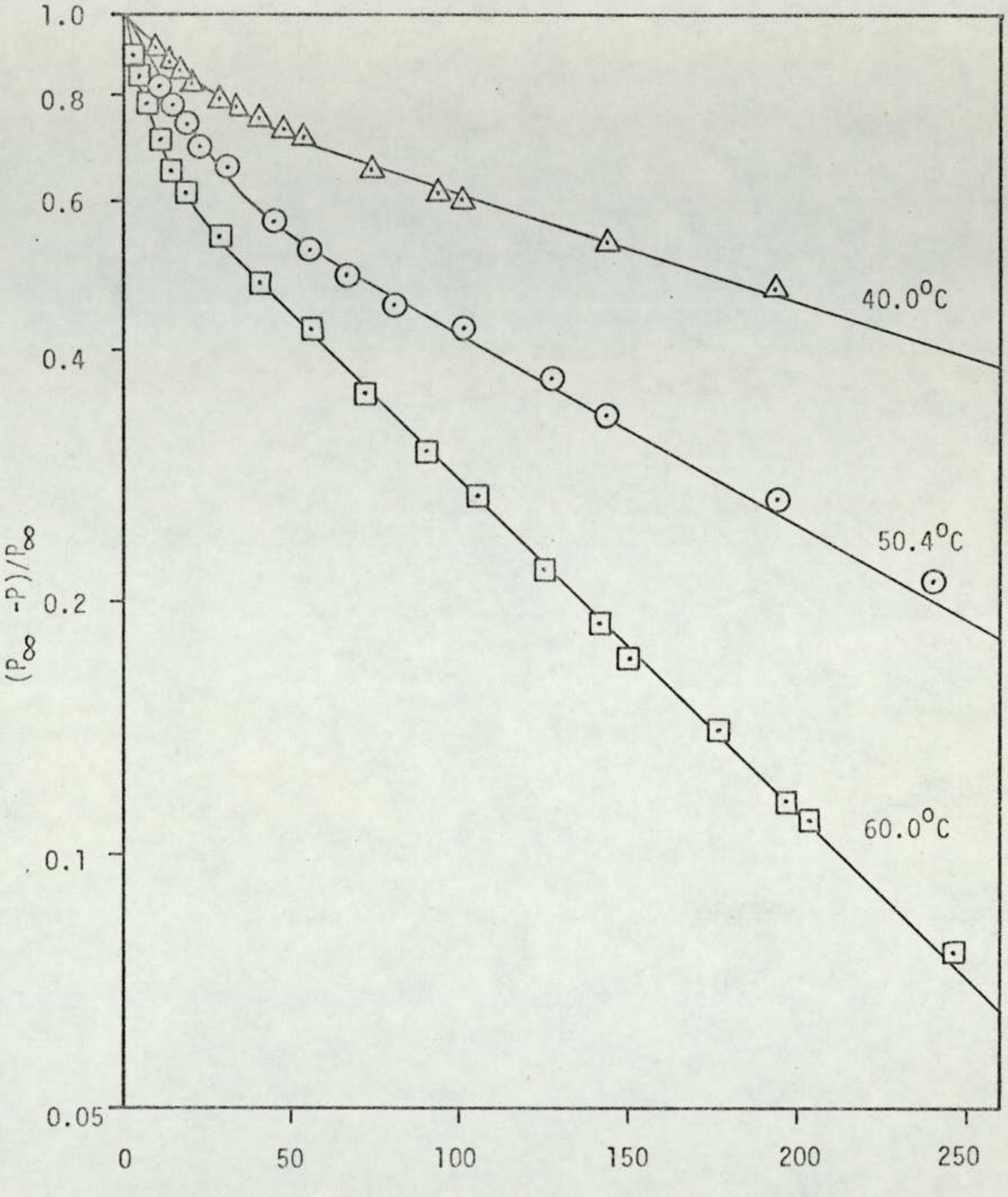


Figure 5.4 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of PFAAC in anisole.

Similar kinetic behaviour was found when anisole was employed as a solvent in the reaction between equimolar (0.25M) PFAAC and pyridine within the same temperature range of 40-60°C. In this set of polymerisations all three reactions (at 40.0, 50.4 and 60.0°C) started with fast reaction rates followed by a change to slow reaction rates which were maintained up to the completion. In comparison with the polymerisation in dimethyl sulphoxide, the change in the reaction rates in anisole started at an earlier stage, at the points where the monomer consumption were at about 20, 30 and 40 per cent at 40.0 50.4 and 60.0°C respectively. Figure 5.4 and Table 5.3 show the first-order plots of log $[(P_\infty - P)/P_\infty]$ versus time and the initial second-order rate constants together with the activation parameters respectively.

Table 5.3

Second-order rate constants (k_2), energy of activation ($E^\ddagger$), pre-exponential factor (A) and entropy of activation ($\Delta S^\ddagger$) for the pyridine initiated polymerisation of PFAAC in anisole at equimolar concentration. $[PFAAC]_0 = [py] = 0.25$ mole.litre^{-1}.

Temperature °C	10^4 k_2 l.mole^{-1}.sec^{-1}.
40.0	5.84
50.4	9.82
60.0	17.7
$E^\ddagger$ (kJ mole^{-1}.)	48.3
A (l.mole^{-1}.sec^{-1}.)	7.7×10^4
$\Delta S^\ddagger$ (J K^{-1}.mole^{-1}.)	-159

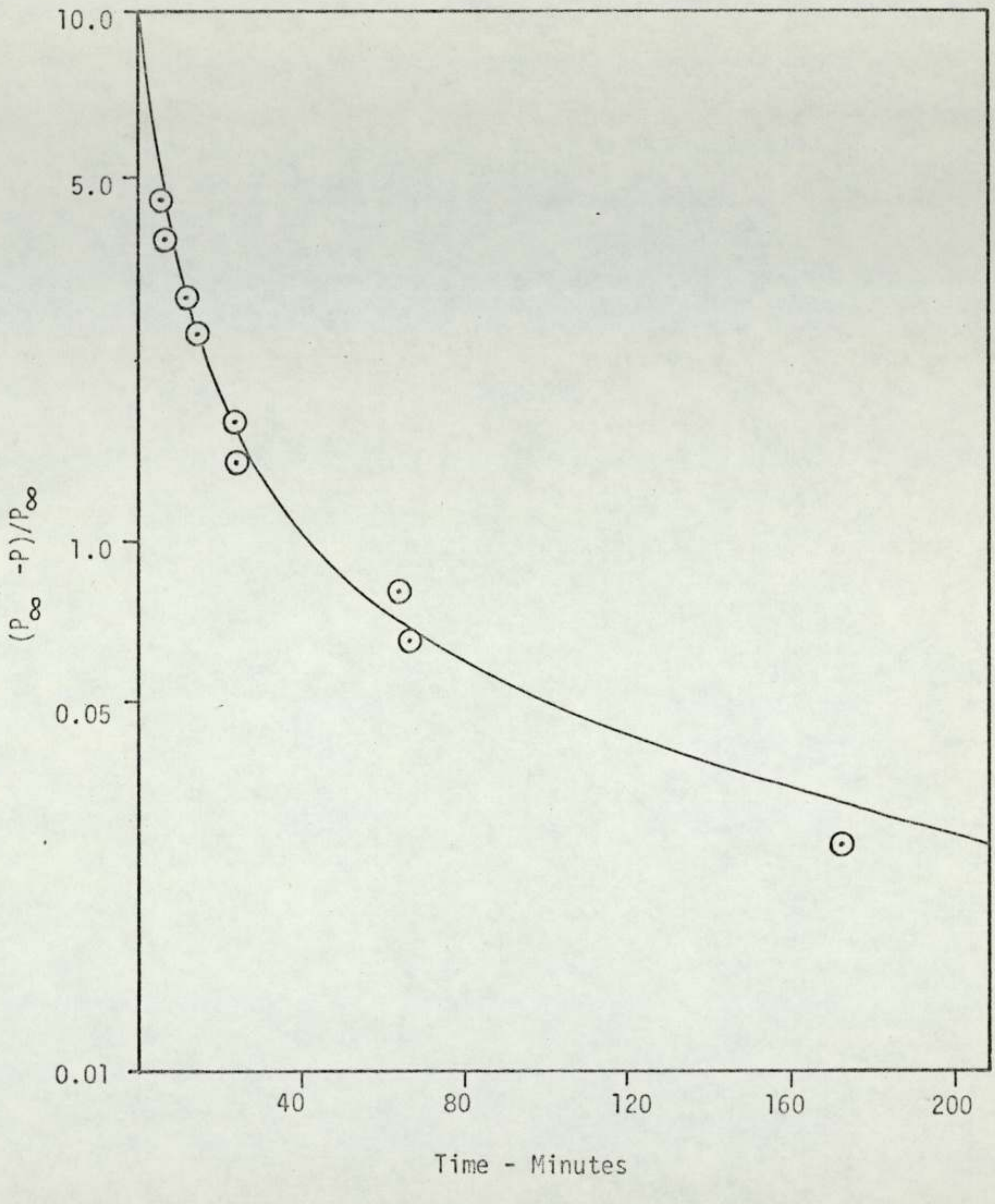


Figure 5.5 A semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of PFAAC in dimethyl sulphoxide in the presence of a partial pressure of carbon dioxide ($\simeq P_\infty$). Temperature = $60.1^{\circ}C$.

In the case of dimethyl sulphoxide as a solvent it was suggested that the deviation in the rate constants of the polymerisation could have been caused by reaction between evolved gaseous carbon dioxide and dimethyl sulphoxide, thus decreasing the pressure of the system since the reacted carbon dioxide cannot enter the gaseous phase.

A kinetic experiment on the reaction between equimolar PFAAC and pyridine (0.25M, 60.1°C) in dimethyl sulphoxide under an atmosphere of carbon dioxide was carried out by the gas evolution technique. The result is shown in Figure 5.5 as the semi-log plot of log $[(P_{\infty}-P)/P_{\infty}]$ versus time.

5.2.2 Pyridine Initiated Polymerisation of AAAC and C' pent AC in Dimethyl Sulphoxide

It was suggested that the presence of a pentafluorophenyl group, which is a strongly electron-withdrawing group, in a ring might be responsible for the deviation of the kinetic behaviour from first order. In order to assess this possibility, AAAC and C' pent AC were used in the reaction with pyridine with dimethyl sulphoxide as a solvent. The results gave the same type of deviation as that observed with PFAAC as shown in Figures 5.6 and 5.7 which contain the plots of log $[(P_{\infty}-P)/P_{\infty}]$ versus time for the reactions of AAAC and C' pent AC with pyridine respectively.

5.2.3 Effect of Co-Solvent on Kinetic Behaviour

It was decided to study the effect of co-solvent between nitrobenzene, which gives first-order behaviour, and dimethyl sulphoxide, which causes a deviation from a simple first-order behaviour of the reaction between an anhydrocarboxylate and pyridine. The co-solvent system of 1:1 mole ratio nitrobenzene-dimethyl sulphoxide was used for the pyridine initiated polymerisation of AAAC at 58.4°C. The

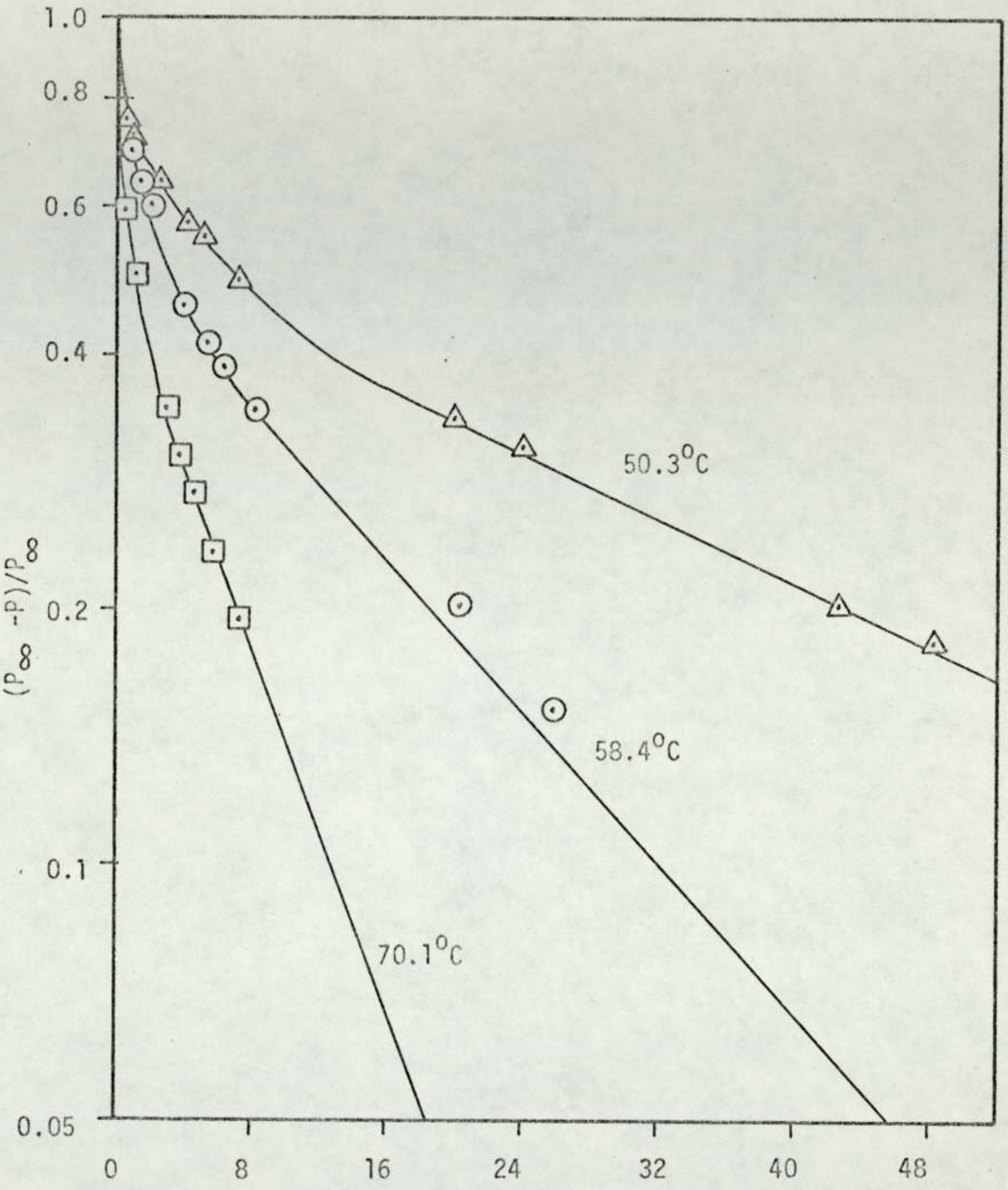


Figure 5.6 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of AAAC in dimethyl sulphoxide. The initial rates of reaction were not able to be calculated.

△ $[AAAC]_0 = [Py] = 0.21$ mole.litre^{-1}.

⊙,⊡ $[AAAC]_0 = 0.19$ mole.litre^{-1}.

$[Py] = 0.25$ mole.litre-1.

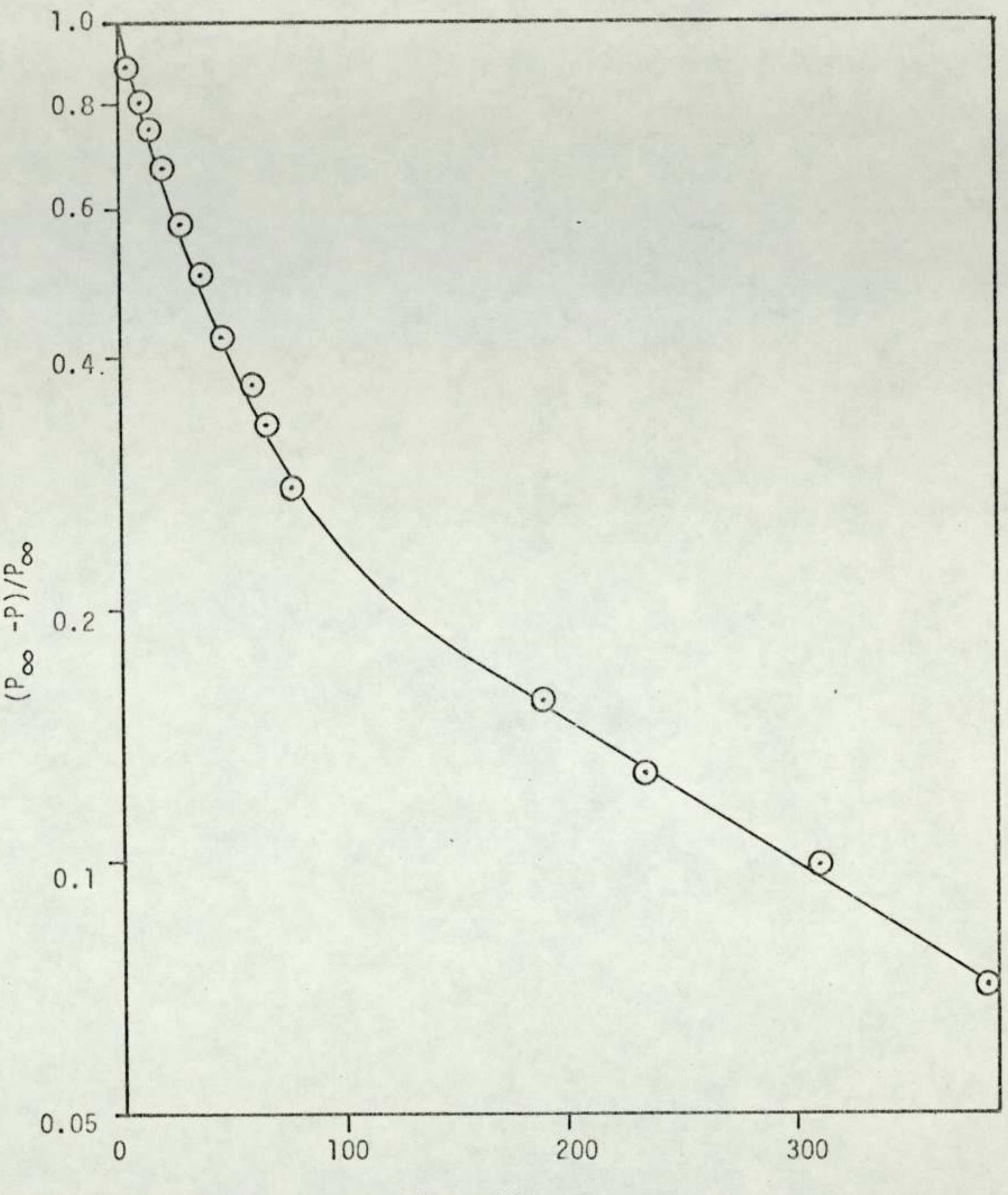


Figure 5.7 A semi-logarithmic plot of $(P_\infty - P)/P_\infty$ for the pyridine initiated polymerisation of C' pent AC in dimethyl sulphoxide at 60.3°C. $[\text{C' pent AC}]_0 = [\text{Py}] = 0.25$ mole. litre^{-1}.

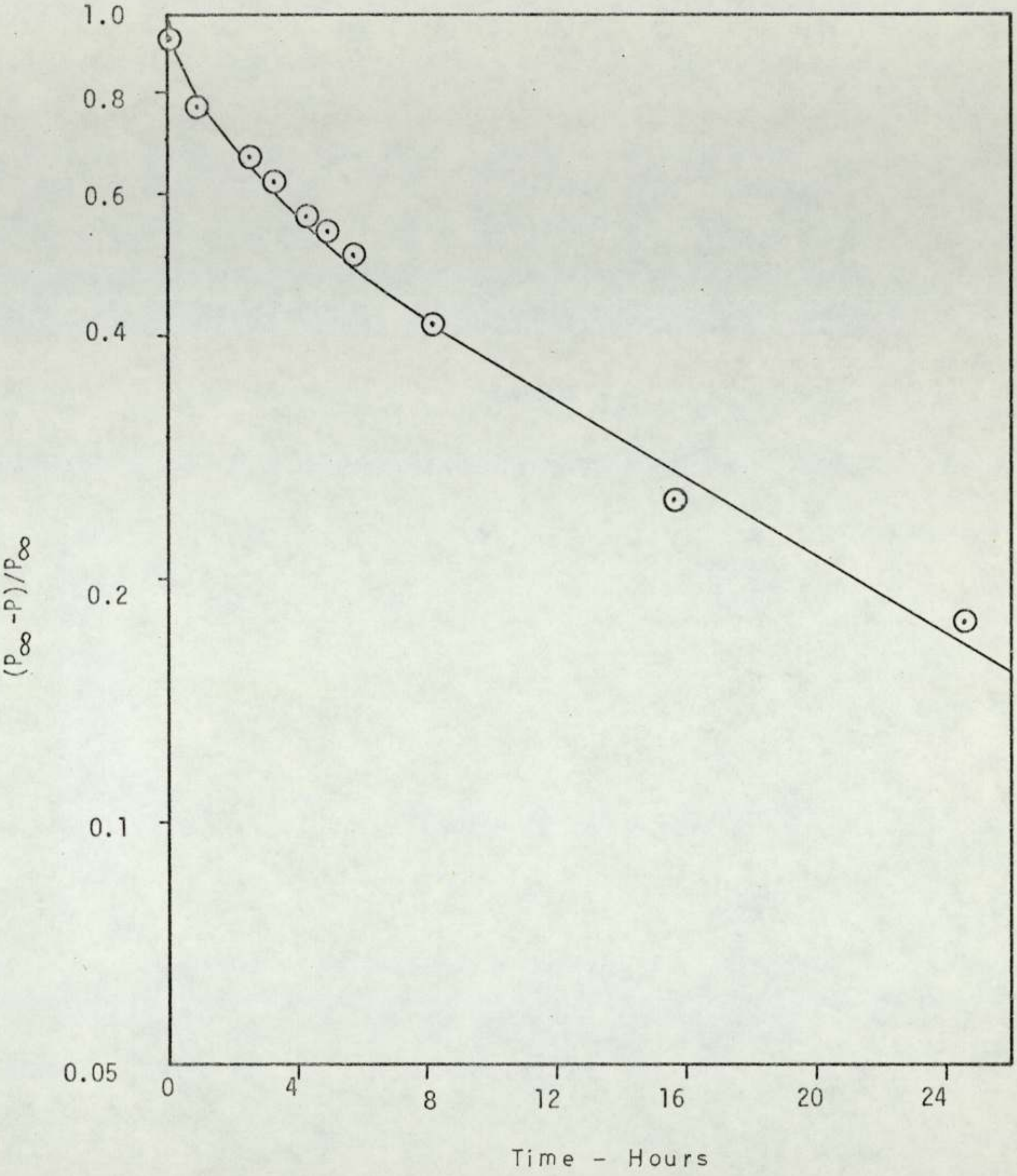


Figure 5.8 A semi-logarithmic plot of $(P_\infty - P)/P_\infty$ for the pyridine initiated polymerisation of AAAC in a 1:1 mole ratio nitrobenzene: dimethyl sulphoxide co-solvent system at 58.4^{o}C.

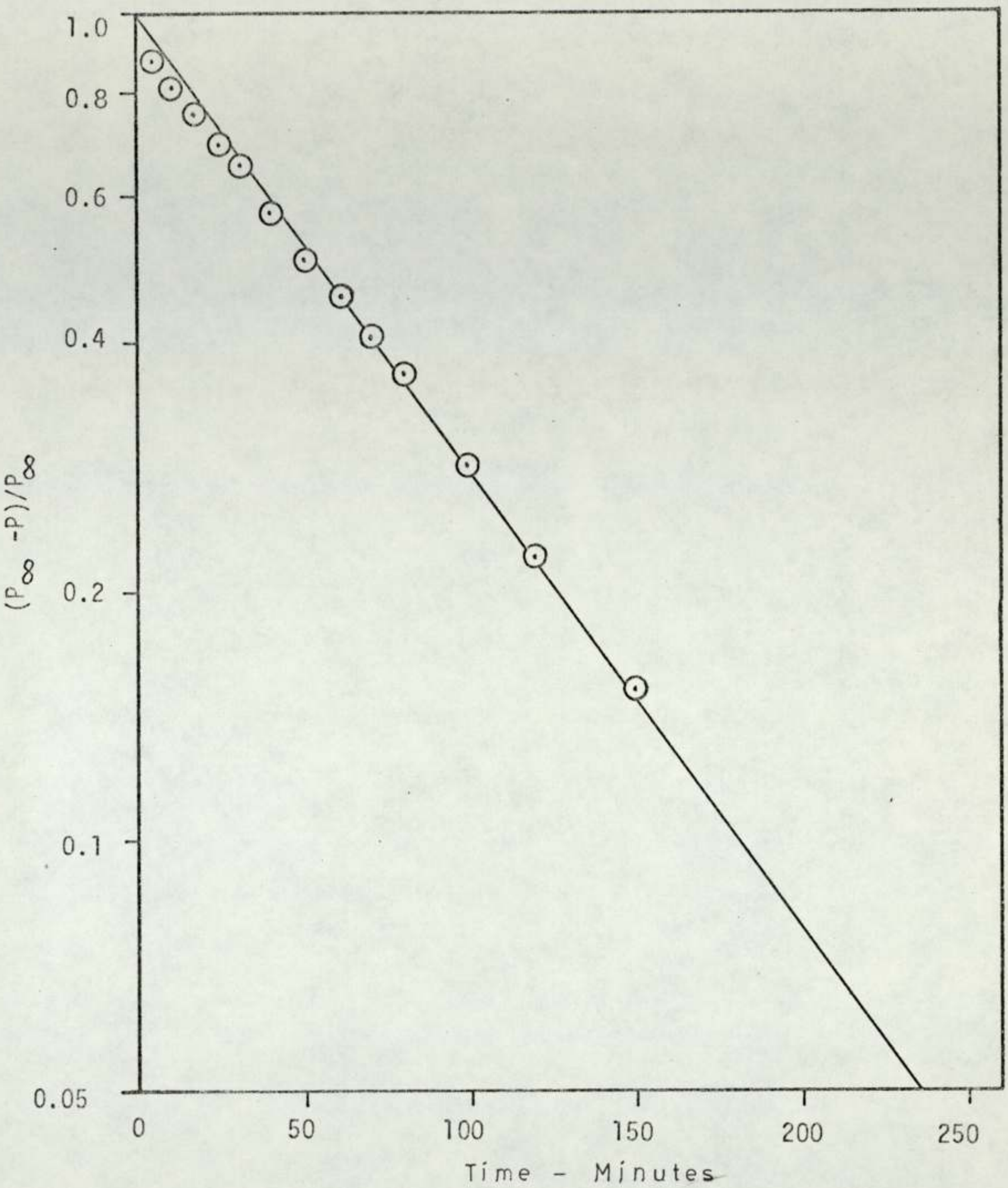


Figure 5.9 A semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the pyridine initiated polymerisation of PFAAC in a 3:2 mole ratio nitrobenzene:dekalin co-solvent system at 60.3°C.

concentration of monomer and initiator were 0.15 and 0.30 M respectively. The resulting curved first-order plot is shown in Figure 5.8.

Since both the solvents which gave deviation from ideal first-order behaviour had fairly polar characteristics, a non-polar solvent was examined. The co-solvent system formed between nitrobenzene and dekalin at 3:2 mole ratio was used in the polymerisation of PFAAC initiated by pyridine at equimolar concentration of 0.25M at 60.3°C. The actual purpose of the experiment was to observe the kinetic pattern of the polymerisation in another solvent, dekalin, but since the solubility of anhydrocarboxylates in this solvent is low it was necessary to use nitrobenzene as a co-solvent. The first-order plot of this reaction gave a good straight line as shown in Figure 5.9.

5.3 Effect of Initiator on Kinetic Behaviour

In the suggested mechanism of pyridine initiated polymerisation of anhydrocarboxylates, the initial step is the attack of the ring nitrogen of pyridine on the C-4 carbonyl of the anhydrocarboxylate ring to form a complex intermediate. This step is believed to be the rate determining step of the polymerisation, in a constant reaction condition the nature of both monomer and initiator govern the formation of the complex intermediate.

In the investigation of the effect of initiator on the kinetic behaviour, the system chosen for all experiments was PFAAC in nitrobenzene at 0.25M within the temperature range of 40-70°C. The initiators used were 2,2' bipyridyl and biphenyl-2-pyridyl methane.

5.3.1 2,2' Bipyridyl Initiated Polymerisation of PFAAC

The polymerisations in nitrobenzene were carried out with equimolar monomer and initiator at 40.0, 49.5 and 60.0°C. The pressure versus time profile of the reactions were found to be

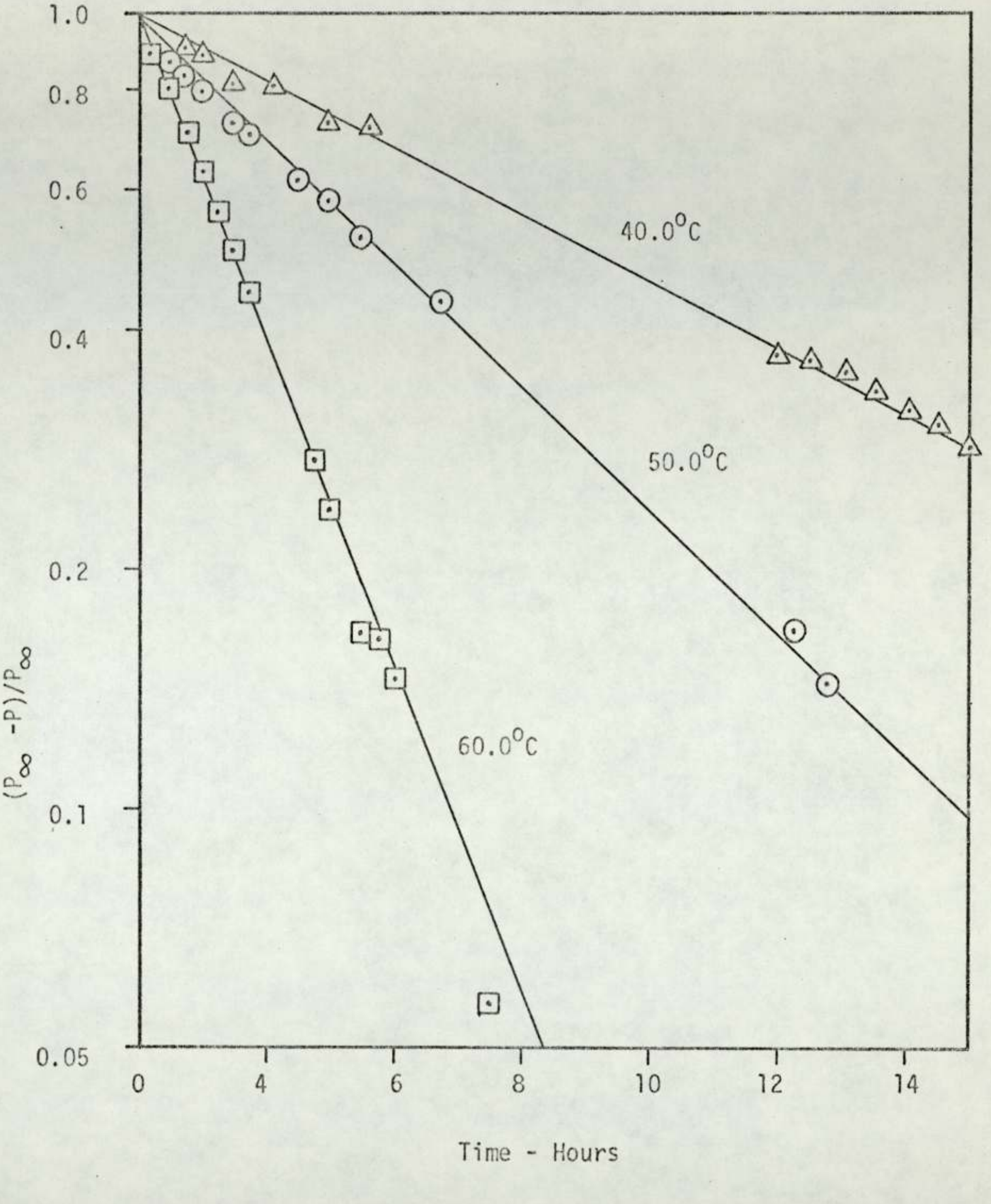


Figure 5.10 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the 2,2'-bipyridyl initiated polymerisation of PFAAC in nitrobenzene.

first order and the semi-log plots (log $[(P_\infty - P)/P_\infty]$ versus time) for the three kinetic runs, presented in Figure 5.11, illustrate the first-order dependence on monomer concentration and the fact that the initiator concentration was sensibly constant throughout the reaction. The derived second-order rate constants of the polymerisations and the activation parameters are given in Table 5.4.

Table 5.4

Second-order rate constants (k_2), energy of activation ($E^{\ddagger}$), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for 2,2'-bipyridyl initiated polymerisation of PFAAC in nitrobenzene. $[\text{PFAAC}]_0 = [\text{initiator}] = 0.25$ mole.litre^{-1}.

Temperature °C	$10^4\ k_2$ l.mole^{-1}.sec^{-1}.
40.0	0.51
49.5	1.05
60.0	2.56
$E^{\ddagger}$ (kJ mole^{-1}.)	69.8
A (l.mole^{-1}.sec^{-1}.)	2.2×10^7
$\Delta S^{\ddagger}$ (J K^{-1}.mole^{-1}.)	-112

5.3.2 Biphenyl-2-Pyridyl Methane Initiated Polymerisation of PFAAC

The polymerisation of PFAAC initiated by biphenyl-2-pyridyl methane in nitrobenzene over the temperatue range 50-70°C was also

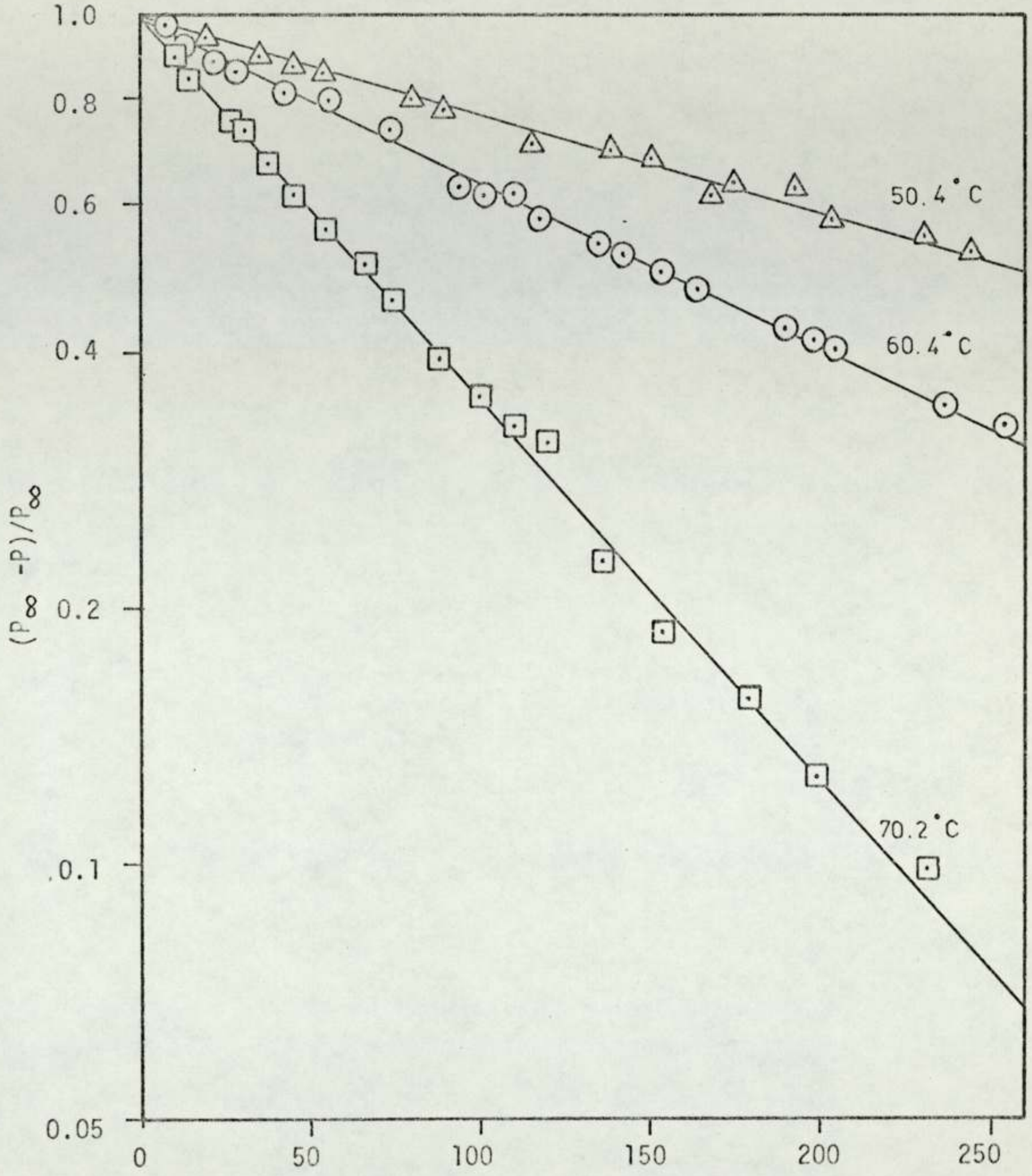


Figure 5.11 Semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the biphenyl-2-pyridyl methane initiated polymerisation of PFAAC in nitrobenzene.

shown to exhibit first-order dependence on monomer concentration with a constant initiator concentration throughout the reaction. Figure 5.11 illustrates the first-order plots, $\log [(P_\infty - P)/P_\infty]$ versus time, of the initiated polymerisation of PFAAC by an equimolar amount of biphenyl-2-pyridyl methane (0.25M) at 50.5, 60.4, and 70.2^{o}C in nitrobenzene. The derived second-order rate constants and the activation parameters are shown in Table 5.5.

Table 5.5

Second-order rate constants (k_2), energy of activation ($E^\ddagger$), pre-exponential factor (A) and entropy of activation ($\Delta S^\ddagger$) for biphenyl-2 pyridyl methane initiated polymerisation of PFAAC in nitrobenzene. $[\text{PFAAC}]_o = [\text{initiator}] = 0.25$ mole.litre^{-1}

Temperature ^{o}C	10^4 k_2 l.mole^{-1}.sec^{-1}.
50.5	1.76
60.4	3.01
70.2	6.89
$E^\ddagger$ (kJ mole^{-1}.)	65.1
A (l.mole^{-1}.sec^{-1}.)	5.2×10^6
$\Delta S^\ddagger$ (J K^{-1}.mole^{-1}.)	-124

CHAPTER 6

MOLECULAR WEIGHT STUDY OF POLY α-ESTERS

The scope of glycollides and substituted glycollides of α-hydroxy acids which have limitations in the synthesis of highly substituted poly α-esters, is greatly extended by the anhydrosulphite and anhydrocarboxylate derivatives of α-hydroxy carboxylic acids which have provided new routes in the synthesis of polymers of this type.

α-hydroxy acid anhydrosulphites have proved to give reasonably high molecular weight (approximately 10^4) poly aliphatic and spiro alkyl substituted poly α-esters(59). There had been little knowledge of, and few studies relating to poly α-esters obtained from α-hydroxy carboxylic acid anhydrocarboxylates especially on the molecular weight aspects before this present work. The work presented in this chapter are results from a series of experiments involving the study of various effects on the molecular weights of poly α-esters obtained from the decomposition of α-hydroxy carboxylic acid anhydrocarboxylates. The related discussion is presented in Chapter 7.

6.1 Gel Permeation Chromatography

Molecular weight determinations of all polymers or decomposition products obtained from the experiments were carried out by Gel Permeation Chromatographic method (G.P.C.) serviced by R.A.P.R.A., Polymer Supply and Characterisation Centre.(77)

The principal of G.P.C. is based on a type of liquid-solid elution column chromatography involving the permeation of solute molecules into rigid porous 'gel' particles. As the dissolved polymer molecules flow through the column they can diffuse into the internal pore structure of the gel to an extent depending on their size and the pore-size distribution of the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded; small polymer molecules penetrate a larger fraction of the interior of the gel. The larger the molecule, therefore, the less time it spends inside the gel, and the sooner it flows through the column. The different molecular species are eluted from the column in order of their molecular size as distinct from their molecular weight, the largest emerging first. Gel Permeation Chromatography provides a simultaneous measurement of molecular size and molecular weight distribution within polymers.

A specific column or set of columns with gel (the most widely used being highly cross-linked polystyrene) of differing pore size is calibrated empirically to give a relationship between retention times or volumes and molecular size of polymer. By means of this, a plot of amount of solute versus retention volume can be converted into a molecular-size distribution curve.

The final product from a G.P.C. analysis is the recorded trace of the chromatogram. Figure 6.1 shows a typical chromatogram from a sample of poly PFAAC obtained from G.P.C. analysis provided by R.A.P.R.A. This trace shows the difference in refractive index of the eluent from the sample columns compared to that from the reference columns. The recorded figure is a function of the concentration and refractive index of the dissolved species eluting, the eluant marker pulses on the trace giving a measure of the elution volume or retention volume (the quantity of solvent that has passed through the sample columns from the point of sample solution injection).

Figure 6.2 shows a set of computed results obtained from the same poly PFAAC sample which gave the chromatogram in Figure 6.1. The format of the results enables the differential molecular weight distribution curve, dW/d log M versus log M to be calculated. The original readings taken from the chromatogram are given in column 1 and 2, the chromatogram height per retention volume increment. The calibration curve is given in column 1 and 3, the molecular weight of polystyrene (standard) per retention volume increment.

Sample of poly α-esters analysed by G.P.C. at R.A.P.R.A. were operated with the G.P.C. Operating Variables shown below:

Flow Rate	1 ml per minute
Solvent	Tetrahydrofuran plus 0.1% 2,6-ditert-butyl- p -Cresol as inhibitor.
Temperature	Ambient.

As the calibration is based on standardised molecular weight of polystyrene, for the interpretation it is assumed that the polymer-poly α-ester- behaves as polystyrene in solution. A closer approximation to the molecular weight of the poly α-ester is achieved by using the "Q" factor which takes account of the different relationship of molecular mass to repeat unit length.

Q = Molecular weight per Å unit of extended chain length

Q for polystyrene = 41.4

Q for poly PFAAC = 63.5

$$\text{M.W. of poly PFAAC} = \text{M.W. of polystyrene} \times \frac{63.5}{41.4}$$

6.2 Effect of Purity

Poly α-esters of PFAAC obtained from pyridine initiated polymerisation had been found to have such a low molecular weight

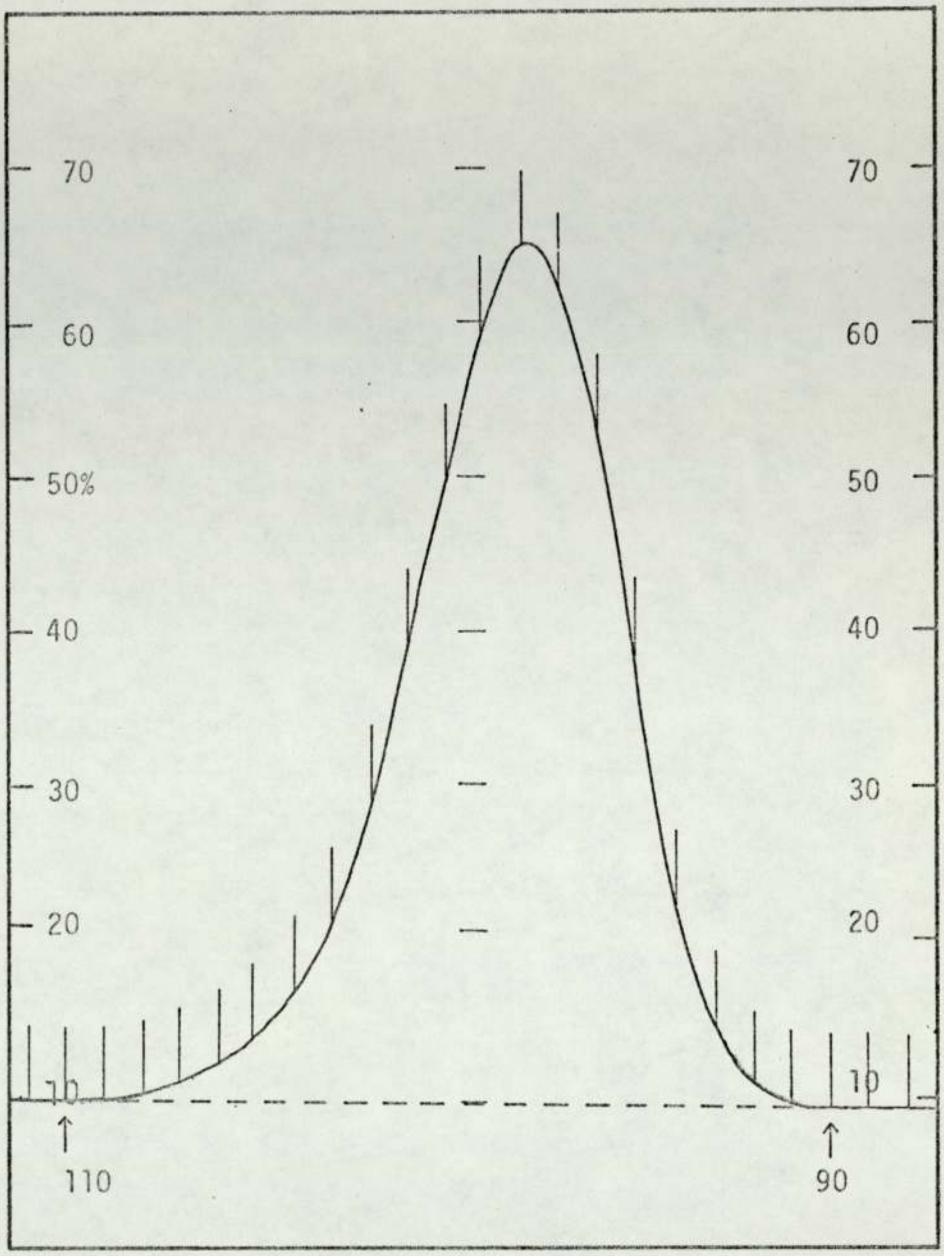


Figure 6.1 An example of a gel permeation chromatogram obtained from the analysis of poly PFAAC.

Concentration 0.2%
Solvent THF
Sensitivity 8X
Temperature 23^{o}C

```
 RETENTION   POLYMER   DW/DV,%     CALIB.       POLYMER      LOGM    DW/DLOGM,%
VOL(COUNTS)  H VALUES  VALUES     M VALUES     M VALUES     VALUES    VALUES

    90         0.00      0.00    1.320E+04    1.320E+04    4.1205      0.00
    91         0.09      0.03    1.000E+04    1.000E+04    4.0000      0.01
    92         1.62      0.47    7.700E+03    7.700E+03    3.8865      0.27
    93         5.46      1.58    5.850E+03    5,850E+03    3.7671      0.93
    94        13.48      3.91    4.500E+03    4.500E+03    3.6532      2.45
    95        26.87      7.79    3.520E+03    3.520E+03    3.5465      5.23
    96        41.33     11.99    2.820E+03    2.820E+03    3.4502      8.84
    97        51.03     14.80    2.300E+03    2.300E+03    3.3617     12.24
    98        52.77     15.30    1.920E+03    1.920E+03    3.2833     14.35
    99        47.41     13.75    1.630E+03    1.630E+03    3.2122     14.54
   100        37.47     10.87    1.410E+03    1.410E+03    3.1492     12.94
   101        26.97      7.82    1.240E+03    1.240E+03    3.0934     10.26
   102        17.50      5.08    1.100E+03    1.100E+03    3.0414      7.24
   103        10.80      3.13    1.000E+03    1.000E+03    3.0000      4.80
   104         6.15      1.78    9.200E+02    9.200E+02    2.9638      2.90
   105         3.44      1.00    8.400E+02    8.400E+02    2.9243      1.71
   106         1.60      0.46    7.600E+02    7.600E+02    2.8808      0.83
   107         0.60      0.18    7.000E+02    7.000E+02    2.8451      0.33
   108         0.22      0.06    6.400E+02    6.400E+02    2.8062      0.12
   109         0.01      0.00    5.850E+02    5.850E+02    2.7671      0.00
   110         0.00      0.00    5.400E+02    5.400E+02    2.7324      0.00


          K1 = 1.200E-04          A1 = 0.710
          K2 = 1.200E-04          A2 = 0.710

          MN = 1.774E+03
          MW = 2.145E+03       MW/MN = 1.21
          MZ = 2.668E+03       MZ/MN = 1.50
          MV = 2.082E+03
     FOR A = 0.710            ONE COUNT = 2.5 MLS
```

Figure 6.2 Computed results giving molecular weight of Poly PFAAC corresponding to the chromatogram shown in Figure 6.1.

Table 6.1

Purification methods for monomer, initiator, and solvent

Chemical	Method	Purification
Monomer (PFAAC)	a	Vacuum sublimation and kept in a dry box for about one year
	b	Vacuum sublimation carried out just prior to use
Initiator (Pyridine)	a	1. Treatment (reflux) with potassium hydroxide. 2. Vacuum distillation
	b	1. Treatment with p-toluene-sulphonic acid (to exclude possible traces of 1^{o} and 2^{o} amine) 2. Treatment with potassium hydroxide 3. Vacuum distillation
Solvent (Toluene)	a	1. Treatment with sodium wire 2. Vacuum distillation

Table 6.2

G.P.C. results of poly PFAAC derived from pyridine initiated polymerisation in toluene at 60°C

Purification Method			Monomer Concentration (Molar)	Mole Ratio PFAAC: Py	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
PFAAC	Pyridine	Toluene							
a	a	No solvent - bulk polymerisation	-	10:4	1243 1278	1402 1705	1.127 1.334	1400 1800	4000 5200
b	a	No solvent - bulk polymerisation	-	1:5	1456	2323	1.595	1800	11500
b	b	No solvent -bulk polymerisation	-	1:10	2925	4084	1.40	3100	20000
b	a	a	0.30	1:8	1257 1286	1618 1633	1.287 1.269	1800 1800	5200 7000
b	b	a	0.30	1:8	2414 2766	2900 3286	1.20 1.19	3100 3100	15000 15000

that the question of purity of the materials used was raised as one of the possible factors concerned. As it is known that the presence of moisture or active hydrogen-containing impurities in systems of the type studied here causes the lowering of molecular weight of the resultant polymer, the materials used in polymerisation were purified in different ways in order to obtain different degrees of purity and enable the study of the effect of purity on molecular weight to be achieved.

Table 6.1 illustrates the methods employed in purification of monomer, initiator and solvent together with the abbreviation corresponding to each method which is to be used to describe the state of purity of the material used in the experiments in Table 6.2 and Table 6.3.

6.3 Effect of Concentration

In pyridine initiated polymerisation of anhydrocarboxylates, the concentration of pyridine itself was one of the factors thought to make some contribution to the molecular weight of the polymers. A series of experiments were conducted and in order to enable a reasonable comparison of results to be made, monomer, initiator and solvent used in the experiments were at their highest purity. Table 6.3 shows the G.P.C. analysis of the polymers obtained.

6.4 Effect of Initiator

Polymerisation of α -hydroxy carboxylic acid anhydrocarboxylates can be achieved with different types of initiators, e.g., substituted pyridine and metal alkoxide. The results from the experiments on the effect of purity and concentration on the molecular weight of polymer obtained from pyridine initiated polymerisation of PFAAC seem to indicate that there is some limit to the molecular weight of the polymers derived by this route. Aseries of experiments was

Table 6.3

G.P.C. analysis results of poly PFAAC derived from pyridine initiated polymerisation in toluene at different pyridine concentration at 60^{o}C. Monomer concentration = 0.3 Mole litre^{-1}.

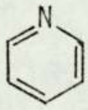
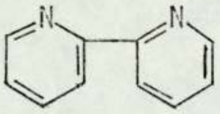
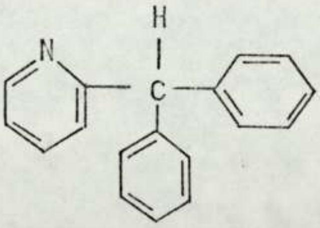
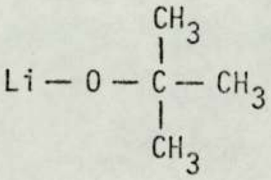
Purification of Monomer, initiator and solvent	Monomer Concentration (Molar)	Mole Ratio [PFAAC]: [Py]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
b, b, a	2.5	1:8	2590	3093	1.19	3100	15000
b, b, a	0.1	3:1	1747	2125	1.22	2350	5200
b, b, -*	-	1:10	2925	4084	1.40	3100	20000

*Bulk polymerisation

carried out in order to gain more knowledge about the relationship between initiator and molecular weight of the decomposition products. Apart from pyridine, the initiators chosen for the experiments were two aprotic bases, a metal alkoxide and a bimetallic oxoalkoxide catalyst of the type recently described by Tessyie(78). The names and structures of the initiators are given in the following table.

Table 6.4

Various initiators employed in polymerisation of α-hydroxy carboxylic acid anhydrocarboxylates.

Initiator	Structure
Pyridine	
2,2'-bipyridyl	
Biphenyl-2-pyridyl methane	
Lithium tertiary butoxide	 $\mathrm{Li-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}$
Bimetallic oxoalkoxide	$(iC_3H_7O)_2Al\text{-}O\text{-}Zn\text{-}O\text{-}Al(OiC_3H_7)_2$

In one experiment a diol, decane-1,10-diol, was employed in addition to pyridine in the hope of doubling the molecular weight obtained. The idea was that in the presence of a diol in pyridine initiated polymerisation, the chain growth could possibly occur at both ends of a diol which should act as a bridge between two growing chains. The result from this experiment together with the rest are shown in Table 6.5. The most consistent conclusion that can be drawn from these experiments is that chain termination rather than initiation of chain growth is responsible for the molecular weight limitation.

6.5 Effect of Monomer Structure

The effect of monomer structure on molecular weight of polymer produced was studied under conditions that were as far as possible, indentical. The results are presented in Table 6.6.

6.6 Effect of Solvent

The nature of the reaction medium was observed to exert a considerable effect on the kinetics of polymerisation (Chapter 5). The molecular weights of the polymers produced at complete conversion were determined and are presented in Table 6.7.

The molecular weight observed with both dimethyl sulphoxide and anisole were substantially lower than those obtained in nitrobenzene despite the fact that all solvents were stringently purified. It was observed that multinodal peaks were obtained when polymers were prepared in dimethyl sulphoxide and anisole but this was found to be simply a function of the ability of the technique to separate the individual low molecular weight species (trimer, tetramer etc).

6.7 Effect of Temperature

The effect of polymerisation temperature on molecular weight was examined with different monomers, and the results shown in Table 6.8. Nitrobenzene was used as the solvent for this comparison

Table 6.5

G.P.C. analysis results of poly PFAAC derived from various initiated polymerisations

Initiator	Solvent	Temperature (^{o}C)	Monomer Concentration (Molar)	Pyridine Concentration (Molar)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
Pyridine	Toluene	60^{o}	0.30	0.1	1747	2125	1.22	2350	5200
Pyridine * Decane-1,10-diol	Tetrahydrofuran	40^{o}	0.30	2.5	1803	1967	1.09	1780	4600
2,2' bipyridyl	Nitrobenzene	60^{o}	0.25	0.25	2564	3097	1.21	2820	10000
Biphenyl-2-pyridyl methane	Nitrobenzene	60^{o}	0.25	0.25	1562	1824	1.17	1920	7700
Lithium tertiary butoxide	Toluene** Tetrahydrofuran	45^{o}	0.30	0.02	2104	2349	1.12	2270	5900
Bimetallic*** oxoalkoxide	Anisole	50^{o}	0.25	0.25	717	819	1.14	840	1920

* $[\text{Decane-1,10-diol}]_0$ = 0.006 mole. litre^{-1}.

** 16.9 ml toluene + 8.1 ml tetrahydrofuran.

*** Low (approx. 20%) conversion due to gelation of reaction mixture.

Table 6.6

G.P.C. results of various poly α-esters derived from pyridine initiated polymerisations at temperature about 60°C

Monomer	Solvent	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
PFAAC	Toluene*	2900	2414	1.20	3100	15000
MAAC	Toluene*	2972	1878	1.58	3100	15000
AAAC	Nitrobenzene**	1774	2114	1.19	1920	7770
C' pent AC	Nitrobenzene**	431	456	1.06	460	1000

* $[\text{Monomer}]_o$ = 0.30 mole. litre^{-1}, $[\text{Py}]$ = 2.5 mole. litre^{-1}

** $[\text{Monomer}]_o$ = $[\text{Py}]$ = 0.25 mole. litre^{-1}

Table 6.7

G.P.C. results of poly α-esters derived from pyridine initiated polymerisations of anhydrocarboxylates in various solvents, $[\text{monomer}]_o = [\text{initiator}] = 0.25$ mole. litre^{-1}

Monomer	Solvent	Temperature ^oC	$\overline{M}_n$	$\overline{M}_w$	M_w/M_n	M.W. at Chromatogram Peak	Highest M.W.
PFAAC	Dimethyl Sulphoxide	60.0	581	628	1.08	640	2820
	Anisole	60.0	1108	1235	1.11	1240 840	5850
AAAC	Nitrobenzene	60.0	1774	2114	1.19	1920	7700
	Dimethyl Sulphoxide	58.4	456	480	1.05	500	1100
	Nitrobenzene* + Dimethyl Sulphoxide	58.4	376	415	1.10	401	1100
C' pent AC	Nitrobenzene	59.3	431	456	1.06	460	1000

* Mole ratio of Nitrobenzene:Dimethyl Sulphoxide =1:1, $[\text{AAAC}]_o = 0.15$M, $[\text{Pyridine}] = 0.30$M.

Table 6.8

G.P.C. results of poly α-esters derived from initiated polymerisation of anhydrocarboxylates at different temperatures. $[\text{Monomer}]_o = [\text{Initiator}]_o = 0.25$ mole. litre^{-1}

Monomer	Initiator	Solvent	Temperature ^oC	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
PFAAC	Pyridine	Dimethyl Sulphoxide	40.2	562	586	1.04	640 and 500	1240
			50.2	518	558	1.08	640 and 460	1630
			60.0	538	584	1.09	640 and 460	1920
		Anisole	60.0	1108	1235	1.11	1240	5850
	2,2' Bipyridyl	Nitrobenzene	40.0	2751	3473	1.21	3520 - 2820	17800
			50.0	2294	2816	1.23	2820	10000
			60.0	2564	3097	1.21	2820	10000
	Biphenyl-2-Pyridyl Methane	Nitrobenzene	50.0	1692	1961	1.16	1920	7700
			60.0	1753	2048	1.17	2300	7700
			70.0	1562	1824	1.17	1920	7700
AAAC	Pyridine	Nitrobenzene	40.0	1072	1191	1.11	1100	3520
			50.0	759	815	1.07	760	1920
			60.0	1774	2114	1.19	1920	10000
		Dimethyl Sulphoxide	50.3	468	492	1.05	500	1000
			58.4	456	480	1.05	500	1100
			70.1	303	336	1.11	540 and 358	760
C' pent AC	Pyridine	Nitrobenzene	50.6	414	436	1.05	464 and 380	1000
			59.3	431	456	1.06	464 and 380	1000
			70.1	439	462	1.05	464 and 380	1000

because it combined good solubility for monomers and polymers throughout the series with "ideal" kinetic behaviour as described in Chapters 4 and 5.

6.8 Effect of Time

The pyridine initiated polymerisation of PFAAC at 40^{0}C was carried out in tetrahydrofuran under a helium atmosphere (the solvent used for G.P.C. analysis) in order that samples could be conveniently analysed during the course of the reaction without either solvent interference or polymer precipitation. It was, of course, necessary to ensure that the reaction had stopped in each of the samples taken at specific times during the polymerisation. This was achieved by addition of methyl iodide which brought about precipitation of a complex in which all the pyridine present was quantitatively incorporated.

It was not, unfortunately, possible to carry out a parallel gas evolution study of the course of the reaction because of the high vapour pressure of T.H.F. However preliminary results obtained by Smith(63) using infrared techniques enabled some assessment of the half life to be made. In the later stages of these studies (Chapter 5) abnormal solvent effects were discussed and it appears likely that the samples were taken over a period in which only around 50% of the monomer decomposed. A final sample representing complete conversion was taken but it appeared that there was a substantial gap (in terms of percent conversion) between this and the penultimate sample. Table 6.9 presents the appropriate results.

The molecular weight distribution appears to vary in a peculiar fashion and these results are paralleled by a subsequent copolymerisation study involving PFAAC and GAAS (Table 6.10). Both sets of results are shown in Figure 6.3.

Table 6.9

G.P.C. results of poly PFAAC from the study of molecular weight with time in tetrahydrofuran at 40.0°C. $[PFAAC]_o = [Py] = 0.25$ mole. litre^{-1}

Reaction Time (Hours)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
0.25	869	1073	1.24	1100	2900
0.50	706	868	1.23	850	2900
0.75	689	881	1.28	850	3600
1.0	790	1016	1.29	1100	2900
1.5	750	1003	1.32	1100	2900
2.0	750	991	1.32	1100	2900
3.0	738	985	1.34	1100	2900
4.5	818	1102	1.35	1400	3600
7.0	855	1163	1.36	1400	2900
30.0	1504	1748	1.16	1780	4600

Table 6.10

G.P.C. results of poly α -ester derived from copolymerisation of PFAAC with GAAS from the study of molecular weight with time in tetrahydrofuran at 40.0°C. $[PFAAC]_o = [GAAS]_o = [Py] = 0.25$ mole. litre^{-1}

Reaction Time (Hours)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
0.25	209	353	1.14	300	2150
1.00	362	403	1.11	323	2650
2.00	350	456	1.30	550, 300, 196	1780
2.8	393	525	1.33	610, 283, 196	4400
4.5	468	587	1.25	610, 268, 196	2650
6.5	463	582	1.25	610	2150
24	502	618	1.23	610	2650
2 weeks	557	641	1.15	610	2150

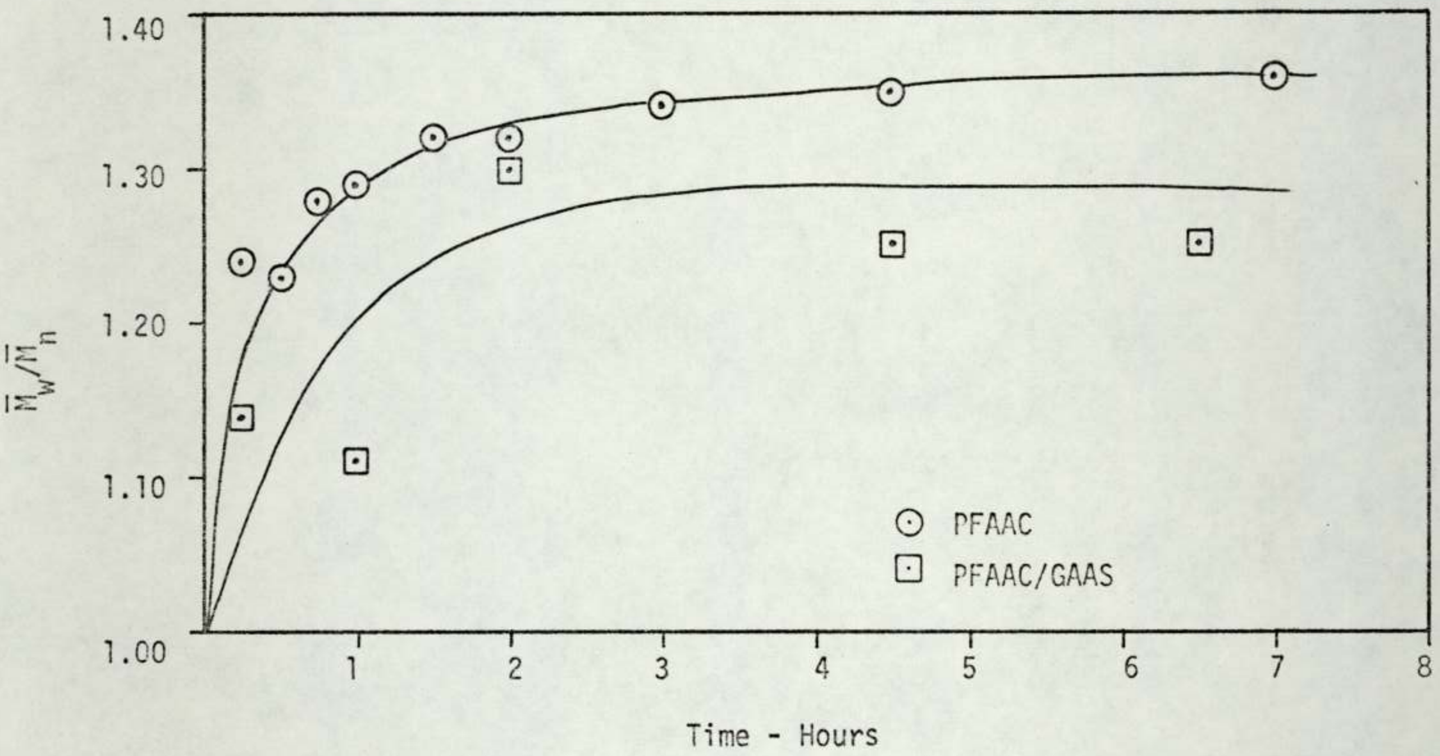


Figure 6.3 The plots of molecular weight distribution versus time for pyridine initiated polymerisations of PFAAC and PFAAC/GAAS.

It is relevant to note at this point that the molecular weight distribution of most samples studied in this work (and taken to complete conversion) lie in the range 1.1 - 1.2. It does appear that two opposing effects are seen in Figure 6.3 due to the fact that residual monomer is present in the samples. On one hand a normal increase in molecular weight distribution is observed as the reaction proceeds but as the monomer disappears towards the end of the reaction the molecular weight distribution decreases sharply.

AAAC was studied in the same way and was, of course, much slower to polymerise. Samples taken up to 48 hours are shown in Table 6.11 together with a typical result obtained for complete conversion at the same temperature and with the same monomer and polymer concentration.

All the experiments were carried out under helium atmosphere using the apparatus shown in Figure 2.7.

6.9 Copolymerisation Study

The copolymerisation of PFAAC with MAAC and GAAC was studied. Because both these monomers are more active than PFAAC greater relative quantities of the latter were used. The molecular weight studies were important because if homopolymerisation of the two monomers used in an experiment occurred it is likely that G.P.C. results would reflect this. There was however no evidence for homopolymerisation from the G.P.C. results, which are summarised in Table 6.12.

6.10 Molecular Weight and End Groups Correlation

The structure of poly α-ester is believed to consist of the repeating unit:

Table 6.11

G.P.C. results of poly AAAC from the study of molecular weight with time in tetrahydrofuran at 40.0°C. $[AAAC]_o = [Py] = 0.25$ mole. litre^{-1}

Reaction Time (Hours)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
0.25	187	188	1.01	188	323
0.50	168	169	1.01	164	268
0.75	176	178	1.00	178	225
1.0	170	171	1.01	164	300
2.0	168	169	1.01	164	268
3.0	169	170	1.01	172	283
4.0	174	175	1.01	172	283
5.0	174	175	1.01	172	323
7.0	180	182	1.01	178	345
9.0	183	185	1.01	178	328
48.0	237	256	1.08	268	805
At complete Conclusion	1100	1172	1.11	1100	3320

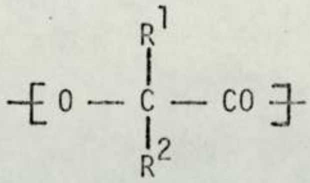
Table 6.12

G.P.C. results of poly α-esters derived from pyridine initiated polymerisation of PFAAC with GAAC and MAAC at 40.0^{o}C in tetrahydrofuran

Comonomer	Mole Ratio $[PFAAC]_o : [Comonomer]_o$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	M.W. at Chromatogram Peak	Highest M.W.
GAAC	100:5	767	886	1.16	840	2820
	100:10	801	874	1.09	840	2300
	100:100	663	716	1.08	700	1410
MAAC	100:50	696	761	1.09	760	1920
	100:100	590	642	1.09	585	1410

$[PFAAC]_o$ = 0.250 mole. litre^{-1}.

$[Py]$ = 0.125 mole. litre^{-1}.



$$-\!\!\left[\,O - \overset{\displaystyle R^1}{\underset{\displaystyle R^2}{C}} - CO\,\right]\!\!-$$

The end groups of the polymer according to the suggested mechanism in Chapter 4, although this is still not clearly conclusive, would be hydroxyl and carboxyl end groups. This fact is confirmed by the presence of the hydroxyl absorption around 3500 cm^{-1} and the carboxylic acid 'shoulder' at 1740 cm^{-1} in the infrared spectra of polymer samples.

For poly PFAAC (derived from pyridine initiated polymerisation of PFAAC) of various molecular weights, the intensities of the methyl absorption at 1388 cm^{-1} relative to the carbonyl absorption, at 1760 cm^{-1}, were calculated. These results, which apart from the decreasing contribution of the terminal carboxyl group with its characteristic extinction coefficient in this region should give a constant ratio, were used to assess the validity of individual spectra for further assessment. Thus the presence of residual petroleum ethers (used in precipitation of polymers) for example produced abnormal values of this ratio and such spectra (which were very few) were discarded.

In addition, the ratio of the hydroxyl absorption (3500 cm^{-1}) to the methyl absorption (1388 cm^{-1}) and the carbonyl ester absorption (1760 cm^{-1}) to the carboxyl carbonyl absorption (1740 cm^{-1}) were calculated and expressed in the form log (absorption, a)/log (absorption, b) shown in Table 6.13.

Figure 6.4 shows the methyl/ester carbonyl ratios and the hydroxyl/methyl ratios. The latter plot unlike that of polymers derived from anhydrosulphites(57) does not show a simple straight line relationship. This implies that the simple hydroxyl/carboxyl

Table 6.13

Relative infrared absorption intensities of methyl, hydroxyl, ester carbonyl and carboxyl carbonyl of a series of different molecular weight poly PFAAC s

Corrected* M.W.	D.P.	Log(Absorption,a)/Log(Absorption,b)			
		a = $-CH_3$ b = -COO-	a = -OH b = -COO-	a = -OH b = -COOH	a - -OH b = $-CH_3$
256	1	0.80	0.94	0.91	1.25
1910	8.1	0.83	0.48	0.61	0.58
2359	10.1	0.84	0.40	0.65	0.48
2553	10.9	0.86	0.48	0.66	0.56
2672	11.4	0.86	0.41	0.71	0.46
4231	18.1	0.89	0.22	0.43	0.32
4475	19.1	0.88	0.39	0.65	0.39

* corrected M.W. = M.W. obtained from G.P.C. x $\frac{63.5}{41.4}$

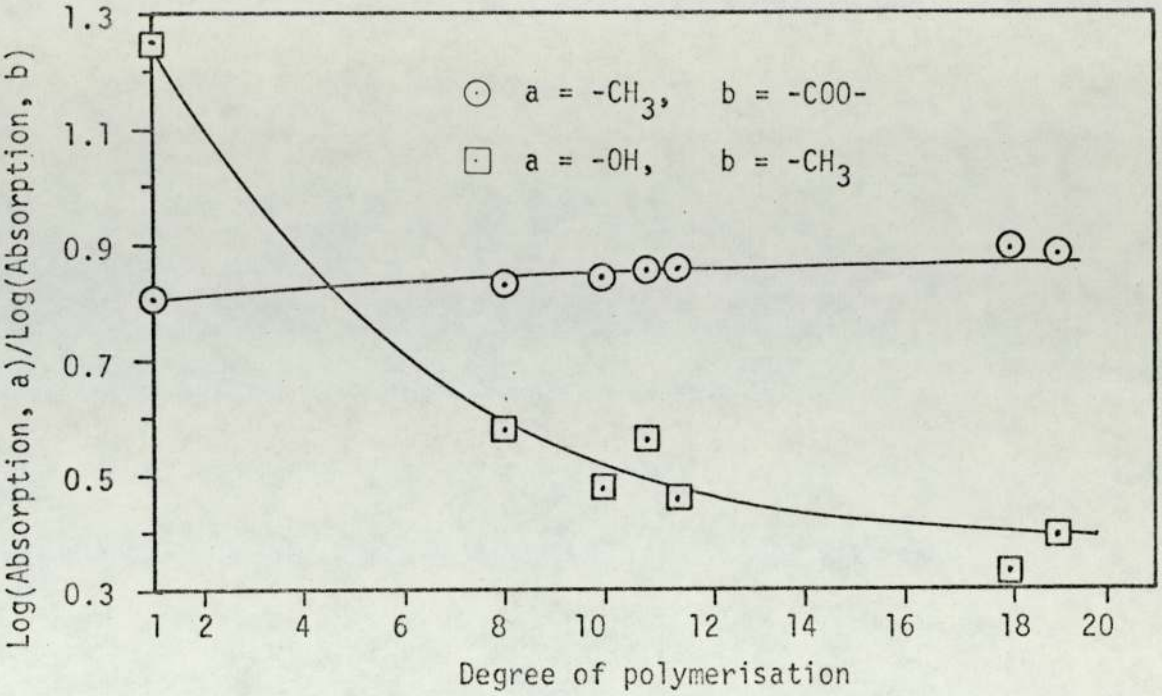


Figure 6.4 The logarithmic ratios of the infrared absorptions of the methyl, ester carbonyl and hydroxyl groups of different molecular weight poly PFAAC.

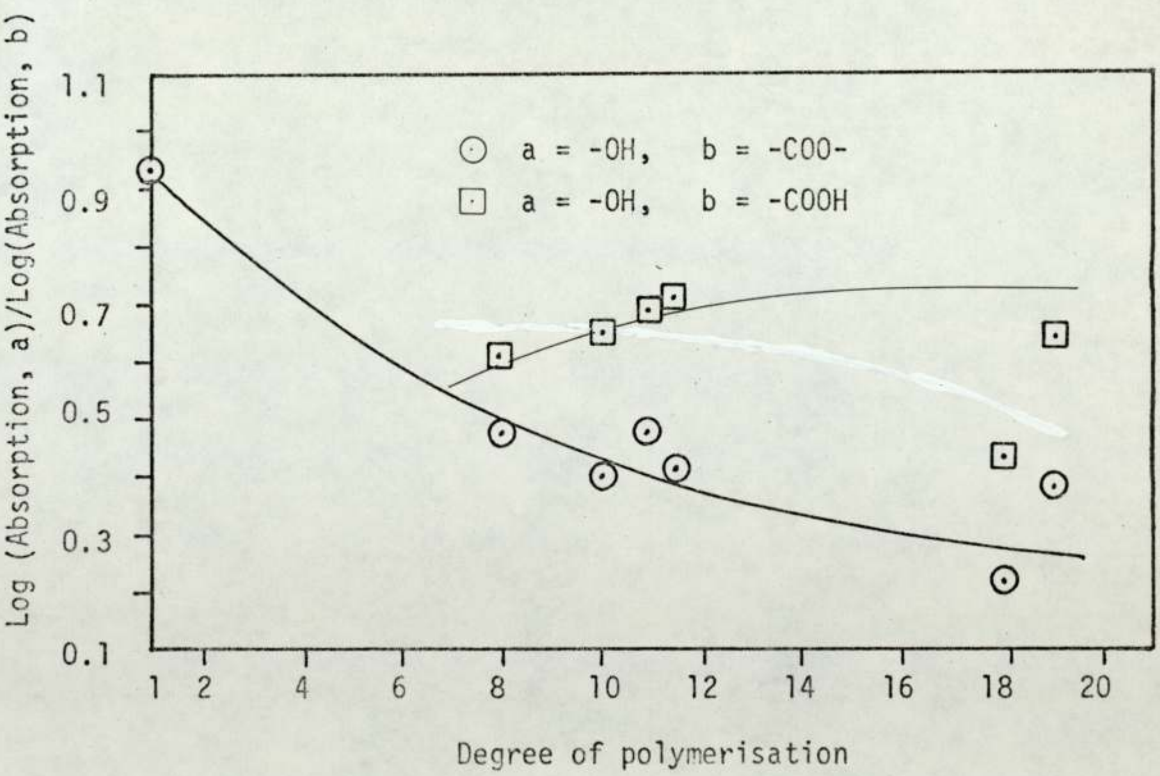


Figure 6.5 The logarithmic ratio of the infrared absorptions of the hydroxyl, ester carbonyl and carboxyl groups of different molecular weight poly PFAAC.

termination suggested by the mechanism previously discussed does not hold. Although the hydroxyl/ester carbonyl ratio (Figure 6.5) shows the expected decrease with increasing D.P. the hydroxyl/carboxyl carbonyl shows a steady increase. This is more remarkable in view of the increasing 'background' contribution to the carboxyl carbonyl from the ester carbonyl as the chain length increases.

The most logical interpretation of these results is that some termination process is present which produces an excess carboxyl group over that predicted by the simple mechanism. Although the parent acid represents the polymer with a D.P. of one it is not a prematurely terminated polymer chain and therefore does not strictly belong on this graph at D.P. equal to one.

One further point of interest is that the polymerisation of PFAAC carried out in the presence of decane-1,10-diol shows abnormal values of all these ratios (relative to those observed in other polymerisations). Thus the spectrum is consistent with a central decane block and the presence of a higher than usual ratio of hydroxyl to carbonyl groups.

The suggestion to be considered in more detail in Chapter 7, therefore, is that although hydroxyl propagation may be responsible for chain growth it does not continue undisturbed until all monomer is consumed. There appears to be rather some process which leads to premature termination of chains which involves the formation of carboxyl groups.

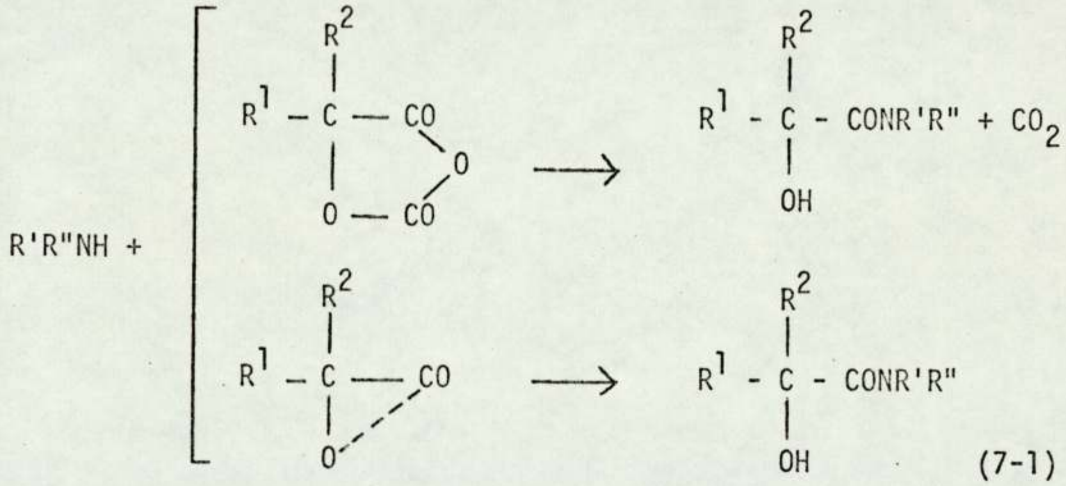
CHAPTER 7

THE TERTIARY BASE INITIATED POLYMERISATION OF α-HYDROXY ACID ANHYDROCARBOXYLATES: DISCUSSION

7.1 Observations and Discussion Based on Results of Chapters 5 and 6

The most plausible base on which the tertiary based initiated polymerisation of α-hydroxy acid anhydrocarboxylates having aromatic and fluoroaromatic substituents can be understood is the mechanism described in Chapter 4. As was indicated there, however, two major problems remain. These are (a) the fact that only relatively low molecular weights have been obtained in these polymerisations and (b) the observed deviation of rate of reaction from first order dependence on initial pyridine concentration. The experimental work contained in Chapter 5 and 6 was designed to investigate some aspects of the mechanism in more detail in an attempt to clarify these problems.

The first point that was examined in detail was the question of purity of monomer, solvent and initiator with particular reference to the presence of residual or adventitious traces of moisture. This point is extremely important since it is well known in the polymerisation of these(63) and related(59) compounds that the presence of moisture governs the molecular weight attained. Section 6.2 shows that beyond a certain level, successive purification steps have no appreciable effect on the molecular weight of the polymer produced. Thus, as can be seen from Table 6.2, in the three bulk polymerisations studied, the lowest $\overline{M}_n$ obtained (1243 and 1278) were in the case where the monomer and initiator employed were at their poorest purity and a slight increase in $\overline{M}_n$ (1456) was the result of purification of the monomer. Hence, the precaution of moisture in the system shows an improvement in the molecular weight attained although not as marked as would be expected from work on anhydrosulphite polymerisation. A bigger increase in $\overline{M}_n$ (2925) was found when the pyridine, used as initiator, had been previously treated with α-toluenesulphonic acid, introduced to eliminate traces of primary and secondary amine impurities present in the pyridine supplied before the normal purifications, refluxing with anhydrous potassium hydroxide followed by vacuum distillation, were carried out. This, of course, indicates that active hydrogen-containing impurities, in the same manner as moisture, govern the molecular weight of the polymer produced.



(7-1)

The primary and secondary amines, which react more rapidly than a hydroxyl group, would react with monomers and α-lactones at a much faster rate than that of the growing chain.

For the polymerisation with toluene as solvent, a similar trend was observed (Table 6.2, i.e., $\overline{M}_n$ increases as the purity increases). This trend is clearly observed from the values of the highest molecular weight obtained from G.P.C. analysis, as the values increased from 4000/5000 (bulk polymerisation, low purity) and 5200/7000 (toluene as solvent, low purity) to 20000 (bulk polymerisation, high purity) and 15000 (toluene as solvent, high purity). It is relevant to note here that the difference in the value of highest molecular weights of 15000 and 20000 corresponds to only one different elution volume unit (Section 6.1) and may be (in this unique study) considered to be of no difference.

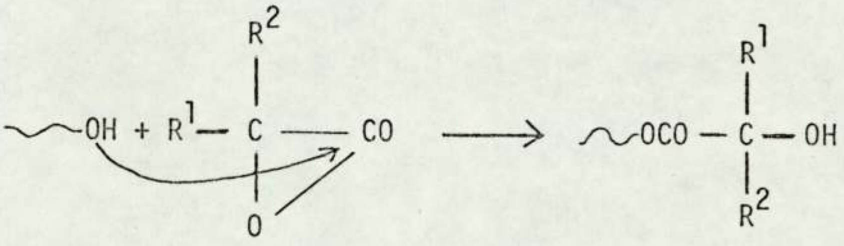
The molecular weight distributions ($\bar{M}_w/\bar{M}_n$) for most cases lie in the range of 1.2-1.3, the two high values of 1.59 and 1.4 were obtained from bulk polymerisations and thought to be caused by the poorly mixed state of the system since the polymerisation took place rapidly as soon as pyridine was introduced onto the solid monomer which was not finely dispersed.

Although some improvement in molecular weight was achieved in these studies it was such a small improvement that the question of limitation of molecular weight by termination of growing chains is raised and will be discussed later in this chapter.

In addition to the aspects of purification discussed above, a comparative experiment was carried out in which the same solvent was used for the polymerisation of both an anhydrocarboxylate and a related class of ring (anhydrosulphite) known to be moisture sensitive. There was no evidence from this experiment to support the view that adventitious moisture was wholly responsible for the low molecular weights obtained in anhydrocarboxylate polymerisation. (This point will be elaborated in due course).

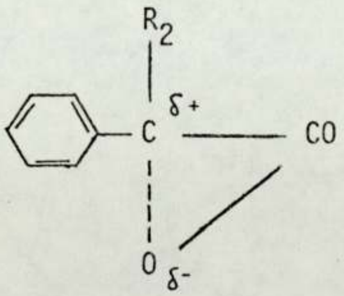
The effect of temperature of polymerisation on the molecular weight of the resulting polymers was examined (Section 6.7, Table 6.8) in the temperature range 40-70^{o}C. No significant variation was found within each series. At this point it is relevant to note that variations studied in initial concentration of monomer and initiator also failed to produce any noticeable effect on molecular weight. The results indicate that the molecular weight of polymer obtained does not depend on the ratio $[M]_0/[I]_0$, monomer initial concentration to initiator initial concentration, which holds in the polymerisation of anhydrosulphites. This can be quite reasonably explained since pyridine is expected to act as a catalyst and does not become a part of a growing chain or polymer. Although it has not been fully demonstrated how the pyridine associates with the ring, nmr studies by Smith (unpublished) indicated the existence of some sort of complex formation in a system containing PFAAC and pyridine.

There are several plausible explanations of the abnormally low molecular weights obtained in these tertiary base initiated polymerisations that could be based on the unique characteristics of aromatic and fluoroaromatic substituents. The first of these involves the fact that the α-lactone is the species proposed as the actual monomer fragment involved in the chain growth step (Equation 7-2), e.g.



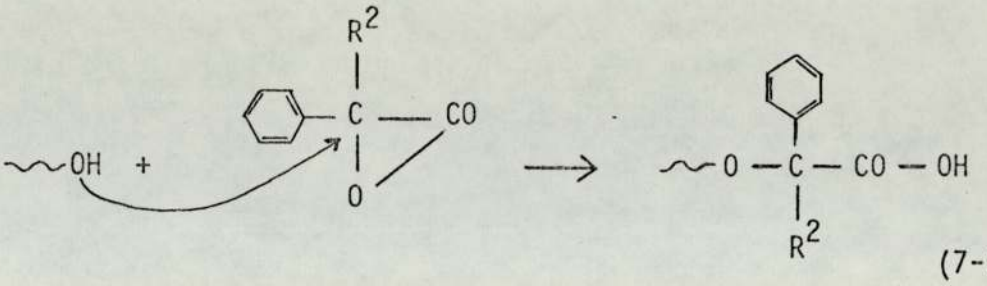
(7-2)

If R^1 and/or R^2 is an aromatic substituent then the polarised form of the α-lactone (XXV) will be resonance stabilised.



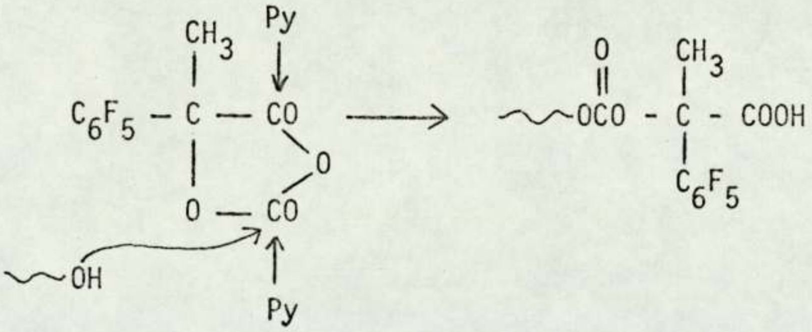
(XXV)

This means that an attack of the type shown in Equation (7-3) will compete with that shown above (Equation (7-2)) and will in effect constitute a chain termination step since the carboxyl group is known (45,46) to be ineffective in chain growth reactions of this type.



(7-3)

A second explanation is related to the activity of the parent monomer rather than that of the derived lactone. Thus, it is possible that because aromatic substituents have conjugative as well as inductive properties the ring will have enhanced activity at the C - 2 carbonyl, i.e.,



(7-4)

The above reaction, Equation (7-4), is analogous to the termination reaction involving uriedo acid formation encountered in N-carboxyl α-amino acid anhydride polymerisation(4) (Equation (1-9)). This is obviously consistent with the carboxyl excess indicated by the infrared study of the polymer end groups, Section 6.10.

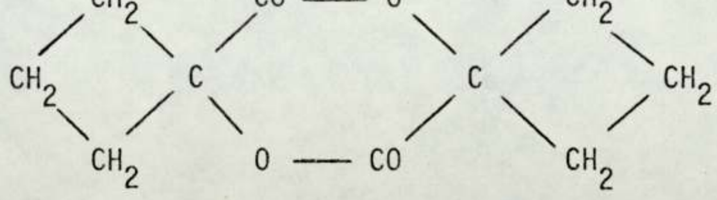
The experiments with the spiro-cyclopentyl anhydrocarboxylate (XIV) were undertaken in order to clarify these possible explanations and the results argue against either of the propositions presented above. The molecular weights of poly C' pent AC (which proved to be one of the easiest monomers to purify) obtained from pyridine initiated polymerisations in nitrobenzene (Table 6.8) over the temperature range 50-70°C are very low compared with those obtained from other initiated polymerisations of the rest of the monomers studied, in fact they are the lowest values ever obtained from this type of polymerisation ($\bar{M}_n$ 430 with the highest molecular weight of 1000). According to the proposition previously suggested, the α-lactone produced by C' pent AC cannot be resonance stabilised because of the absence of an aromatic group in the molecule, thus any type of approach similar to Equation (7-3) by a hydroxyl terminal from a growing chain would not be favoured. The same applies to the reaction similar to Equation (7-4), the C-2 carbonyl in C' pent AC ring is less activated by the inductive effect from the spirocyclopentyl group and by the complete absence of any conjugation effect.

For these reasons, C' pent AC was expected to give a higher molecular weight polymer than those of aromatic and fluoroaromatic substituted monomers, but the results, as can be seen, were quite the opposite and seem to suggest at first sight that the two propositions are incorrect when this particular monomer is dealt with.

The work carried out with C' pent AC allows direct comparison of anhydrosulphite and anhydrocarboxylate rings to be drawn. Polymerisation of both monomers in rigorously purified nitrobenzene demonstrated that whereas the pyridine initiated polymerisation of C' pent AC produced molecular weights in the order of only 10^2-10^3, thermal polymerisation of C' pent AS (spiro-cyclopentyl anhydrosulphite) produced polymer having a molecular weight in excess of 15000. Addition of pyridine to anhydrosulphites has been used as a low temperature ($< 0^{\circ}$C) method for removal of acid chloride impurities. It does, however, especially at room temperature and above produce rapid decomposition and discolouration with the formation of products which include low molecular weight polymer(68). Unfortunately, the acidic nature of the anhydrosulphite monomer and especially that of its gaseous decomposition product (sulphur dioxide) make absolutely comparative studies of anhydrocarboxylates and anhydrosulphites with tertiary bases impossible.

Thermal decomposition of C' pent AC in nitrobenzene was carried out at 102°C in order to provide direct comparison with C' pent AS. Figure 7.1 shows that the decomposition is a straightforward first-order reaction with a very slow, as expected, reaction rate of 2.4×10^{-7} sec^{-1} ($t_{\frac{1}{2}} \simeq$ 800 hours). The most striking result was the extremely low molecular weight of the product, $\overline{M}_n \simeq 200$. Since both monomer and solvent employed were rigorously purified, this, together with the 'well behaved' properties of nitrobenzene as solvent, makes it quite reasonable to suggest that the nature of the α-lactone derived from the monomer together with its very slow rate of production might be responsible for the abnormally low molecular weight product (which corresponds to exclusive 'dimer' formation).

It was found that C' but AS (spiro-cyclobutyl anhydrosulphite) produced only the dimeric cyclic glycollide (XXVI) on thermal decomposition.



(XXVI)

This was attributed to the fact that the bond angles are constrained by the spiro-cyclobutane group in such a way as to make this the favoured product. It appears that in the case of the spiro-cyclopentane ring the principle that high dilution conditions favour the formation of cyclic products applies. Thus, when C' pent AS is thermally

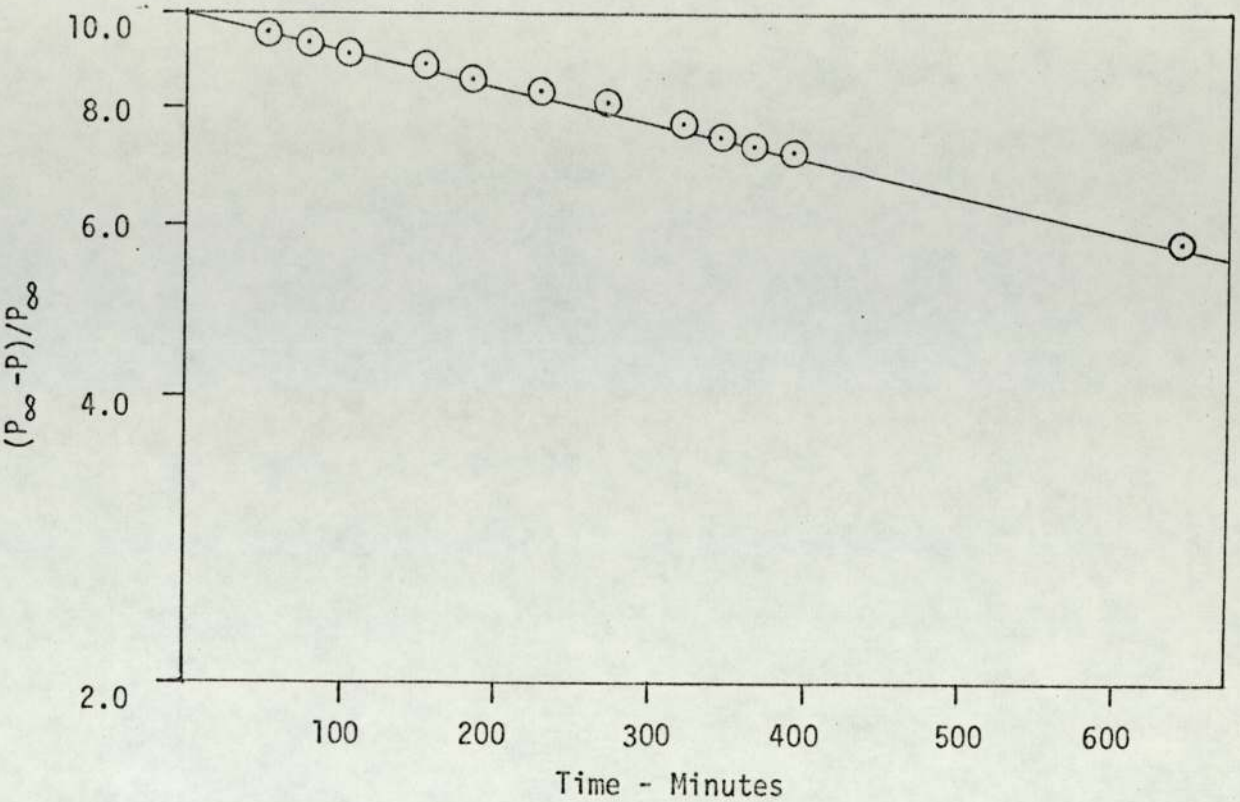


Figure 7.1 A semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the thermal decomposition of C' pent AC in nitrobenzene at 102^oC. (First-order rate constant, k_1, = 2.4×10^{-7} sec^{-1}.).

decomposed the α-lactone is generated relatively rapidly and polymers of molecular weight $\simeq$ 15000 are formed. In the case of the analogous anhydrocarboxylate, the rate of generation is approximately 10^3 times slower and cyclic dimer formation is favoured. Pyridine initiated decomposition of C' pent AC, on the other hand, generates the lactones at a similar rate to that occurring in the thermal polymerisation of C' pent AS, but the products have molecular weights of only 500-1000. Similar molecular weights are obtained when C' pent AS is treated with pyridine. This seems to suggest that the lactone is particularly susceptible to some chain termination process in the presence of pyridine.

Although activation of the C-2 carbonyl by aromatic substituents is clearly not responsible for the molecular weight limitation and kinetic deviations described above, this does not mean that the C -2 carbonyl reactions described do not themselves occur. Indeed, it is consistent with the observed fact that molecular weights obtained from C' pent AC are somewhat lower than those from PFAAC and AAAC to suggest that the difference between C - 4 and C - 2 carbonyl activity is less in the former case. Thus in C' pent AC the absence of inductive activation would in this case mean that the relative activity of the C - 2 carbonyl (in relation to that at the C- 4) would be somewhat higher than in the case of PFAAC and AAAC. This argument should also apply to the unsubstituted GAAC and although the polymer produced from this monomer is insoluble in the solvent used for G.P.C. studies (tetrahydrofuran) its glass transition temperature is some 150°C lower than that of high molecular weight polymer produced by an alternative route. This does suggest that the molecular weight of the polymer is low.

There is then in these results nothing to suggest that the reaction shown in Equation (7-3) does not occur. Similarly, it is consistent with the observed results to suggest that the C - 2 carbonyl (and thus, this termination reaction) is more effective in monomers having substituents which possess little or no electron withdrawing capability.

The effect of initiator structure has been examined and, in particular, the effect of using tertiary bases that are more sterically hindered than pyridine (Chapter 5). The results clearly show similar kinetic behaviour to that encountered with pyridine. Factors affecting their reactivity will now be considered in conjunction with structural factors affecting monomer reactivity.

With nitrobenzene as a reaction medium, the initiators show similarity in their initiated polymerisation patterns in the following ways.

(a) First-order dependence on initial initiator concentration throughout the reaction in the temperature range studied.

(b) Similarity in energy of activation, entropy of activation and frequency factor was observed as shown in Table 7.1.

(c) Reaction rates are, as expected, influenced by the nature of initiators and the nature of monomers, as governed by steric and electronic factors.

Table 7.1, which includes some of Smith's results(63) for comparison, shows that for initiated polymerisation of anhydrocarboxylates at approximately the same temperature (60^{o}C), MAAC, with phenyl and hydrogen substituents, reacts rapidly (k_2 = 0.12 litre. mole^{-1}. sec^{-1}.) while AAAC, with phenyl and methyl substituents, reacts at a much slower rate ($k_2 = 1.67 \times 10^{-4}$ litre. mole^{-1}. sec^{-1}.). It can be seen from this that the presence of a methyl group, which occupies more space than a hydrogen atom, severely hinders nucleophilic attack at the C-4 carbonyl, resulting in a marked reduction in the reaction rate. PFAAC, which has one methyl and a strongly electron-withdrawing pentafluorophenyl as substituents, reacts at a faster rate than does AAAC ($k_2 = 14.3 \times 10^{-4}$ litre. mole^{-1}. sec^{-1}.). In this case the presence of a pentafluorophenyl group increases the susceptibility of the C-4 carbonyl to a nucleophilic attack and it is a pure electronic effect since the pentafluorophenyl group, approximately the same size as a phenyl group, would contribute a similar steric factor to that of a phenyl substituent. A marked

Table 7.1

Second-order rate constants (k_2), energies of activation ($E_a^{\ddagger}$), pre-exponential factors (A) and entropies of activation ($\Delta S^{\ddagger}$) for tertiary base initiated polymerisations of anhydrocarboxylates in nitrobenzene

Monomer	Initiator	$10^4 k_2$ litre.mole^{-1}.sec^{-1}. (Temperature ^oC)	$E_a^{\ddagger}$ kJ. mole^{-1}.	A l.mole^{-1}.sec^{-1}.	$\Delta S^{\ddagger}$ J.K^{-1}.mole^{-1}.
PFAAC	Pyridine*	14.3 (60.3)	62.5	6.9 x 10^6	-127
	2,2'-bipyridyl	2.56 (60.0)	69.8	2.2 x 10^7	-112
	Biphenyl-2-pyridyl methane	3.01 (60.4)	65.1	3.2 x 10^6	-124
AAAC	Pyridine	1.67 (60.0)	73.3	6.5 x 10^{-7}	-103
C' pent AC	Pyridine	4.35 (59.3)	55.0	2.5 x 10^5	-149
MAAC*	Pyridine	0.12 (60.0)	48.3	4.3 x 10^6	-133

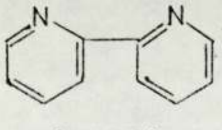
* From reference 63

steric effect on the reaction rates is seen in the pyridine initiated polymerisation of C' pent AC, a second-order rate constant, $k_2 = 4.35 \times 10^{-4}$ litre. mole^{-1}. sec^{-1}., is almost 3 times faster than that of AAAC. The spiro-cyclopentyl substituent is restricted according to its cyclic nature and, therefore, provides a less hindered reaction path (less steric hindrance) for the approaching pyridine molecule, resulting in a faster reaction rate.

In this polymerisation series, MAAC, PFAAC, AAAC and C' pent AC with pyridine, it is observed that the steric factor exhibits more effect in controlling nucleophilic attack than does the electronic factor as can be seen in the values of their energies of activation, 48.3, 62.5, 73.3 and 55 k J. mole^{-1} respectively. PFAAC, although having a faster rate of reaction than that of C' pent AC, exhibits a higher free energy of activation (62.5 k J. mole^{-1}) than does C' pent AC (55 k J. mole^{-1}); this is, of course, the result of a higher energy of the transition state (activated complex) of the highly sterically hindered PFAAC-pyridine adduct.

2,2'-bipyridyl and biphenyl-2-pyridyl methane were used as initiators for the polymerisation of PFAAC in nitrobenzene which was selected as a solvent because of the good kinetic behaviour of polymerisations observed in this solvent. As was stated earlier the kinetic parameters, e.g. reaction rate, energy of activation, were of the order expected from the steric and electronic factors associated with these initiators.

2,2'-bipyridyl (XXVII) apart from its low basicity (compared with pyridine, $pK_a = 5.17$) is considered to be quite sterically hindered

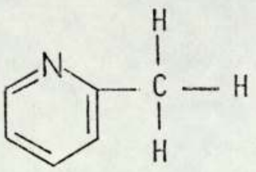


$pK_a = 4.44$

(XXVII)

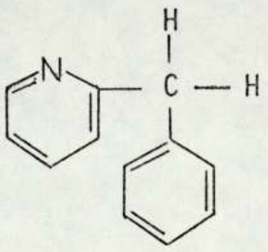
in relation to its nucleophilic attack on the C-4 carbonyl of PFAAC which already has two substituents of a considerable size. Although this initiator possesses a structural element of :N-C-C-N: consisting of two nuclophilic nitrogen centres in the molecule, it appears that the balance between the electronic and steric effects results in a slower rate of reaction and a higher free energy of activation compared with those of pyridine.

The basicity of biphenyl-2-pyridyl methane (XXX) with a biphenylmethyl group as substituent on an ortho position, was estimated from its place in the series shown below to be approximately 4.6.



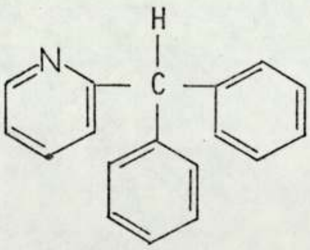
$pK_a = 5.96$

(XXVIII)



$pK_a = 5.13$

(XXIX)



(XXX)

The balance between steric and electronic effects can now be demonstrated for attacking base as it has previously been for monomers of different structures with a given base (Section 4.3). By taking pK_a values to represent the electronic (or intrinsic reactivity) factor for the base and E_s values ascribed to groups of different sizes from the Taft equation, some basis for correlation is obtained. This is considered to be legitimate since neither the Taft nor Hammet equations are entirely applicable in this case and the pK_a values take no account of the sort of steric effects encountered in these reactions. The results of Smith$^{(63)}$ together with those obtained in the present work with PFAAC were examined and found to conform with the empirical equation

$$\ln (k/k_0) = apK_a + bE_s \qquad (7\text{-}5)$$

where k_0 is the rate obtained with the unsubstituted ring (i.e. pyridine).

For convenience, the equation is used in a more customary form,

$$\log k = a\ pK_a + bE_s + \text{constant} \qquad (7\text{-}6)$$

E_s values were used for substituents in the 2 and 6 position only (i.e., 4-methyl substituent, for example, is considered to make no steric contribution). The most suitable values of a and b for this series of reactionswere shown to be approximately 2 and 1 respectively. Figure 7.2 shows the semi-logarithmic plot of the second-order rate constant, k_2, versus the combined electronic and steric effect, $apK_a + bE_s$, obtained from steric and electronic factors of the substituents at the 2 and 6 positions.

There is evidence of lower molecular weight in polymers initiated by the sterically hindered 2,2'-bipyridyl and biphenyl-2-pyridyl methane as compared to those obtained with pyridine (Table 6.8). It is possible that this bears some relationship to the lower molecular weights obtained with C' pent AC as compared to those from PFAAC and AAAC, which difference, it has been suggested, may be a function of the relative activity of C-4 and C-2 carbonyls. Thus, the effect of increased steric hindrance in the attacking tertiary base is to affect its ability to approach the C-4 carbonyl very much more than at the

Table 7.2

Electronic and polar factors for 2, 6 substituted pyridines employed in the polymerisation of PFAAC in nitrobenzene

Substituted Pyridine	2, 6 substituents	pK_a *	E_s *** (Total)	2 $pK_a + E_s$	10^3 k_2 $1.mole^{-1}.sec.^{-1}$
Pyridine	H, H	5.17	2.48	12.72	1.43
2-methylpyridine	H, CH_3	5.97	1.24	13.18	2.17
2,6-dimethylpyridine	CH_3, CH_3	6.75	0	13.5	1.91
4-methylpyridine	H, H	6.02	2.48	14.54	2.95
4-(t-butyl)-pyridine	H, H	5.99	2.48	14.46	2.84
2-ethylpyridine	H, C_2H_5	5.97	1.17	13.11	1.38
2-(n-propyl)-pyridine	H, n-C_3H_7	5.97	0.88	12.82	1.42
2,2'-dimethoxypyridine	OCH_3, OCH_3	1.5**	-0.2	2.8	0.017
Biphenyl-2-pyridyl methane	H, $-CH(C_6H_5)_2$	4.6	-0.5	8.7	0.30
2,2'-bipyridyl	H, $-C_5H_4N$	4.44***	-0.75	8.15	0.25

*Obtained from reference 74

**Approximation was made from references 74 and 75

***Obtained from reference 76

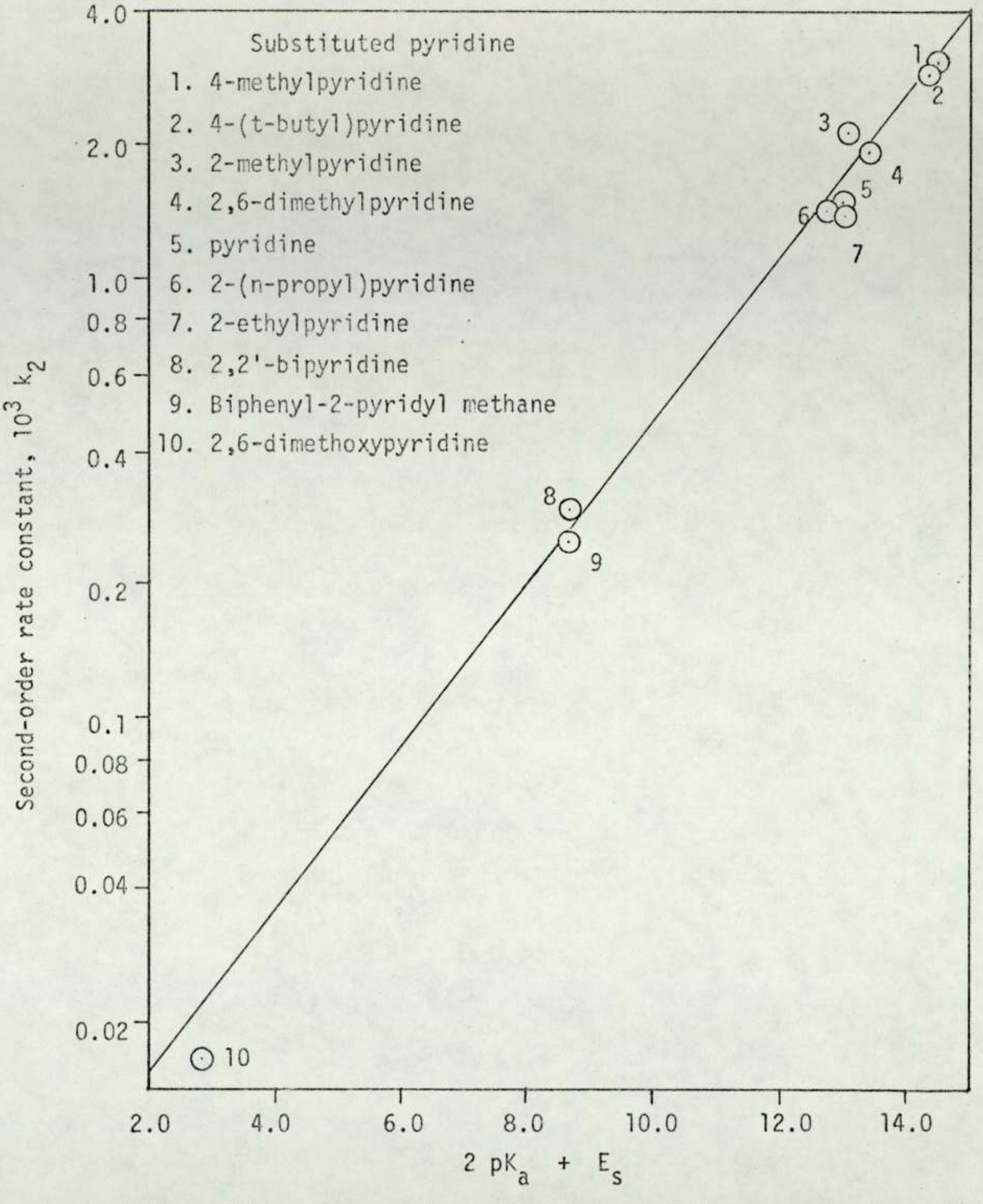


Figure 7.2 A semi-logarithmic plot of the second-order rate constant (k_2) versus the polar and steric factor ($2pK_a + E_s$) of the pyridines used in the polymerisations of PFAAC in nitrobenzene at 60°C.

C-2. It may be that this provides a clue to the nature of the termination step in the sense that there may be some correlation between lowering of molecular weight and the susceptibility to attack of the C-2 carbonyl (related to that at the C-4).

The strangest results and those that were most difficult to interpret were obtained on investigating the effect of solvent on the kinetics of the tertiary base initiated polymerisation and on the molecular weight of the resultant polymers.

The unexpected decrease in reaction rates (Figures 5.3-5.8) for the pyridine initiated polymerisation of the anhydrocarboxylates studied, always occurred when dimethyl sulphoxide and anisole were used as a solvent or a co-solvent. There are some particular points which are considered to be relevant to mention here.

(a) In the pyridine initiated polymerisation of PFAAC, the slow-down of the rate of reaction was found to occur at an earlier stage when anisole was a solvent compared with when dimethyl sulphoxide was used (Figures 5.4 and 5.3 respectively).

(b) When C' pent AC was initiated-polymerised with dimethyl sulphoxide as a solvent, the change in the reaction rate occurred at a much later stage and was not as marked as when PFAAC was the monomer. The first-order plot (Figure 5.7) shows a rather smooth curve at the changeover point.

(c) This changing in the rate of reaction is less marked when nitrobenzene (which always gives good kinetics behaviour) was used as a co-solvent (Figure 5.8).

To explain this strange behaviour, several propositions were suggested and considered,

i) Carbon dioxide, produced during the reaction, reacts in some way with the solvent.

ii) In the presence of these solvents, dimethyl sulphoxide or anisole, the evolved carbon dioxide reacts with pyridine thereby reducing its effective concentration as the reaction progresses.

iii) Pyridine reacts, in some way, with the solvents.

iv) The solvent interferes with the attack of pyridine at the monomer carbonyl in a manner that causes a decrease in the rate of attack.

v) In the presence of these solvents, the overall course of the mechanism is changed and the stoichiometry of the reaction modified.

The proposition (i) reflects the idea that after a certain quantity of gaseous carbon dioxide is produced it reacts or associates with the solvent and stays in a liquid phase, hence, the pressure of the gas registered on a manometer is low and, therefore, it appears as if the reaction is retarded. This proposition, however, was disregarded after an experiment aiming to confirm it failed to provide any support for the hypothesis. The experiment on the effect of carbon dioxide (Section 5.2.1, Figure 5.5) was made on the pyridine initiated polymerisation of PFAAC under a partial pressure of carbon dioxide in dimethyl sulphoxide and the second-order rate constant (taken from the initial rate) obtained was virtually the same for the polymerisation without the presence of carbon dioxide pressure. This experiment similarly demonstrates that proposition (ii) is untrue. Another reason for the invalidity of the proposition (i) is the normal kinetic behaviour of the decomposition of a series of anhydrocarboxylates with benzyl alcohol using dimethyl sulphoxide and anisole as co-solvents(63). There was no sign of a decrease in the reaction rate throughout the reaction.

No analytical evidence could be found for any change in stoichiometry or products of the reaction (proposition (v)) apart from the lower molecular weights of polymers produced in these solvents. Similarly, the fact that the activation energies obtained from initial and final rates in these reactions are similar to each other (Figure 7.3) and of the same order as those obtained in nitrobenzene suggests strongly that it is the rate only and not the mechanism that is affected.

This leaves only propositions (iii) and (iv). One problem with both of these explanations is the fact that pyridine and solvent, and monomer and solvent were separately pre-mixed well before the reactions were carried out. There seems to be no possibility, therefore, that the observed time-dependence (as distinct from a simple first-order reaction that is slower or faster than expected) can be produced by monomer-solvent or pyridine-solvent interactions.

There is, however, one remaining possibility. The abnormal slowing down in rate corresponds to high pyridine:monomer ratio (since monomer is consumed and pyridine is not) as the reaction progresses. Abnormally low rates at high pyridine:monomer concentrations have been observed in nitrobenzene with both PFAAC(63) and AAAC. It may well be that deviation from first-order behaviour with respect to pyridine concentration is more marked in these solvents (dimethyl sulphoxide and anisole) and that what we are observing is simply a reflection of this.

The solvent characteristics that seem to promote these deviations - whatever their origins - are a high ratio of solvent donicity (the ability of solvents to donate electrons) to solvent dielectric constant. The former will produce association of solvent and, e.g., monomer whereas the latter leads to a randomly dissociated system.

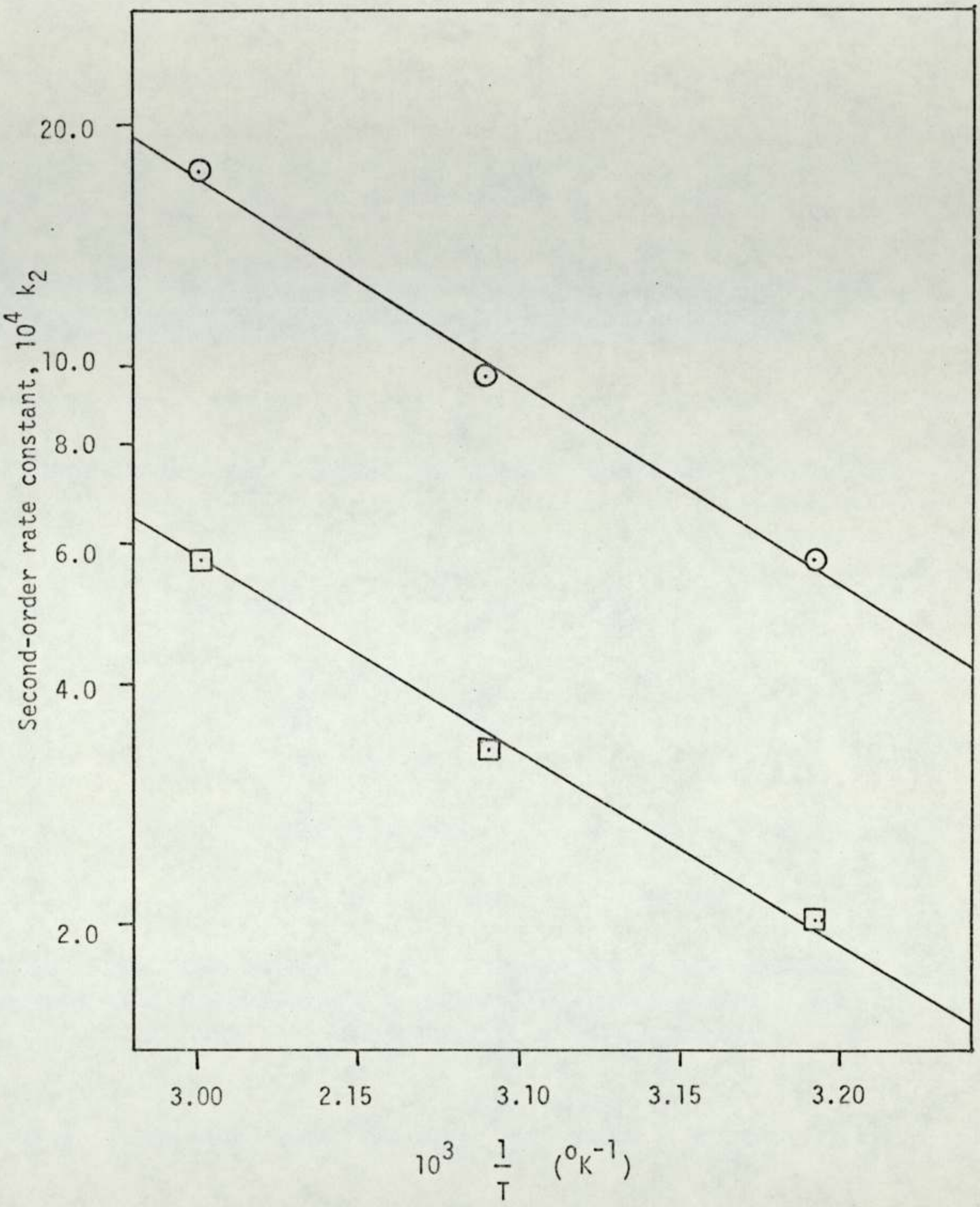


Figure 7.3 Arrhenius plots of initial, ⊙ , and final, ⊡ , second-order rate constants for the pyridine initiated polymerisation of PFAAC in anisole.

The electron-donating power and the electron-accepting power of an organic liquid are considered(79) to correspond to the proton-attracting force and the electron-accepting power respectively and are defined as the relative difference of the O-D or the C=O absorption band observed in the compound from that in benzene which is a reference compound. Table 7.3 gives these values together with the dielectric constants of the solvents or co-solvent system used in the present work.

A common factor that all the solvent systems, which give a change in reaction rate, possess is a rather high ratio of the electron-donating power to either its electron-accepting power or dielectric constant. Nitrobenzene, with good kinetic behaviour, has a rather low ratio compared with those which give a change in reaction rates. Dekalin is given electron-donating and -accepting power equal to zero (as compared with n-hexane or n-heptane which have nearly zero values as does benzene), and, therefore, gives the two ratio values of the co-solvent system of 3:2 mole ratio nitrobenzene:dekalin equal to those of nitrobenzene itself. This co-solvent system of nitrobenzene and dekalin gives a good kinetic behaviour (Figure 5.9) similar to those having nitrobenzene as solvents.

Although there is little knowledge of the effects of the electron-donating/-accepting powers or their ratio on the tertiary base initiated polymerisation of anhydrocarboxylates, it is observed, and worth mentioning here, that the early changes in reaction rates correspond to the higher values of the ratio of the electron-donating power to the electron-accepting power.

7.2 Conclusions

In this chapter so far we have discussed the implications of the various experimental results of Chapters 5 and 6 with no attempt

Table 7.3

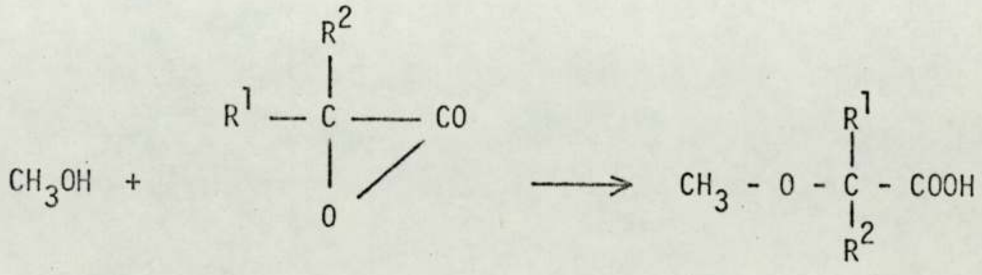
The electron-donating powers, electron-accepting powers and dielectric constants of the solvents and co-solvents employed

Solvent System	Electron-* donating power (A)	Electron-* accepting power (B)	Dielectric Constant (C) (approx)	$\frac{A}{B}$	$\frac{A}{C}$
Nitrobenzene	21	9.0	35.8	2.3	0.59
Dimethyl Sulphoxide	141	8.2	48	17.1	2.9
Anisole	26	1.4	4.4	18.5	5.9
Nitrobenzene:Dimethyl Sulphoxide (1:1 mole ratio)	81	8.6	42	9.4	1.9
Nitrobenzene:Dekalin (3:2 mole ratio)	4.2	1.8	22	2.3	0.19

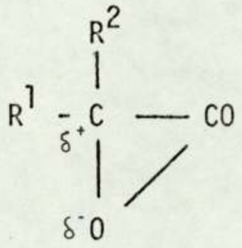
*Obtained from reference 79

to draw an overall conclusion, for example, with respect to the termination step. Although pyridine and other bases almost certainly interact with the C-2 as well as the C-4 carbonyls of the anhydrocarboxylate ring and although this can explain observed deviation from first-order kinetic dependence on pyridine concentration, it seems an inadequate basis for a chain-termination step. Thus, it is reasonable to assume the C-2 interaction will impede the leaving group (carbon dioxide) and lead to a relative reduction in the expected rate just as long alkyl substituents, R^1, in anhydrosulphites(53) are known to bring about the same effect. On the other hand, the attack of hydroxyl groups at the C-4 carbonyl of the anhydrocarboxylate ring is many orders of magnitude lower than the rate of attack at the derived lactone carbonyl(64,65). Since attack at the C-2 carbonyl is in turn a much less preferred reaction to attack at the C-4 carbonyl, it is inconceivable that 'wrong attack' at the C-2 of the ring can provide an effective termination step in a chain growth reaction which consists of addition of α-lactone units to the growing chain.

There is, however, a substantial body of evidence to suggest that the termination step involved 'wrong addition' of the lactone itself. First, there is a known(79) reaction of an α-lactone with methanol corresponding to the required 'wrong addition'.

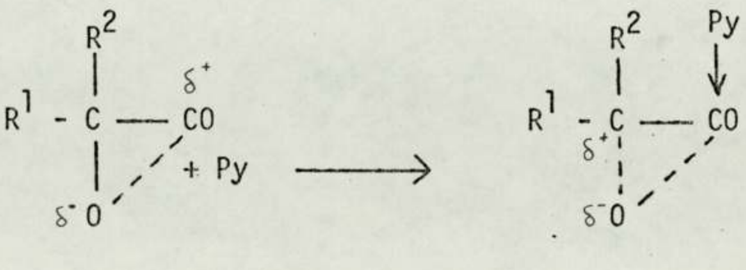


Secondly, the comparative results obtained with thermal polymerisation of C' pent AS and the pyridine initiated polymerisation of C' pent AC which take place at similar rates indicate that identical α-lactones polymerise to very different molecular weights in the presence and absence of pyridine. Similarly, anhydrosulphites which produce polymers having molecular weights of over ten thousand produce only low molecular weight polymers in the presence of pyridine(68). These observations are substantiated by results obtained with PFAAC and PFAAS which also suggest that in the absence of pyridine, α-lactones with aromatic substituents produce polymers of lower molecular weights than those with aliphatic substituents. The tendency to undergo 'wrong addition' can be readily envisaged to be increased with polarisation of the type:



which will be favoured when R^1 or R^2 is an aromatic substituent.

Since pyridine interacts with the anhydrocarboxylate C-4 carbonyl it will certainly interact in a similar way with the derived α-lactone. This will alter the polarisation of the lactone and could well explain the difference in molecular weights produced in the absence of pyridine, i.e.



Presumably interaction of pyridine with α-lactones possessing aromatic substituents will occur at the α-carbon as well as at the carbonyl. This could well be the basis for the observation that polymers from such α-lactones are not as dramatically affected by the presence of pyridine as are those produced from C' pent AC. Similarly more sterically hindered initiators will be less able to interact with the α-carbon thereby favouring even further the 'wrong addition'.

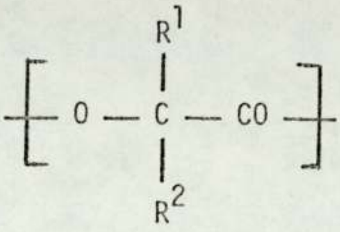
This basis for understanding the origin of a termination reaction that produces polymers with the observed excess of carboxyl end groups has one further advantage. Since the interaction of pyridine with the parent anhydrocarboxylate ring reflects the interaction with the lactone, the fact that abnormal kinetic behaviour with solvents such as dimethyl sulphoxide and anisole also produces low molecular weight polymers is not unexpected. It seems possible, therefore, on the basis of these suggestions to accommodate all the experimental observations although the connections are, of course, far from being completely proved.

CHAPTER 8

PROPERTIES OF AROMATIC PHENYL AND PERFLUOROPHENYL SUBSTITUTED POLY α-ESTERS

8.1 General Characteristics

The polymers as prepared are, on the basis of evidence discussed in previous chapters, linear poly α-esters having the repeat unit

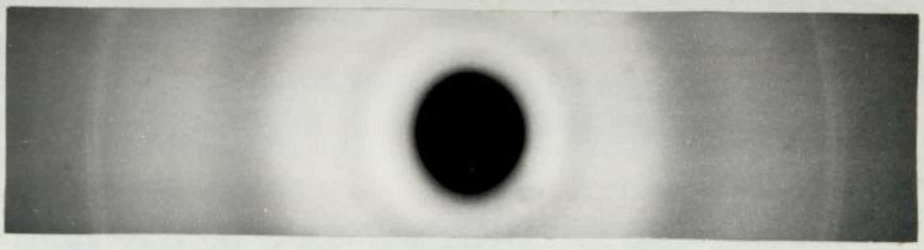


$$\left[O - \overset{R^1}{\underset{R^2}{C}} - CO \right]$$

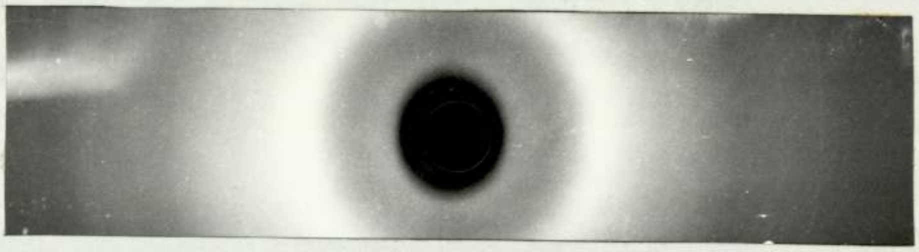
and with hydroxyl/carboxyl end groups although not necessarily on a 1:1 basis. Thus it appears that, in general, polymers will have an excess of carboxyl over hydroxyl end group.

The polymers prepared are all unsymmetrical (i.e. $R^1 \neq R^2$) and as such predominantly amorphous. A special case exists with spiro-cyclopentyl substituted poly α-ester. This polymer has been prepared from the anhydrosulphite monomer and due to the difficulty of packing the cyclopentyl ring in this short repeat unit polymer it is also amorphous. Figure 8.1 shows the X-ray powder photographs of some polymer samples.

Although crystalline poly α-esters [poly (glycollic acid), $R^1 = R^2 = H$, poly (α-hydroxy isobutyric), $R^1 = R^2 = CH_3$] are relatively insoluble materials, those described in this thesis are soluble in a wide range of organic solvents including chloroform, tetrahydrofuran, cyclohexanone etc.



Poly PFAAC



Poly MAAC

Figure 8.1 X-ray powder photographs of poly α-esters

8.2 Differential Scanning Calorimetric Studies

The polymers were studied by differential scanning calorimetry in order to determine the value of transitions such as glass transition temperature, T_g, and melting temperature, T_m. The traces were not as well characterised as those obtained from carbon backbone polymers such as poly(methyl methacrylate) (P.M.M.A.), polystyrene (P.S.) etc., but it was possible to make reasonable assignments of T_g. The values given for T_m do not of course correspond to true crystalline melting points but,rather softening points being the relatively broad transitions corresponding to the transformation from solid to fluid state. The values quoted in Table 8.1 are the average of several successive determinations. For comparison, values of glass transition temperatures were determined for poly GAAS and poly DMAS. These are 330-345^{o}K and the approximate melting points of both polymers lie in the range of 493-543^{o}K.

Table 8.1

D.S.C. results of glass transition temperature T_g- and melting temperature, T_m, for poly α-esters

Polymers	T_g (^{o}K)	T_m (^{o}K)
Poly MAAC	330-348	No distinct trace shown (thought to closely follow T_g)
Poly AAAC	358-360	500-520
Poly PFAAC	430-432	510-525

The effects seen here are fairly straightforward. Poly(glycollic acid) packs extremely well and the interchain distance is at a minimum as for crystalline fibre forming polymers. A change from planar zig-zag conformation [poly(glycollic acid)] to helix conformation [poly(α-hydroxy isobutyric acid)] is thought to occur in order to accommodate the two methyl groups. Some corresponding increase in glass transition temperature accompanies this change. All the remaining polymers described here pack in a random fashion and the interchain distance is not uniquely in the 5Å range. Thus one phenyl and one hydrogen substituent polymer (poly MAAC) has a glass transition temperature very similar to that of poly(glycollic acid). The phenyl groups although producing in principle, greater steric hindrance to rotation, are badly packed and exert little overall effect. We see here the effect of one large substituent unsymmetrically introduced but producing at the same time an increase in interchain distance. The energy barrier to rotation as seen here is very similar to that of the unsubstituted chain.

Unsymmetrical disubstitution does however cause a rise in glass transition temperature, thus poly AAAC ($T_g = 360^{o}K$) shows an increase over the value for poly MAAC since no further increase in interchain distance can be expected and a steric hindrance of a methyl and phenyl group substituted at the same carbon atom become appreciable.

The most significant feature in the glass transition temperatures recorded here is the high glass temperature of poly PFAAC. Undoubtedly this results from the interaction of the polar backbone with the polar pentafluorophenyl substituent and to some extent the polar-polar repulsion between the pentafluorophenyl substituents. It is important to note that the pentafluorophenyl group is similar in size to the phenyl group and it appears that the increase in glass transition temperature in going from poly AAAC to poly PFAAC is almost exclusively a polar effect.

This result is all the more interesting in the light of the fact that polystyrene and poly(pentafluorostyrene) show little difference in glass transition temperature. Here of course no polar backbone is involved and the aromatic substituent is attached to a carbon containing an α-hydrogen.

8.3 Surface Properties

The surface free energies of the polymers were examined by the method of Owens and Wendt(81) which is a sessile drop contact angle technique involving methylene iodide and water thereby enabling the separate polar and dispersive components of the surface free energy of the substrate to be determined. The results are shown in Table 8.2 together with values of the reference polymers, poly(ethylene) (P.E.), poly(tetrafluoroethylene) (P.T.F.E.), poly(ethyleneterephthalate) (P.E.T.) and poly(methyl methacrylate) (P.M.M.A.).

The difference in surface properties of P.E., P.T.F.E. are well known. The characteristically low surface energy of P.T.F.E. is used commercially in such applications as "frictionless" bearings and non-stick domestic pan linings. On the other hand the increase in surface free energy on moving from the non-polar polyethylene to the ester containing polymers, P.E.T. and P.M.M.A. is reflected in the figures shown in the table.

Although it is not possible to make direct comparison of the changing polar and dispersive contribution of surface free energies of polymers with changes in the gross chemical structure, some general trends can be clearly seen. Thus, in moving from P.E. to P.T.F.E. a considerable drop in the dispersive component (γ_D) coupled with a distinct increase in the polar component (γ_P) is observed. Similarly the change in structure from P.E. to P.M.M.A.

Table 8.2

Computed results for poly α-ester surface free energies: dispersive free energy (γ_D), polar free energy (γ_P) and total surface free energy (γ_T) as determined by the sessile contact angle involving water and methylene iodide

Polymer	Contact Angle		Surface Free Energy - dynes/cm		
	Water	Methylene Iodide	γ_D	γ_P	γ_T
Poly MAAC	82.0	19.0	46.29	1.84	48.13
Poly AAAC	86.0	21.0	46.50	0.98	47.49
Poly PFAAC	88.0	35.0	40.82	1.20	42.02
Poly DMAS	83.0	20.0	46.18	1.62	47.81
Poly C' hex AS	85.0	23.0	45.57	1.26	46.84
P. E. *	94	52	32	1.1	33.1
P.T.F.E. *	108	88	12.5	1.5	14
P.E.T. *	81	38	37.8	3.5	41.3
P.M.M.A. *	80	41	35.9	4.3	39

* Quoted values from reference (81)

for example, results in a major increase in the polar component.

Turning now to the results obtained with the poly α-esters (which are incidentally the first surface study on polymers of this family), this shows some changes in the balance of polar and dispersive components with the three polymers, poly AAAC, poly C'hex AS and poly(α-hydroxy isobutyric acid) α-ester but a figure for the total surface free energy in each case that falls within the range 47.3 ±.6 5. Lying outside this range are poly MAAC (the only polymer having an α-hydrogen atom which will markedly reduce shielding of the backbone) which has a somewhat higher surface free energy of 48.13. At the other extreme the pentafluorophenyl substituted polymer shows a decrease in surface free energy to 42.02.

A more detailed consideration of the polar and dispersive contribution to surface free energy is interesting and instructive. Thus the change from poly AAAC to poly PFAAC is accompanied by a distinct drop in the dispersive component (γ_D) and a slight rise in the polar component (γ_P). This is, of course, parallelled to the change observed on moving from P.E. to P.T.F.E. The magnitude of the overall change is however much smaller. This is consistent with the fact that surface and interfacial properties of aromatic and fluoroaromatic compounds are much more similar to each other than is the case with their aliphatic counterparts.

The highest polar contribution in all the poly α-ester studies is found in the case of poly MAAC having as it does one side of the chain shielded only by α-hydrogens. The next highest is found in the case of disubstituted but highly crystalline poly(α-hydroxy isobutyric acid) ($R^1 = R^2 = CH_3$) possessing as it does a helical structure. The next highest polar contribution is found with spirohexyl substituted polymer which has two α-methylene groups whose conformation is constrained by the fact that they are held in a spiro system.

Thus the major contribution to the polarity of the surface comes from the ester backbone itself. This again is quite consistent with the P.E., P.M.M.A. and P.E.T. results shown in the table. Such contributions are expected to be virtually the same, however, in the cases of poly AAAC and poly PFAAC.

8.4 Mechanical Properties

The mechanical properties of the polymers were studied using a microindentation technique initially designed for use with paint films. This technique has been developed using the theory of Hertz relating to the elastic deformation of thin films with spherical indentor(82). A direct plot of log load versus log indentation for a 1/16 inch spherical indentor on the polymer samples are shown in Figure 8.2.

By use of the Hertz equation

$$\frac{E}{1-\nu^2} = \frac{3}{34} \frac{mg}{\frac{1}{2}h^{3/2}} \qquad (8\text{-}1)$$

and the relationship connecting rigidity modulus (G) with Young's modulus (E) and Poisson's ratio (ν) (in this case 0.35), values of G and E for poly PFAAC and poly AAAC together with P.S. and P.M.M.A. for comparison were determined. The results are shown in Table 8.3.

The figures also include results obtained on the polymers after UV exposure. The general level of moduli obtained are of the order expected and as can be seen slightly higher than both P.S. and P.M.M.A.

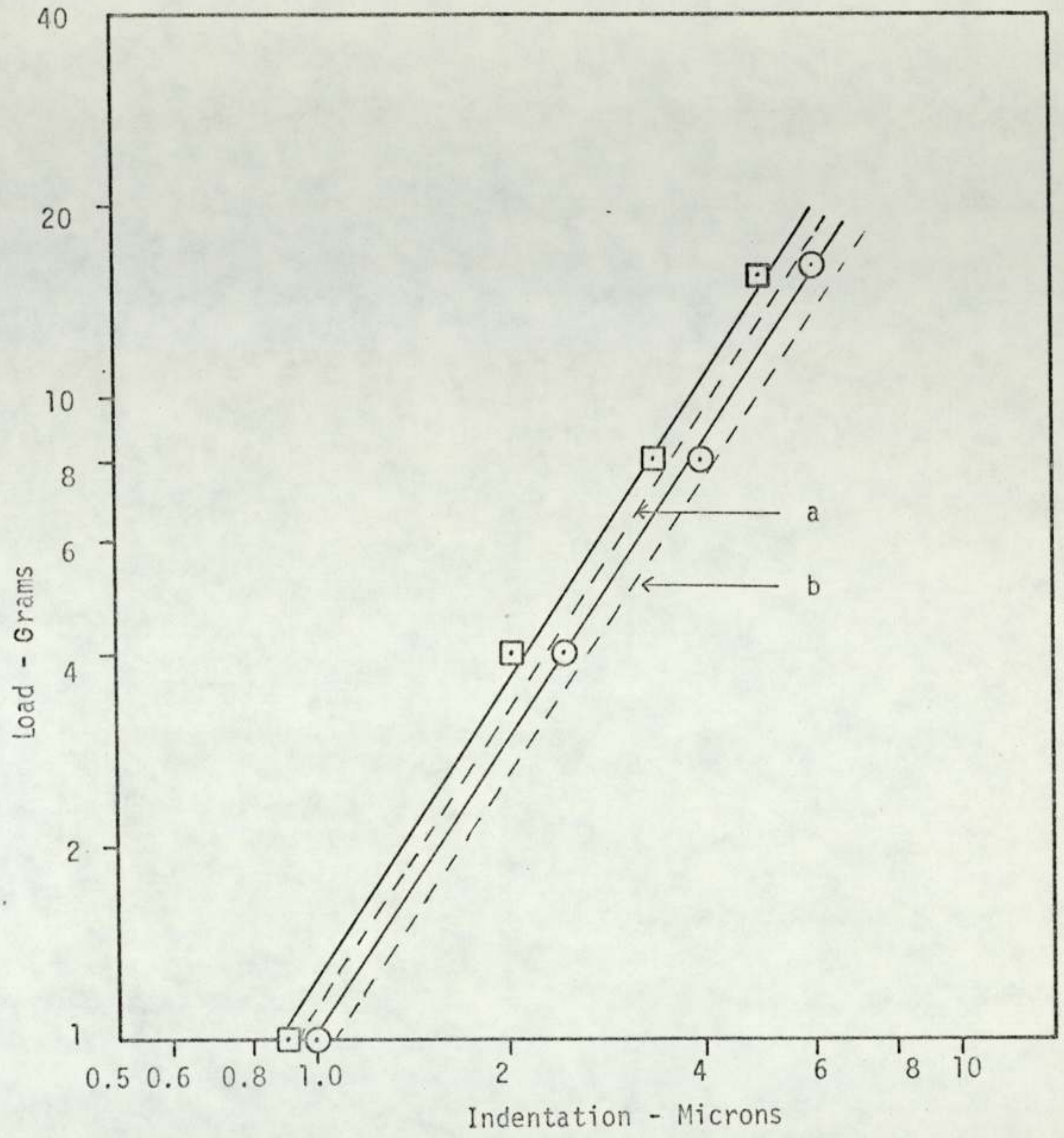


Figure 8.2 Logarithmic plots of load versus indentation for a 1/16 inch spherical indentor on the polymer sample.

Dotted lines show position of undegraded polymers

(a) Poly PFAAC
(b) Poly AAAC

⊡ Degraded Poly PFAAC
⊙ Degraded Poly AAAC

Table 8.3

Mechanical properties of poly α-esters. Values of Young's modulous (E) and Rigidity modulous (G) as obtained from the Hertz Equation in conjunction with the relationship

Polymer	Young Modulous E, (dyne.cm^{-2})	Rigidity Modulous G, (dyne.cm^{-2})
Poly AAAC	5.5×10^{10}	2.03×10^{10}
Poly PFAAC	6.5×10^{10}	2.4×10^{10}
Poly AAAC (after 5000 hrs)	6.0×10^{10}	2.22×10^{10}
Poly PFAAC (after 6000 hrs)	7.3×10^{10}	2.77×10^{10}
Polystyrene	2.8×10^{10}	1.05×10^{10}
Poly(methyl methacrylate)	2.9×10^{10}	1.05×10^{10}

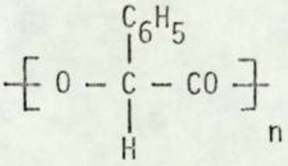
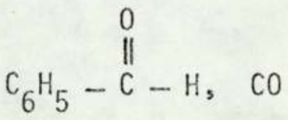
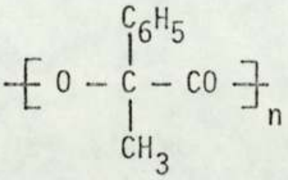
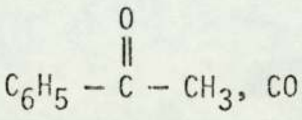
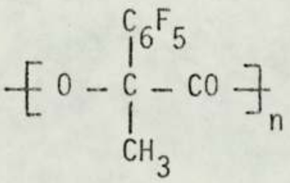
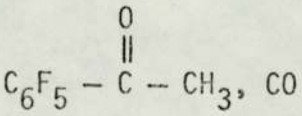
8.5 Thermal and U.V. Degradation

8.5.1 Thermal Degradation

The thermal degradation of poly α-esters has been extensively studied(83-89) and a general pattern established. No work has been carried out previously on degradation of aromatic and fluoroaromatic substituted poly α-esters. A preliminary pyrolysis-glc study has been undertaken and the major degradation products are identified as shown in Table 8.4.

Table 8.4

Major degradation products from thermal decomposition of a series of poly α-ester as identified by GLC technique

Poly α-ester	Major Decomposition Products
poly MAAC  $\left[O - \overset{C_6H_5}{\underset{H}{C}} - CO \right]_n$	Benzaldehyde and Carbon Monoxide  $C_6H_5 - \overset{O}{\overset{\|}{C}} - H$, CO
poly AAAC  $\left[O - \overset{C_6H_5}{\underset{CH_3}{C}} - CO \right]_n$	Acetophenone and Carbon Monoxide  $C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_3$, CO
poly PFAAC  $\left[O - \overset{C_6F_5}{\underset{CH_3}{C}} - CO \right]_n$	Pentafluoroacetophenone and Carbon Monoxide  $C_6F_5 - \overset{O}{\overset{\|}{C}} - CH_3$, CO

The only tentative conclusion that can be drawn is that there is no major difference in degradation mechanism between aromatic and fluoroaromatic substituted poly α-esters.

8.5.2 UV-Degradation Studies

Films of poly AAAC and poly PFAAC were exposed in a UV-cabinet designed to give an intense near-solar distribution of light wavelengths. The samples were monitored from time to time by means of goniophotometry and the deterioration described in terms of changes in the derived parameters which are associated with this technique$^{(90-94)}$. A typical goniophotometric trace for one of the samples studied is shown in Figure 8.3.

The sequence of changes in gloss factor (G F) on UV-exposure of the poly PFAAC sample are shown in Figure 8.4 and can be seen to follow an apparently cyclic pattern. The initial increase in GF during the first 100 hours exposure, indicating as it does an early improvement in the state of the film surface, is indicative of an equilibration period during which the sample undergoes an initial flow while adjusting to the slightly higher than ambient temperature (approx. 35°C) inside the UV-cabinet. Over the next 400 hours exposure, however, the GF is seen to decrease fairly rapidly before subsequently tailing off to an interim minimum value after 900 hours. It is interesting to note at this stage that of the two goniophotometric parameters which makes up the GF term (viz. $GF = I_S - I_d / W_{\frac{1}{2}}$), it is the changes in specular reflectance (I_S) as seen in Figure 8.5, rather than those in the peak width at half-height ($W_{\frac{1}{2}}$) (Figure 8.6) which appear to influence the GF term the most in these early stages. However, on comparing the graph of peak area (peak area $\simeq I_S \times W_{\frac{1}{2}}$, for "triangular" shaped peaks), Figure 8.7, alongside those of I_S (Figure 8.5) and $W_{\frac{1}{2}}$ (Figure 8.6),

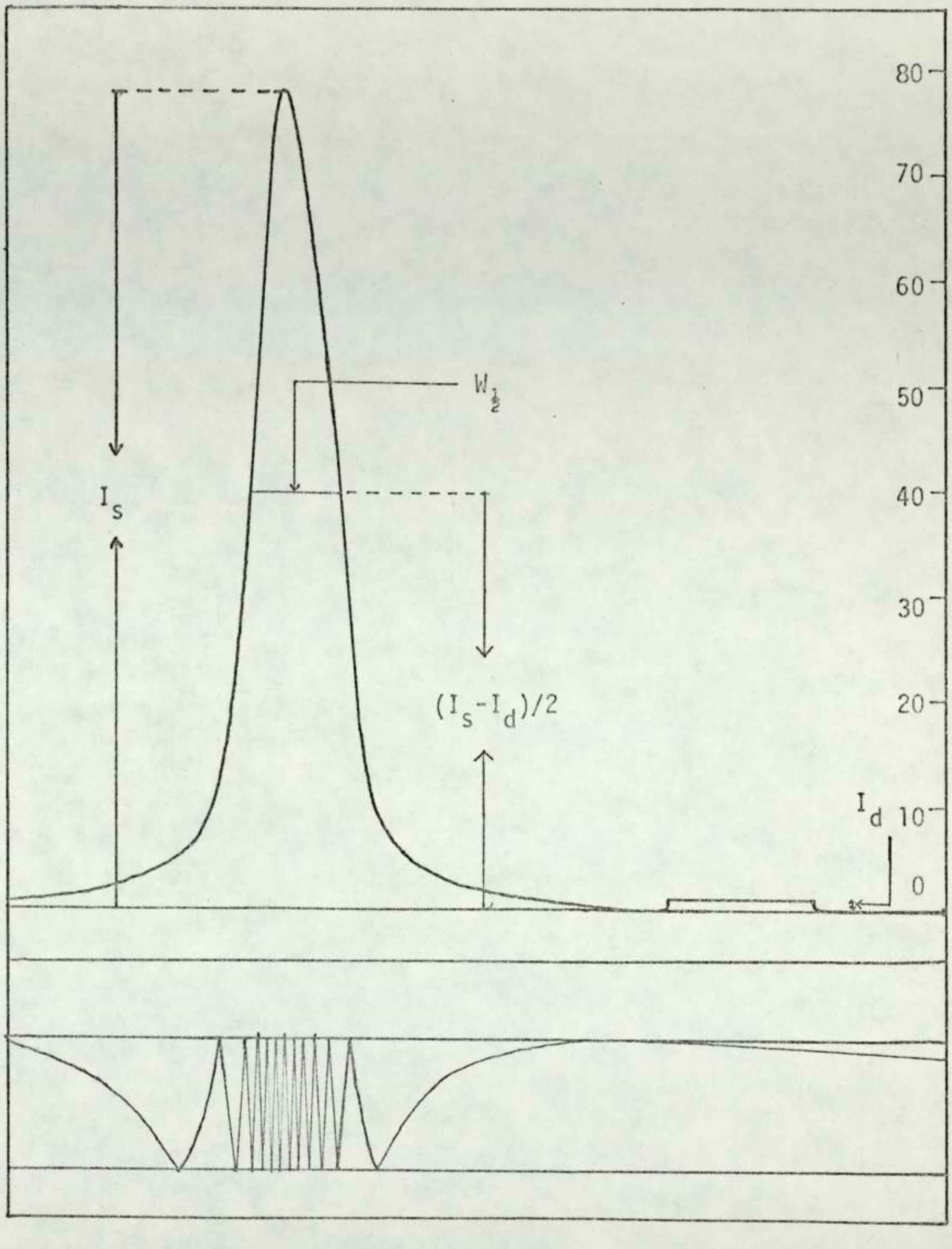


Figure 8.3 A typical goniophotometric curve relating, in this case, to an unaged poly PFAAC film sample - showing the various derivable parameters referred to in the text.

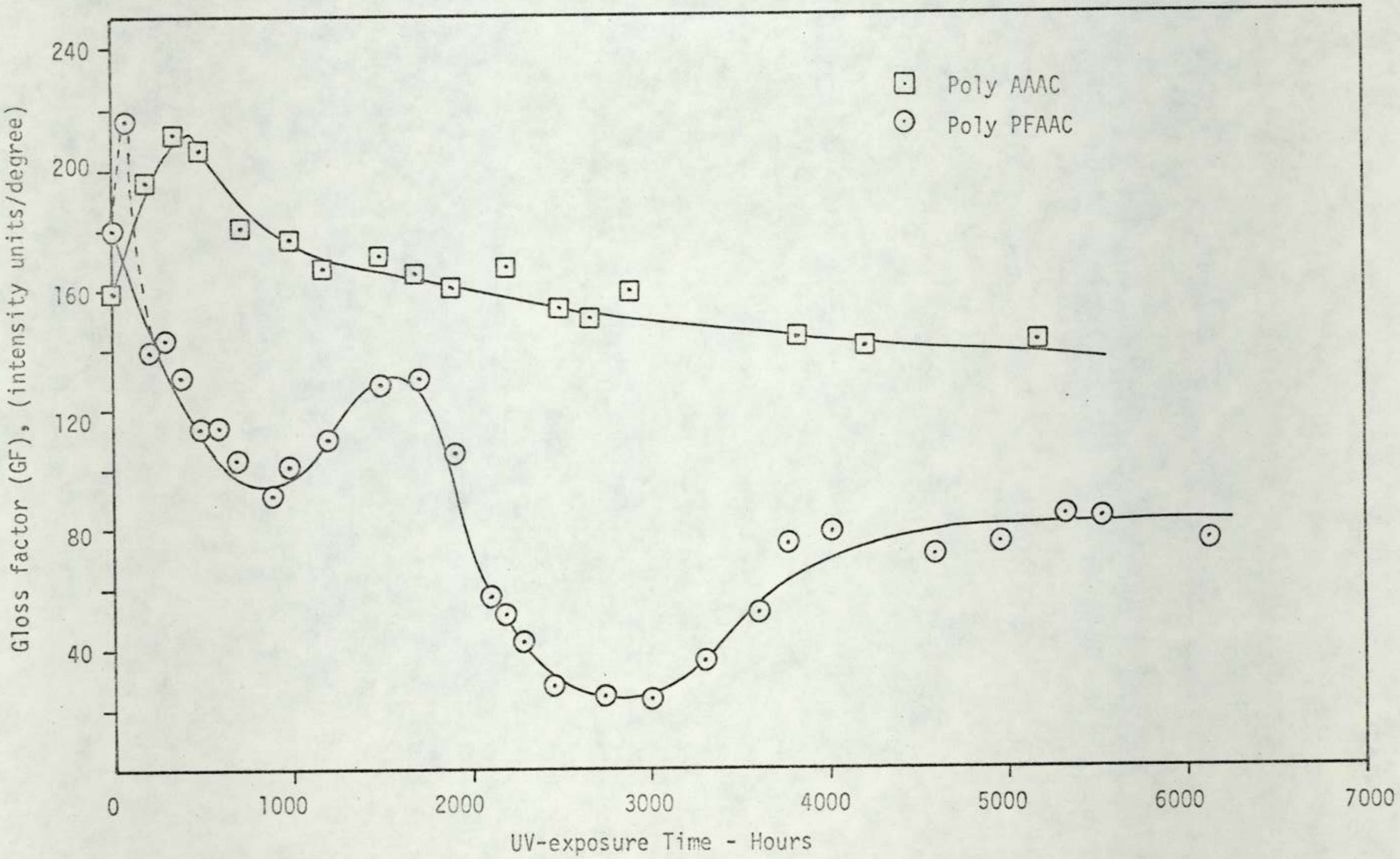


Figure 8.4 Goniophotmetric plots showing variations in gloss factor with length of UV-exposure for Poly AAAC and Poly PFAAC films.

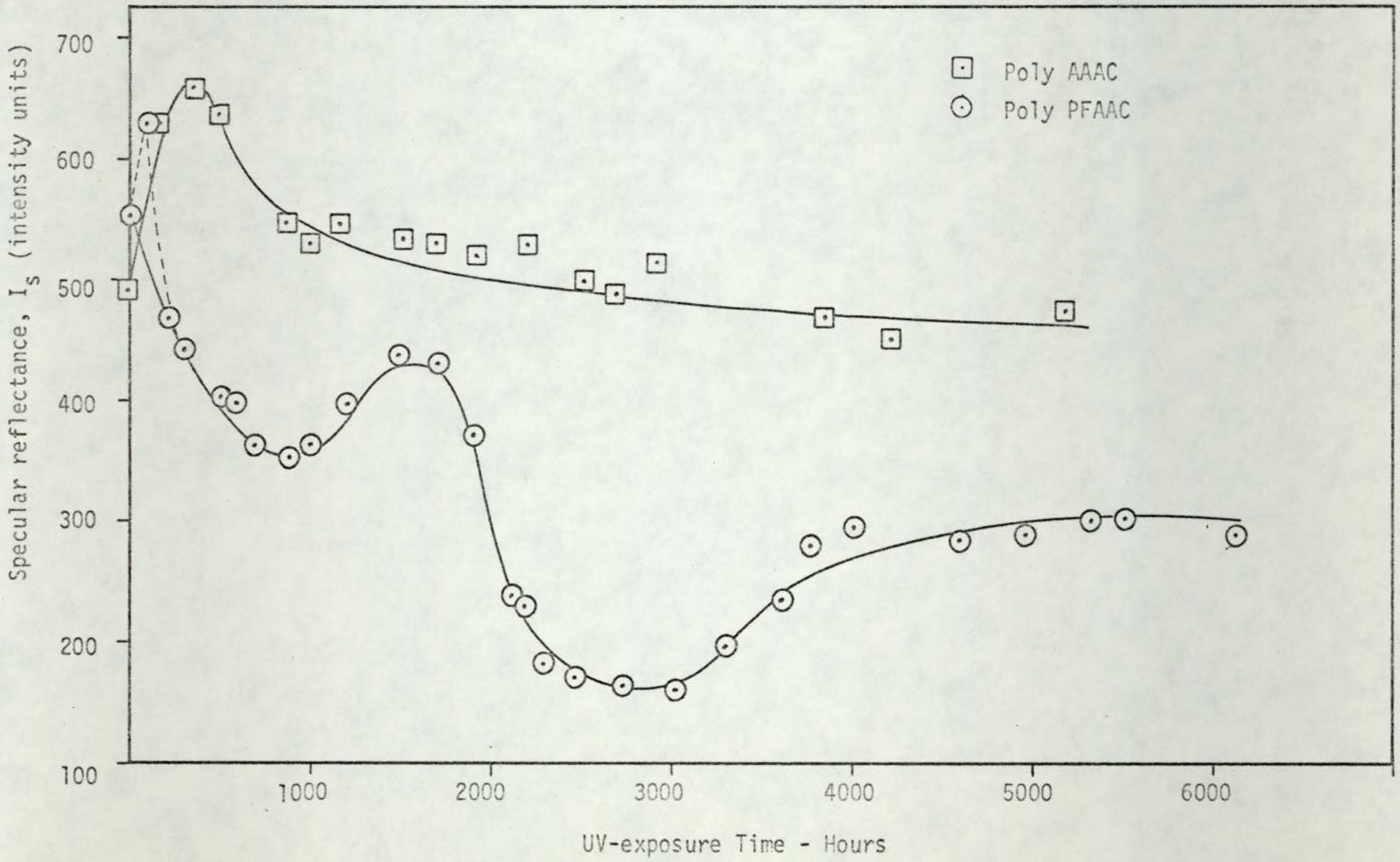


Figure 8.5 Goniophotometric plots showing changes in specular reflectance (I_s) with UV-exposure time for Poly AAAC and Poly PFAAC films.

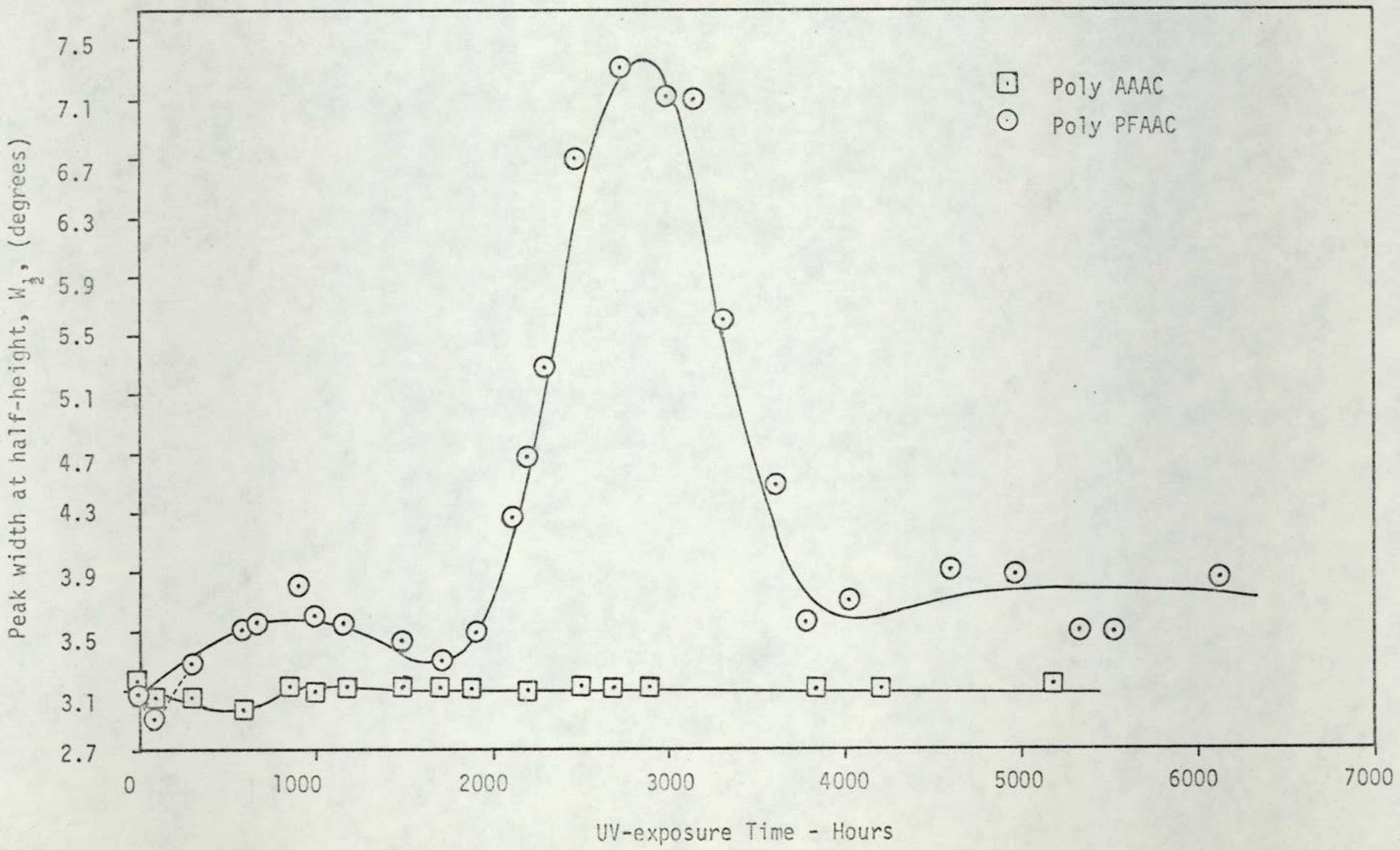


Figure 8.6 Goniophotometric plots showing variations in the peak width at half-height ($W_{\frac{1}{2}}$) with UV-exposure time for Poly AAAC and Poly PFAAC films.

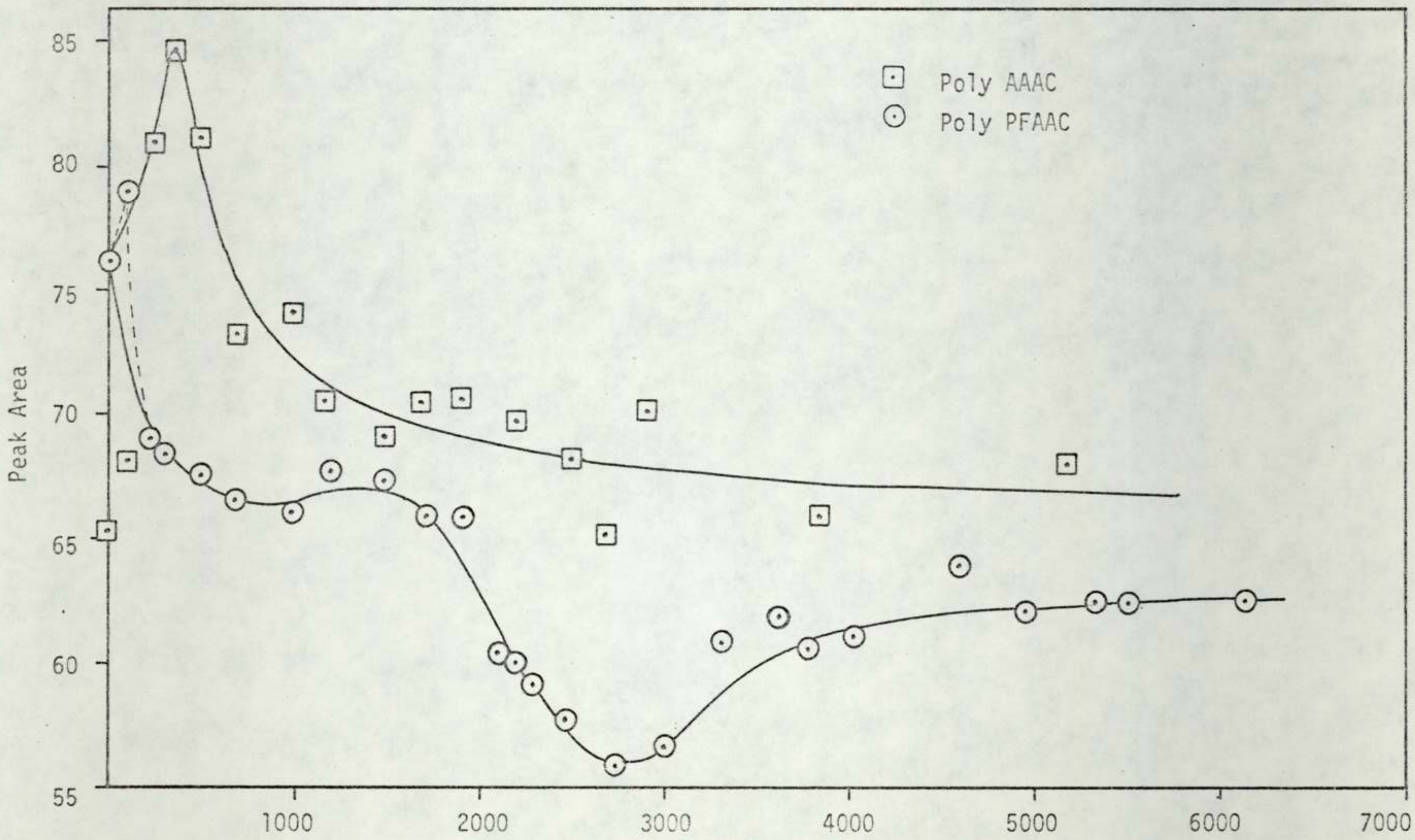


Figure 8.7 Goniophotometric plots showing change in peak area with UV-exposure time for poly AAAC and poly PFAAC films.

there is a suggestion that towards the end of this deteriorative period, the overall surface changes can be at least partially characterised by a slight broadening of the goniophotometric peak (i.e., increase in $W_{\frac{1}{2}}$) which is genuinely representative of surface roughening.

All of this can be readily interpreted from light reflection(95) theory as being evidential of a fairly rapid build up in the density of surface MICROimperfections (i.e., defects of an order of size $\leqslant$ wavelength of incident light) up as far as 500 hours exposure. However, as these surface irregularities increase in size as well as number, the goniophotometric data obtained suggests that after a further 400 hours these defects are beginning to assume an order of size $\geqslant$ wavelength of incident light whereupon as MACROdefects they are able to bring about an angular divergence of the specular beam and hence a broadening of the goniophotometric peak.

This deteriorative period is then seen from Figure 8.4 to be followed by a period, similar in length, of apparent surface improvement during which the gloss factor recovers approximately 33% of its previous loss. Similar theoretical considerations to those described previously interpret these results as indicating that this ageing period sees the gradual erosion of a proportion of the surface MICROdeterioration leading to a recovery in specular reflectance (I_S) and hence gloss. This "surface-mending" phase, however, would not be expected to include clearance to the same extent of the more largely-developed irregularities which are likely to be retained in the samples otherwise apparently "renewed" surface. Indeed, this carry-over of residual MACROdefects represents the largest single difference between the initial equilibrated surface (i.e., after 100 hours) and this "quasi-restored" state.

The following section of the exposure period (i.e., 1700 — 3500 hours) exhibits a similar cycle of ageing to that previously discussed. However, the surface profile changes occurring within this periodic deterioration/recovery pattern are relatively more exaggerated within this second cycle, the most significant manifestation being in the peak-width at half-height ($W_{\frac{1}{2}}$) changes. This illustrates the greater trancursion of surface defect size across the so-called MICRO-MACRO "boundary" as sensed by the goniophotometer during the terminal stages of ageing.

Finally, the extended exposure of the sample to just over 6000 hours showed relatively little further change indicating that, by this time, the sample had attained an apparently stable state with respect to further surface profile variations.

It can be concluded from this UV-ageing study of poly PFAAC that clear films of the polymer, whilst exhibiting an apparently cyclic pattern of ageing behaviour, are nevertheless relatively stable towards UV-degradation when compared with commercial polymer films such as those made from polyethylene and polypropylene over a 4000 hours exposure period.

Following on from poly PFAAC, the UV-degradation of its non-fluorinated analogue, poly AAAC, was studied and the goniophotometric results for this polymer are presented in Figures 8.4-8.7 alongside those of poly PFAAC for comparison. As with poly PFAAC previously, an initial increase in gloss factor (Figure 8.4) occurred on exposure which could again be contributed to an equilibration of the sample within the UV-cabinet. In the case of poly AAAC, however, this initial improvement in the state of the film surface, at the expense of the MICROirregularities originally present in the unexposed sample, continued over the first 400 hours of exposure with the increases in GF being wholly accounted for by corresponding increases in the specular reflectance (I_s). After this equilibration period was completed, the following 500 hours UV-exposure induced a gradual build-up in the density of surface MICROirregularities (as with poly PFAAC) to about the same degree as had been originally present in the unexposed, but unequilibrated state. In contrast to poly PFAAC, however, the constancy throughout of the peak width at half-height ($W_{\frac{1}{2}}$) values (Figure 8.5) indicated that these MICROdefects were not "graduating" in time to what the goniophotometer regarded as MACROdefects before the subsequent and now familiar recovery period set in. This slight recovery period lasting from between 900 and 1300 hours ageing could also be fully explained in terms of what were exclusively I_s changes (Figures 8.4-8.7). Finally, a relatively very slow and gradual decrease in I_s and hence GF, amounting to only about 10-15% over the remaining 3900 hours up to the end of the exposure, was observed.

On comparison of these two polymers studied, it would be easy to conclude that on the evidence of (a) the longer induction period of poly AAAC prior to the onset of degradation and (b) the relatively shorter duration and lesser extents to which film deterioration proceeds for poly AAAC prior to recovery, that the poly AAAC is inherently more UV-stable than its fluorinated analogue. However, it is probably more accurate to conclude that both of these polymers, each having a molecular weight of around 2000, appear to be fairly UV-stable over the length of time for which they were exposed, deriving this stability from their polyester backbones. In addition to this, it is conceivable that the pentafluorophenyl substituent in poly PFAAC in some way makes available a slightly more inviting degradative route along which this particular polymer can proceed.

Microindentation studies before and after exposure (time = 0 to time $\simeq$ 6000 hours) show relatively little change. The most obvious conclusion is that little or no change to the backbone structure either by cleavage of substituents or cross-linking had taken place.

8.6 Copolymerisation Studies

Some initial attempts were made to copolymerise PFAAC with other anhydrocarboxylate monomers.

(a) PFAAC-MAAC Copolymer

Since PFAAC is known to be less reactive than MAAC in relation to its rate of polymerisation under given tertiary base initiation conditions, PFAAC was copolymerised with equimolar and sub-equimolar quantities of MAAC. The products were isolated in the normal way and infrared spectra taken. There was no apparent difference in properties of the copolymer as one might expect since the gross behaviour of the two homopolymers is similar. The changes in infrared spectra (Figure 8.8) in the aromatic C-H and conjugation regions (3000-3150 cm^{-1} and 1600 cm^{-1}) show increases in incorporation of MAAC as the comonomer composition changes.

Because separation of two soluble homopolymers such as poly MAAC and poly PFAAC is difficult, it is impossible to be sure that the materials produced were copolymers rather than a mixture of homopolymers. Preparation of larger quantities and, e.g., D.S.C. studies might have established this had time been available. A second system was examined however, in which the properties (particularly solubility and X-ray diffraction behaviour) of the homopolymers were quite different.

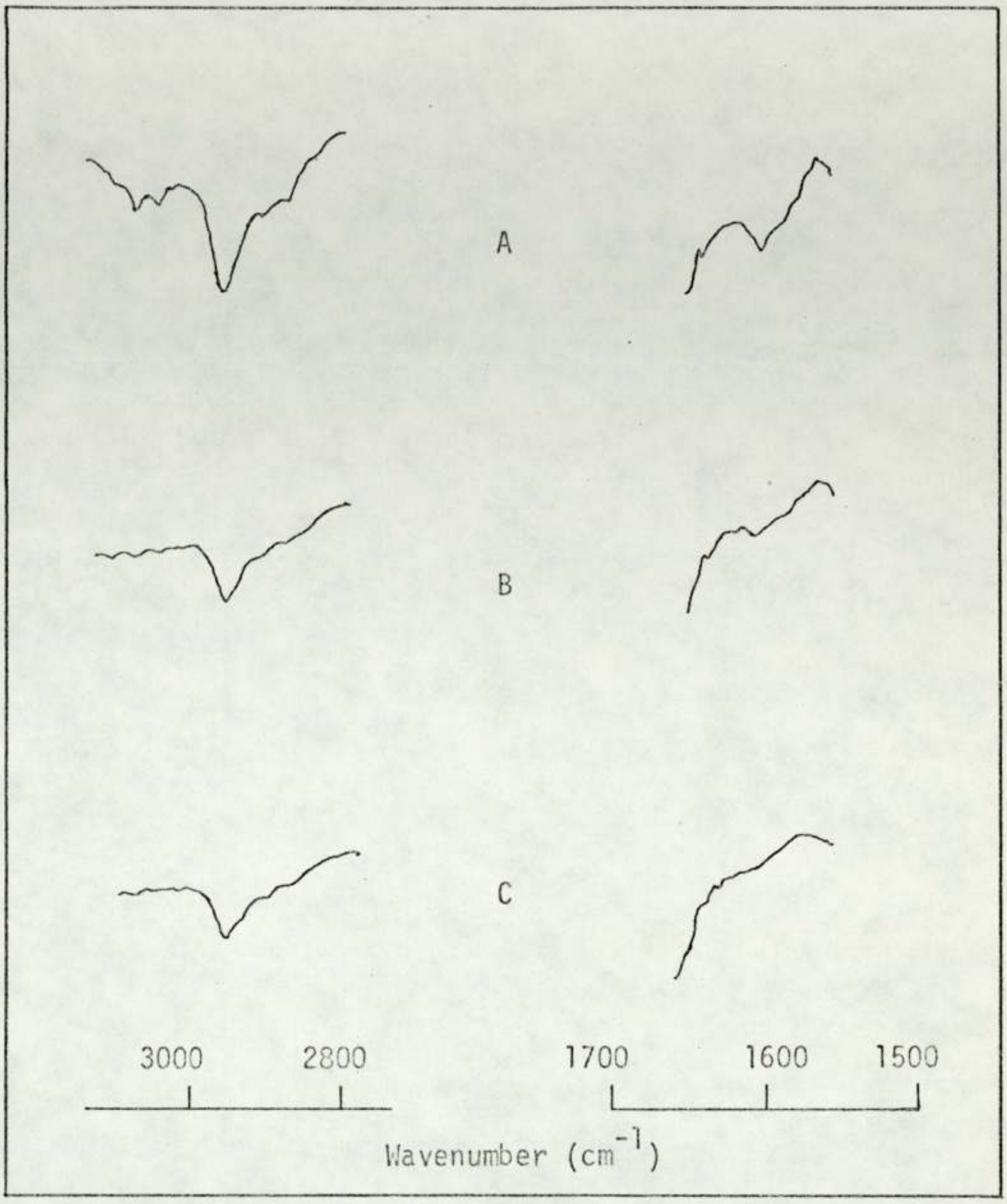


Figure 8.8 Aromatic C-H absorption peaks from the infrared spectra of polymers obtained from pyridine initiated copolymerisations of PFAAC and MAAC

A [PFAAC] : [MAAC] = 1:1
B [PFAAC] : [MAAC] = 2:1
C [PFAAC] : [MAAC] = 10:1

(b) PFAAC-GAAC Copolymer

Copolymerisations were attempted at various molar ratios and the products isolated. In this case the infrared characteristics of poly GAAC were insufficiently distinctive to detect its incorporation in this way. X-ray powder photographs were taken however in the hope that this might demonstrate incorporation of the GAAC unit. Unfortunately no such evidence was obtained. In retrospect the much greater reactivity of GAAC compared to PFAAC (and indeed to MAAC) makes it probable that all the GAAC monomer would disappear before any appreciable amount of PFAAC could react.

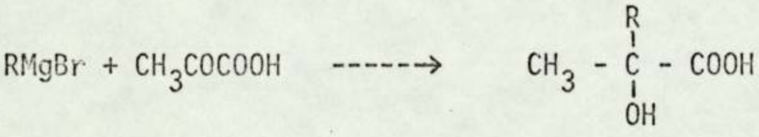
It became obvious in the course of this part of the work that the greater range in reactivity of anhydrocarboxylates in pyridine initiation as compared to the relative similarity in rates of the thermal polymerisation within the series of substituted anhydrosulphites makes copolymerisation studies difficult in the former case although they are relatively simple in the latter.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

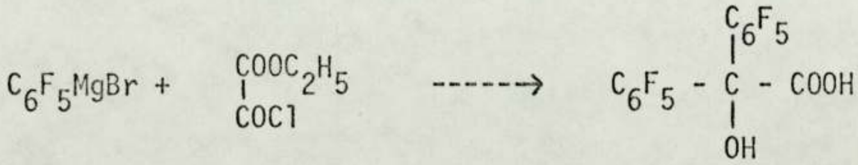
9.1 Summary and Conclusions

The synthetic work described in the early part of this thesis was concerned mainly with anhydrocarboxylates with fluorine-containing substituents and their α-hydroxy acid precursors. As far as anhydrocarboxylate synthesis is concerned, an improved procedure has been developed which involved the use of lower temperatures and higher concentrations than previous workers had employed. The major advantages were in reduced reaction time and improved yield and purity of the product. Most of the effort in synthetic work was expended on α-hydroxy acid synthesis. In Grignard reactions involving pyruvic acid, i.e.,



$$RMgBr + CH_3COCOOH \dashrightarrow CH_3 - \underset{OH}{\overset{R}{C}} - COOH$$

the purity of pyruvic acid was found to be of vital importance but extremely difficult to assess in a convenient manner. Colour and viscosity were found to be the only reliable indicators. In the attempted synthesis of decafluorobenzilic acid from the reaction of ethyl oxalyl chloride with pentafluoro magnesium bromide:



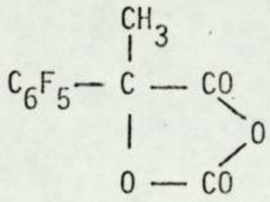
$$C_6F_5MgBr + \begin{matrix} COOC_2H_5 \\ | \\ COCl \end{matrix} \dashrightarrow C_6F_5 - \underset{OH}{\overset{C_6F_5}{C}} - COOH$$

low yields are obtained even under the most favourable reaction conditions. The most important competitive products were thought to be perfluoropinacol, perfluoropinacolone and perfluorobenzilide.

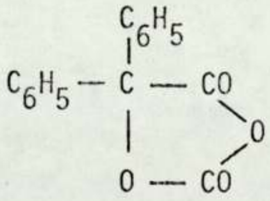
Their formation was minimised by preparing the copper(II) salt of the desired product, decafluorobenzilic acid, concurrently with the hydrolysis of the Grignard complex. This produced a low overall yield but greater purity of the product.

Attempts to synthesise the related fluoroaliphatic acid, bis-(trifluoromethyl)glycollic acid, by the cyanohydrin route from hexafluoroacetone were unsuccessful.

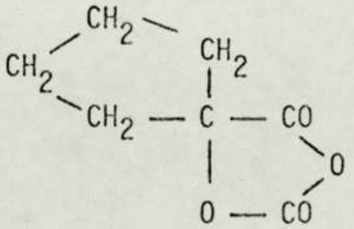
Kinetic and related work described in this thesis was concerned with establishing the relative effects of phenyl and pentafluorophenyl substituents in anhydrocarboxylate polymerisation. The pyridine initiated polymerisation of PFAAC:



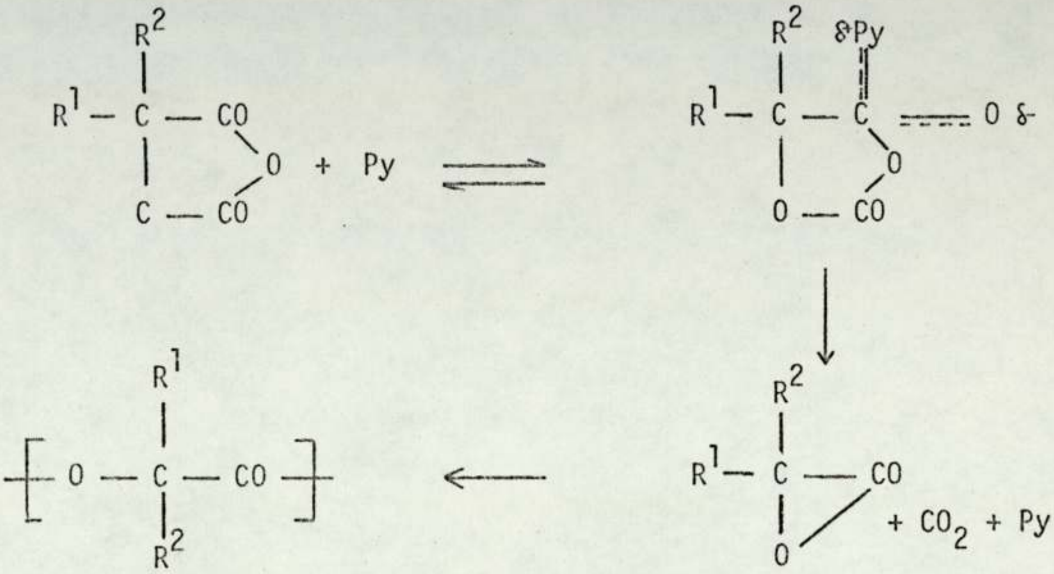
had been previously studied by Smith(63) and this work was extended and used as a comparative basis for the study of AAAC:



and C' pent AC:



Similar kinetic behaviour was observed in all three cases. The rate of polymerisation was found to be first order in monomer and first order in pyridine (although with some deviation at high pyridine concentrations). Pyridine was not consumed during the reaction and poly α-esters having both hydroxyl and carboxyl groups were formed. A simplified mechanism can be envisaged which accounts for these observations:



It was found that ring polymerisability could be related to both steric and polar effects using the Taft equation:

$$\log k_2 = 1.88\,\sigma^* + 1.29\,E_s + \text{constant}$$

No specific activation effects were found to be associated with aromatic rings other than these described by the Taft polar and steric substituent constants. The observed order of reactivity with pyridine is:

PFAAC > C' pent AC > AAAC

In a similar way, the structure of the tertiary base was found to be related to its effectiveness as an initiator in this reaction by considering (a) pK_a values and (b) the steric effect of substituents in the 2 and 2' positions. By assigning Taft steric (E_s) values to the latter, good correlation was obtained using the equation:

$$\log k_2 = 2\,pK_a + E_s + \text{constant}$$

Whereas uncomplicated kinetic behaviour with respect to monomer concentration was observed in nitrobenzene, and mixtures of this solvent with dekalin, abnormalities were encountered with both dimethyl sulphoxide and anisole. These took the form of deviations from first-order behaviour. As the reaction progressed beyond (say) 50% conversion, the rate diminished markedly and progressively below the level predicted by first-order dependence. Despite this, similar kinetic parameters were observed in the initial 'well behaved' portion to those found in nitrobenzene. Molecular weight studies produced further anomalies. Although it had been anticipated that inadequate purification was responsible for the relatively low molecular weights produced in the initial studies of PFAAC polymerisation carried out by Smith(63), rigorous purification procedures demonstrated that this was not the case.

The balance of evidence suggests a termination step, involving the α-lactone and enhanced by the presence of pyridine, that produces polymers having an excess of carboxyl groups over the 1:1 hydroxyl: carboxyl ratio encountered in poly α-esters prepared from related ring systems.

It is thought most likely that this involves 'wrong addition' of the growing chain to the α-carbon of the lactone. The polarisation that governs this is related to both the substituents at the α -carbon and the interaction of the tertiary base with the lactone.

9.2 Suggestions for Further Work

The work described in this thesis has established general areas in which mechanistic peculiarities exist. More detailed studies are necessary to correlate abnormalities in kinetic behaviour with the production of low molecular weight polymer and the possible existence of a termination step.

A more precise technique is needed for measurement of end group concentration in low molecular weight polymer. High resolution nuclear magnetic resonance spectroscopy should be able to provide this although it may be necessary to undertake C^{13} fourier transform work in order to get the required precision.

The deviation from first-order kinetic behaviour in pyridine may well prove to be a conclusive link in the mechanistic work. More detailed studies of the effect of tertiary base concentration need to be carried out, (a) with various (sterically hindered) initiators, and (b) in various solvents. Similarly, the effect of bases which are less active than pyridine (e.g., biphenyl-2-pyridyl methane) on molecular weights of anhydrosulphites should be studied in more detail in order to examine more carefully the hypothesis that pyridine-lactone interaction can enhance wrong addition.

Further evidence could also be obtained by studying initial rates of reaction in a series of experiments in which the initial base concentration was kept constant but the initial monomer concentration varied in such a manner as to correspond to significant points on the 'abnormal' kinetic curves obtained with anisole or dimethyl sulphoxide.

The synthetic work should obviously be continued in an attempt to improve the yield of decafluorobenzilic acid. The properties of the derived anhydrocarboxylate and its polymer would be of obvious interest.

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